

**Development of In-situ Nanocrystalline NiCoCrAlTaY Coatings
by Cold Spray on a Single-Crystal Nickel-base Superalloy
for Gas Turbine Applications**

By

Deliang Guo

A thesis submitted in partial fulfillment of the requirements for the degree
of Doctor of Philosophy in Advanced Materials and Manufacturing

Department of Mechanical Engineering

Faculty of Engineering

University of Ottawa

© Deliang Guo, Ottawa, Canada, 2021

Abstract

MCrAlY coatings are commonly applied as the bond coat in TBCs used in modern gas turbines. Cold spray (or CS), characterized by low process temperature and high particle impact velocity, has been demonstrated as a promising alternative to thermal spray processes, such as air plasma spray (APS) and high velocity oxygen fuel (HVOF), for manufacturing MCrAlY coatings. **The general objective of the thesis research is to characterize CS deposition on a single-crystal nickel-base superalloy and to develop low-cost/high-performance NiCoCrAlTaY coatings using the CS technique.**

Several individual studies were carried out with each having a specific focus towards achieving the general research objective. CS deposition of NiCoCrAlTaY coatings **using nitrogen** was first examined to verify the feasibility of replacing the expensive helium gas typically used as the CS process gas. Several materials were used as the substrates, and the effects of substrate materials and surface preparation on coating microstructure and properties were investigated. **Recycling of non-deposited powder particles** was then explored to reduce the costs associated with the feedstock powder. A cost model that includes the economics of powder recycling was developed for the CS process, showing that the use of nitrogen and powder recycling could potentially be cost-effective for CS deposition of MCrAlY coatings.

A CS process that can produce **in-situ nanocrystalline NiCoCrAlTaY coatings** was proposed to develop coatings with enhanced oxidation performance. This CS approach utilizes conventional commercial powders instead of pre-milled nanocrystalline powders. Detailed characterization using the scanning electron microscope (SEM), scanning transmission electron microscope (STEM), and X-ray diffraction (XRD) was carried out to investigate the microstructure of the resulting CS NiCoCrAlTaY coatings, single-crystal substrate, and their interface. Isothermal oxidation performance of the CS NiCoCrAlTaY coatings was evaluated at 1100°C for 1h to 500h. Results revealed that the nanostructure promoted the α -Al₂O₃ scale formation and sustained α -Al₂O₃ scale growth, suggesting **good isothermal oxidation performance**.

Finally, the **effects of different processing sequences** on CS NiCoCrAlTaY coating characteristics and short-term isothermal oxidation performance were investigated.

Specifically, CS deposition of NiCoCrAlTaY coatings was carried out on single-crystal superalloy substrates that underwent various degrees of full heat treatments prior to being coated. The remaining superalloy heat treatments required were then performed on the coated samples after the CS deposition. The microstructures of the superalloy substrates and CS NiCoCrAlTaY coatings were characterized after each heat treatment. Isothermal oxidation performance of the coated samples following different sequences was evaluated at 1100°C for 2 hours. The results suggested a promising processing sequence that could potentially further improve the oxidation performance of CS NiCoCrAlTaY coatings.

Preface

Some of the thesis research results were presented in the format of peer-reviewed journal articles. These articles were reprinted in the thesis with permissions from the corresponding copyright owners, Springer Nature and Elsevier. My contributions as well as of the co-authors to each of the journal articles are summarized below.

I have co-authored (first author) the journal article entitled “Cold Spray MCrAlY Coatings on Single-Crystal Superalloy Using Nitrogen: Properties and Economics” presented in section 5.2 (pages 83-97) with Mr. Daniel MacDonald, Dr. Linruo Zhao, and Dr. Bertrand Jodoin. I have performed the pertinent experiments and examinations, including sample preparations, metallographic analysis, as well as microstructural and mechanical characterization. In addition, I have developed the cost model for the CS process that incorporates powder recycling. I have also prepared the original manuscript, including the production of all the tables and figures, and made the necessary revisions based on the co-authors’ comments. Mr. MacDonald, the second author, has helped produce some of the coating samples and provided great discussions on developing the cost model. He also reviewed the manuscript and provides insightful feedback on the organization of the tables and figures. Dr. Zhao, the third author, has participated in the discussion of the results and reviewed the manuscript. Dr. Jodoin, my thesis supervisor, has guided me throughout the study and provided invaluable discussions on the presentation and interpretation of the experimental and analytical results. He has also reviewed the manuscript and directed me on improving the structure, conciseness, and readability of the manuscript, as well as on preparation and submission of the manuscript. All the co-authors agreed that I should be the first author as I contributed the most to the technical/scientific content of the article.

I have co-authored (first author) the journal article entitled “Cold Spray for Production of In-Situ Nanocrystalline MCrAlY Coatings – Part I: Process Analysis and Microstructure Characterization” presented in section 6.1 (pages 99-111) with Dr. Yin Wang, Dr. Ruben Fernandez, Dr. Linruo Zhao, and Dr. Bertrand Jodoin. I have conducted the pertinent experiments and produced all the samples for the study as well as prepared the specimens for metallographic analysis, SEM characterization, and mechanical testing. In addition, I have

drafted the original manuscript, including the production of all the SEM and TEM figures as well as the tables, and made the necessary revisions based on the co-authors' comments. Dr. Wang, the second author, has provided communication and coordination during the TEM samples preparation and characterization. She also provided valuable explanations and discussions on the TEM results production and interpretation. Dr. Fernandez, the third author, has provided great discussions on the elaboration of the TEM characterization results and reviewed the manuscript. Dr. Zhao, the fourth author, has participated in the discussion of TEM results interpretation and provided insightful feedback regarding the manuscript. Dr. Jodoin, my thesis supervisor, has guided me throughout the study and provided invaluable discussions on the presentation and interpretation of the experimental and analytical results. He has also reviewed the manuscript and directed me on improving the structure, conciseness, and readability of the manuscript, as well as on preparation and submission of the manuscript. All the co-authors agreed that I should be the first author as I contributed the most to the technical/scientific content of the article.

I have co-authored (first author) the journal article entitled "Cold Spray for Production of In-Situ Nanocrystalline MCrAlY Coatings – Part II: Isothermal Oxidation Performance" presented in section 6.2 (pages 113-127) with Dr. Linruo Zhao and Dr. Bertrand Jodoin. I have conducted the pertinent experiments and produced all the samples for the study. I have also performed the oxidation tests and prepared the resulting samples of each condition for metallographic analysis as well as microstructure and composition characterization. All the results presented in the article were outcomes of these experiments and characterization. In addition, I have drafted the original manuscript, including the production of all the tables and figures, and made the necessary revisions based on the co-authors' comments. Dr. Zhao, the second author, has provided great discussions on the elaboration of the isothermal oxidation results. He also provided insightful feedback regarding the manuscript and contributed to the manuscript revisions. Dr. Jodoin, my thesis supervisor, has guided me throughout the study and provided invaluable discussions on the presentation and interpretation of the experimental and analytical results. He has also reviewed the manuscript and directed me on improving the structure, conciseness, and readability of the manuscript, as well as on preparation and submission of the manuscript. All the co-authors agreed that I should be the first author as I contributed the most to the technical/scientific content of the article.

Acknowledgements

I would first like to thank my supervisor, Prof. Bertrand Jodoin, for his great guidance and continuous support throughout my Ph.D. study. It would not be possible for me to reach where I am without his help, encouragement, and enlightenment. I am forever grateful for the opportunities of joining the group and getting to know and learn from him not just in the research context but also in everyday life. Thank you for being a great supervisor and mentor!

I wish to express my gratitude to Dr. Linruo Zhao for his involvement and guidance throughout my study. His expertise on thermal barrier coatings, gas turbines, and material science in general has enlightened me in the field and is of great help to my research work. I enjoyed and cherished the valuable discussions we had each time. I am also privileged to have known and worked with Dr. Weijie Chen. His insightful direction and suggestions both in the technical field and in my professional career development are greatly appreciated. I would also like to thank Dr. Yin Wang for her help with TEM sample preparation and characterization that are crucial to my study.

Many thanks to the technical officers at the Mechanical Engineering machine shop, Leo Denner, Paul Burberry, John Perrins, and Stanley Weedmark, for their help with sample preparation and experimental apparatus design and fabrication. They are always a source of solutions whenever there is an issue in our research projects. I also acknowledge the help and service provided by the department administration team, Dr. Natalie Baddour, Michelle Le Gallez, and Manon St-Jean.

Huge thanks to Ruben Fernandez, Daniel MacDonald, and Chengming Luo, for their friendship and tremendous help both in and outside the lab. Thanks are also extended to my colleagues, Roghayeh Nikbakht, Tyler Samson, Patrick Richer, Antoine Bacciochini, Patrick Trahan, Maryam Razavipour, Saeed Rahmati, Aleksandra Nastic, Alexanna Hawkins, Rocio Dominguez, Amir Daoud, and Justin Perry, for creating such a nice work environment and making this a fun journey.

Lastly, I wish to express my great appreciation to my parents and sister for their unconditional love, support, and encouragement. To my lovely wife Lu, you are the backstage hero of all the things I have achieved; I couldn't have completed the study without your love, companion, and support. I can't wait to turn this page and enter the next phase of our life in all the years to come. A special thanks to Hector for giving me many excuses to procrastinate. The time we spent and the joys we had have made me realize that life is so beautiful!

Table of Contents

Abstract.....	ii
Preface.....	iv
Acknowledgements	vi
List of Tables.....	ix
List of Figures.....	x
Chapter 1 Introduction.....	1
1.1 Background.....	1
1.2 Motivation and General Objectives	10
1.3 Outline of the Thesis	12
Chapter 2 Literature Review	14
2.1 Fundamentals of Oxidation and Resistance.....	14
2.2 MCrAlY Materials Justification.....	20
2.2.1 Addition of Chromium.....	20
2.2.2 Addition of Reactive Elements	21
2.2.3 Variations of MCrAlY systems	23
2.3 Scale Growth and Failure Mechanism.....	24
2.3.1 Transport Mechanism of Oxide Growth	25
2.3.2 Failure Mechanism	29
2.4 Factors Affecting the Oxidation Performance	35
2.4.1 Exposure Conditions.....	35
2.4.2 Coating Characteristics	36
2.4.3 Manufacturing Processes	38
2.5 Cold Gas Dynamic Spray	40
2.5.1 Process Overview	40
2.5.2 Gas Dynamic Principles.....	43
2.5.3 Particle Impact and Bonding.....	55

Chapter 3 Research Objectives.....	59
3.1 Deposition of NiCoCrAlTaY Coatings by Cold Spray Using Nitrogen	60
3.2 Powder Recycling and Process Economics	60
3.3 Production of In-situ Nanocrystalline MCrAlY Coatings by Cold Spray	61
3.4 Isothermal Oxidation Evaluation	62
3.5 Processing Adjustment.....	63
Chapter 4 Methodology	66
4.1 Feedstock Powder	66
4.2 Substrate and Preparation	68
4.3 Cold Spray Deposition.....	70
4.4 Oxidation Evaluation	71
4.5 Materials Characterization	72
Chapter 5 Cold Spray Deposition of NiCoCrAlTaY Coatings Using Nitrogen	73
5.1 Coating Deposition	73
5.2 Coating Properties and Process Economics.....	82
Chapter 6 Production of In-Situ Nanocrystalline NiCoCrAlTaY Coatings by Cold Spray	98
6.1 Process Analysis and Microstructure Characterization.....	98
6.2 Isothermal Oxidation Performance	112
Chapter 7 Processing Adjustment of Cold Spray NiCoCrAlTaY Coatings on Single-Crystal Superalloys.....	128
7.1 Superalloy Heat Treatments and Cold Spray Deposition	128
7.2 Isothermal Oxidation Performance	134
Chapter 8 Conclusions.....	139
Future Work	143
Reference	145
Appendix.....	160

List of Tables

Table 1.1 Alloy composition of some typical nickel-base superalloys in the form of wrought, cast and single-crystal (wt. %) [2-6]	3
Table 2.1 Speed of sound for several common gases under standard ambient condition (25 °C, 100 kPa)	50
Table 4.1 Nominal composition of the Amdry 997 powder and CMSX-4 superalloy substrate (wt. %)	66
Table 4.2 Mean and percentile particle sizes for the NiCoCrAlTaY powder	68
Table 4.3 Heat treatment conditions for the superalloy substrate and MCrAlY coatings	69
Table 5.1 Parameters for CS deposition of NiCoCrAlTaY coatings using nitrogen.....	73
Table 5.2 Microhardness of feedstock NiCoCrAlTaY powder, Al 6061, IN 625, and CMSX-4 substrates (HV _{0.3})	75
Table 7.1 Microhardness of CMSX-4 substrates under different heat treatment conditions and characteristics of CS NiCoCrAlTaY Coatings deposited on the substrates.....	131

List of Figures

Figure 1.1 Evolution of superalloy temperature capability over the 1940-2010 period.....	1
Figure 1.2 Turbine blades with grain structure in the form of (a) equiaxed, (b) columnar, and (c) single-crystal	2
Figure 1.3 Overview of Cr concentration in some typical nickel-base superalloys	5
Figure 1.4 Oxidation performance of different generations of single-crystal superalloys (cyclic oxidation testing of 1h holding at 1100°C).....	6
Figure 2.1 Schematic of a continuous oxide scale and diffusion of the reactants	15
Figure 2.2 Schematic of linear and parabolic growth of oxide scales	17
Figure 2.3 Order-of-magnitude parabolic rate constants for the growth of several oxides	18
Figure 2.4 Thermokinetic map of various oxide scales showing parabolic rate versus free energy of formation. Optimum performance for stable slow-growing scales in lower right.	19
Figure 2.5 Notional ternary diagrams showing the influence of chromium addition on the scale make-up: (a) symmetric, idealized; (b) asymmetric, real.	20
Figure 2.6 Effect of sulfur content on the oxidation performance of alloy PWA1480	22
Figure 2.7 Optimum coating compositions in relation to oxidation and hot-corrosion resistance	24
Figure 2.8 Bulk diffusivity data for oxygen and aluminum diffusion in Al_2O_3	26
Figure 2.9 Schematic diagram showing the outward diffusion of reactive elements along grain boundaries of an $\alpha\text{-Al}_2\text{O}_3$ scale	28
Figure 2.10 Schematic diagram showing the chemical failure of the protective scales	29
Figure 2.11 Schematic of cracking and spallation initiation in the protective scale under tensile stresses	31
Figure 2.12 Schematic of two possible routes leading to crack initiation and scale spallation for protective scales under compression	33
Figure 2.13 Schematic diagram of a typical cold spray system.....	40
Figure 2.14 Schematic showing the evolution of pressure (p), temperature (T) and velocity (v) of a gas flowing through a de-Laval nozzle.....	41
Figure 2.15 Subsonic to supersonic flow through a converging-diverging nozzle.....	45
Figure 2.16 Flow characteristics in a converging-diverging nozzle for varying back pressure	46

Figure 2.17 Calculated profiles of (a) plastic strain and (b) flow stress along the particle radial path for two impact velocities.....	56
Figure 2.18 SEM images showing the rollups and the vortices at the interface of (a) Cu on Al6061 substrate (b) Ni on Al substrate.....	57
Figure 3.1 Flowchart showing the CMSX-4 superalloy substrate conditions prior to CS deposition.....	64
Figure 3.2 Flowchart showing different sequences of superalloy heat treatments and CS deposition.....	65
Figure 4.1 (a) Morphology and (b) microstructure of the NiCoCrAlTaY powder	67
Figure 4.2 Particle size distribution of the NiCoCrAlTaY powder.....	67
Figure 4.3 (a) As-received CMSX-4 bar and (b) CMSX-4 disk after EDM cutting.....	68
Figure 4.4 Grit blasted (a) Al6061, (b) IN625, (c) CMSX-4, and (d) ground CMSX-4 substrates	70
Figure 4.5 Overview of (a) the CS system and (b) the spray gun.....	71
Figure 5.1 CS NiCoCrAlTaY coatings deposited on three substrate materials: (a, b) Aluminum alloy 6061, (c, d) Inconel alloy 625 polycrystalline nickel-base superalloy, and (e, f) CMSX-4 single-crystal nickel-base superalloy.	74
Figure 5.2 Thick NiCoCrAlTaY coating produced by CS using nitrogen on a CMSX-4 substrate: (a) secondary electron (SE) image, and (b) backscattered electron (BSE) image.	76
Figure 5.3 CS NiCoCrAlTaY coatings deposited on CMSX-4 substrates with different surface preparation: (a) grit blasting, and (b) grinding.	77
Figure 5.4 Morphology and microstructure of NiCoCrAlTaY powders from different production batches: (a, c) batch X and (b, d) batch Y.....	78
Figure 5.5 Topview and cross-section SEM images of CS NiCoCrAlTaY coatings produced from (a, c, e, g) batch X powder, and (b, d, f, h) batch Y powder	79
Figure 5.6 Topview and cross-section SEM images of CS NiCoCrAlTaY coatings produced from the batch Y powder using adjusted spray parameters ($T_{\text{gas}} = 400^{\circ}\text{C}$ and $T_{\text{powder}} = 400^{\circ}\text{C}$)	81
Figure 7.1 BSE images showing the microstructures of the CMSX-4 superalloy substrates after (a) SHT, (b) SHT+PA, and (c) SHT+PA+SA	129
Figure 7.2 BSE image showing the primary γ' phase and the secondary γ' phase within the γ -matrix channel.....	130

Figure 7.3 CS coating deposition on CMSX-4 substrates with different heat treatments: (a) SHT, (b) SHT+PA, and (c) SHT+PA+SA	131
Figure 7.4 BSE images showing the microstructures of coated SHT samples after ageing: (a) PA and (b) PA+SA.	133
Figure 7.5 BSE images showing the microstructure of coated SHT+PA sample after SA: (a) overview and (b) high magnification revealing the presence of a thin TGO layer.	133
Figure 7.6 Flowchart showing three different sequences of superalloy heat treatments and CS coating deposition	135
Figure 7.7 BSE images showing the microstructures of NiCoCrAlTaY coatings after 2h oxidation at 1100°C following (a, b) Sequence 1, (c, d) Sequence 2, and (e, f) Sequence 3	136
Figure A.1 Metallographic sample preparation equipment: (a) sectioning (Struers Secotom-10), (b) mounting (Struers LaboPress-3), and (c) grinding and polishing (Struers TegraPol-31, TegraForce-5, and TegraDoser-5)	160
Figure A.2 Laboratory furnace (Lindberg/Blue M™, Thermo Scientific™) for superalloy heat treatments and isothermal oxidation evaluation	161
Figure A.3 In-house powder reclamation apparatus: (a) open view without the front panel, and (b) enclosed setup during an actual spray.	161
Figure A.4 Laser diffraction analyzer (Microtrac S3500, Nikkiso, Japan) for particle size distribution analysis	162
Figure A.5 Laser Doppler velocimetry meter (ColdSprayMeter, Tecnar, Canada) for particle velocity distributions analysis.....	162
Figure A.6 Stylus surface roughness tester (SRG-4000, Phase II Plus, USA)	163
Figure A.7 Vickers Microhardness Tester (Duramin-1, Struers, Denmark)	163
Figure A.8 Optical microscope (NMM-800TRF, Kingdak, China) equipped with digital camera and image analysis software (Vision Lite, Clemex, Canada) for coating porosity and thickness measurement	164
Figure A.9 Three-dimensional optical microscope (VHX-2000, Keyence, Osaka, Japan) for general sample examination.....	164
Figure A.10 Scanning electron microscope (SEM) (EVO-MA10, Zeiss, Germany) equipped with energy-dispersive X-ray spectrometer (EDS) (INCA-x-act, Oxford Instruments, UK) for microstructure and chemical composition characterization.....	165
Figure A.11 Gold sputter (Desk IV, Denton Vacuum, Moorestown, USA) for depositing a thin conductive layer on samples prior to SEM examination	165

Chapter 1 Introduction

1.1 Background

Gas turbines with enhanced efficiency and improved environmental performance have been pursued since the inception of this industry. A higher turbine entry temperature (TET), from a thermodynamic point of view, is always desirable as it leads to higher engine efficiency and better engine performance. However, a higher TET inevitably imposes severe demand on the thermal capability of materials that comprise hot-section components of the gas turbines (e.g., combustor liner, turbine blades, and nozzle guide vanes), and requests the development of innovative technological solutions to accommodate the ongoing challenges.

Nickel-base superalloys are the dominant materials for the hot-section components due to their excellent physical properties and chemical stabilities at elevated temperatures ($>0.5T_m$) [1]. They have been the center of extensive research and development efforts in the field of high-temperature materials for gas turbines applications. The advancement in processing and alloying of superalloys has significantly increased their temperature limitation over the past decades, as shown in Fig. 1.1.

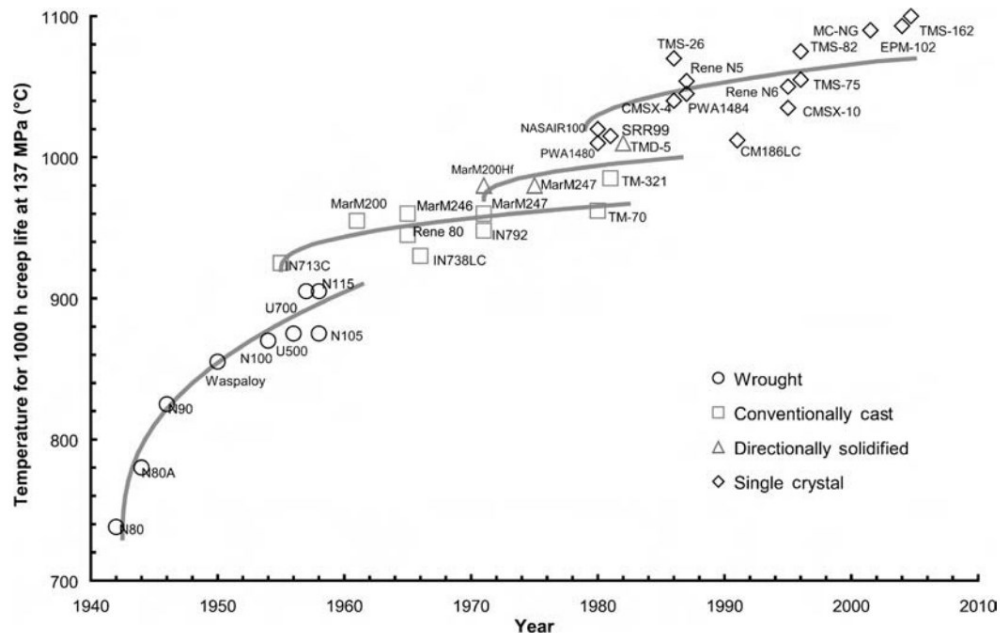


Figure 1.1 Evolution of superalloy temperature capability over the 1940-2010 period. Reproduced from [2] with permission of Cambridge University Press through PLSclear.

The gradual increases of temperature capability were realized through alloy development, while the larger temperature leaps were accomplished through manufacturing innovations. Innovative manufacturing processes have led to the well-known microstructure evolution of the superalloys, i.e., equiaxed grains from conventional casting, columnar grain structure and single crystal from directional solidification technique (see Fig. 1.2). This change in superalloy microstructure has dramatically improved the creep resistance of superalloys at elevated temperatures as grain boundaries that facilitate creep deformation are gradually eliminated. As a result, elements such as boron (B) and carbon (C), which were traditionally added in the superalloys to strengthen the grain boundaries, are not necessary anymore and thus have been removed from the composition of single-crystal superalloys. Meanwhile, the concentration of other alloying elements has been continuously modified to better accommodate the microstructure changes to achieve optimum properties and performance at elevated temperatures. Table 1.1 summarizes the compositions of some typical nickel-base superalloys along with the development of wrought and cast superalloys [2-6]. The composition of single-crystal superalloys categorized by different generations is also included in the table.

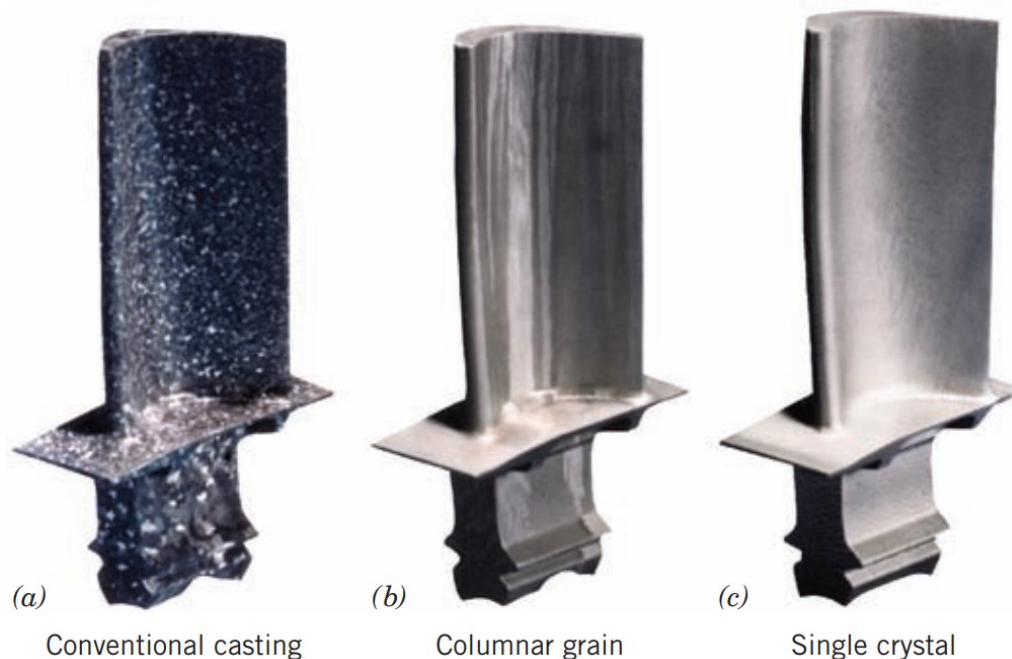


Figure 1.2 Turbine blades with grain structure in the form of (a) equiaxed, (b) columnar, and (c) single-crystal. Republished from Ref. [7] with permission of John Wiley & Sons - Books; permission conveyed through Copyright Clearance Center, Inc.

Table 1.1 Alloy composition of some typical nickel-base superalloys in the form of wrought, cast and single-crystal (wt. %) [2-6]

	Ni	Cr	Co	Mo	W	Al	Ti	Ta	Hf	C	B	Zr	Fe	Nb	Re	Ru
<i>Wrought superalloys</i>																
Hastelloy X	Bal.	22.0	1.5	9.0	0.6	0.25	-	-	-	0.10	-	-	18.5	-	-	-
Haynes 242	Bal.	8.0	2.5	25.0	-	0.25	-	-	-	0.15	0.003	-	2.0	-	-	-
Inconel 625	Bal.	21.5	-	9.0	-	0.2	0.2	-	-	0.05	-	-	2.5	3.6	-	-
Nimonic 105	Bal.	15.0	20.0	5.0	-	4.7	1.2	-	-	0.13	0.005	0.10	-	-	-	-
René 41	Bal.	19.0	11.0	1.0	-	1.5	3.1	-	-	0.09	0.005	-	-	-	-	-
RR1000	Bal.	15.0	18.5	5.0	-	3.0	3.6	2.0	0.5	0.027	0.015	0.06	-	1.1	-	-
Udimet 720	Bal.	17.9	14.7	3.0	1.25	2.5	5.0	-	-	0.035	0.033	0.03	-	-	-	-
Waspaloy	Bal.	19.5	13.5	4.3	-	1.3	3.0	-	-	0.08	0.006	-	-	-	-	-
<i>Cast superalloys</i>																
GTD-111	Bal.	14.0	9.5	1.5	3.8	3.0	5.0	3.15	-	0.10	0.014	0.007	-	0.07	-	-
IN-738LC	Bal.	16.0	8.5	1.75	2.6	3.4	3.4	1.75	-	0.11	0.01	0.04	-	0.9	-	-
Mar-M247	Bal.	8.0	10.0	0.6	10.0	5.5	1.0	3.0	1.5	0.15	0.015	0.03	-	-	-	-
PWA 1422	Bal.	9.0	10.0	-	12.0	5.0	2.0	-	1.5	0.14	0.015	0.10	-	1.0	-	-
René 125	Bal.	9.0	10.0	2.0	7.0	1.4	2.5	3.8	0.05	0.11	0.017	0.05	-	-	-	-
<i>Single-crystal superalloys</i>																
1st generation																
CMSX-3	Bal.	8.0	5.0	0.6	8.0	5.6	1.0	6.0	0.10	-	-	-	-	-	-	-
PWA 1480	Bal.	10.0	5.0	-	4.0	5.0	1.5	12.0	-	-	-	-	-	-	-	-
René N4	Bal.	9.0	8.0	2.0	6.0	3.7	4.2	4.0	-	-	-	-	-	0.5	-	-
2nd generation																
CMSX-4	Bal.	6.5	9.0	0.6	6.0	5.6	1.0	6.5	0.10	-	-	-	-	-	3.0	-
PWA 1484	Bal.	5.0	10.0	2.0	6.0	5.6	-	9.0	0.10	-	-	-	-	-	3.0	-
René N5	Bal.	7.0	8.0	2.0	5.0	6.2	-	7.0	0.20	-	-	-	-	-	3.0	-
3rd generation																
CMSX-10	Bal.	2.0	3.0	0.4	5.0	5.7	0.2	8.0	0.03	-	-	-	-	0.1	6.0	-
René N6	Bal.	4.2	12.5	1.4	6.0	5.75	-	7.2	0.15	0.05	0.004	-	-	-	5.4	-
TMS-75	Bal.	3.0	12.0	2.0	6.0	6.0	-	6.0	0.10	-	-	-	-	-	5.0	-
4th generation																
MC-NG	Bal.	4.0	-	1.0	5.0	6.0	0.5	5.0	0.10	-	-	-	-	-	4.0	4.0
PWA1497	Bal.	2.0	16.5	2.0	6.0	5.55	-	8.25	0.15	0.03	-	-	-	-	6.0	3.0
TMS-138	Bal.	3.2	5.8	2.9	5.9	5.8	-	5.6	0.10	-	-	-	-	-	5.0	2.0
5th generation																
TMS-162	Bal.	3.0	5.8	3.9	5.8	5.8	-	5.6	0.09	-	-	-	-	-	4.9	6.0
TMS-173	Bal.	3.0	5.6	2.8	5.6	5.6	-	5.6	0.10	-	-	-	-	-	6.9	5.0
TMS-196	Bal.	4.6	5.6	2.4	5.0	5.6	-	5.6	0.10	-	-	-	-	-	6.4	5.0

Several general trends of the composition refinement can be realized in addition to the evolution of C and B that is previously mentioned:

- i. While refractory elements, such as tungsten (W) and tantalum (Ta), are not commonly employed in wrought superalloys, considerable amounts of these elements are added in almost all the cast superalloys. On the contrary, elements such as molybdenum (Mo), titanium (Ti), iron (Fe), niobium (Nb), which are alloyed to some wrought superalloys at appreciable quantities, are either reduced to a modest level (Mo, Ti) or completely excluded (Fe, Nb) in the cast superalloys, especially in the single-crystal forms. Hafnium (Hf), on the other hand, is more common in the cast superalloys though it is normally in low concentration.
- ii. Rhenium (Re) and ruthenium (Ru) are employed for the development of high-temperature high-strength single-crystal superalloys. In fact, the generations of single-crystal superalloys are conventionally determined by the level of Re and Ru contents. The second- and third-generation superalloys are characterized by approximately 3% Re and 5-6% Re without Ru addition, whereas the fourth- and fifth-generation distinguish themselves from the previous generations by alloying Ru in the composition, containing 2-4% and 5-6% Ru, respectively, while keeping Re at a level of 4-7%.
- iii. Aluminum (Al) concentration is seen to increase from wrought superalloys to cast superalloys and stabilize at 5-6% for the single-crystal superalloys.
- iv. Chromium (Cr) content is dramatically reduced along with the development of cast superalloys, from 15%-22% in the wrought superalloys to 2%-5% in the latest single-crystal superalloys.

Figure 1.3 displays the chromium concentrations of typical nickel-base superalloys. Cast superalloys, especially the single-crystal superalloys, contain a significantly low level of Cr in comparison to wrought superalloys. As corrosion resistance of the superalloys relies on the selective oxidation of Cr or Al to promote the protective oxides scale on the surface, lack of sufficient Cr and Al contents renders the superalloys susceptible to environmental attacks, such

as oxidation and hot corrosion [1]. This would result in surface degradation and eventually lead to mechanical failure of the components.

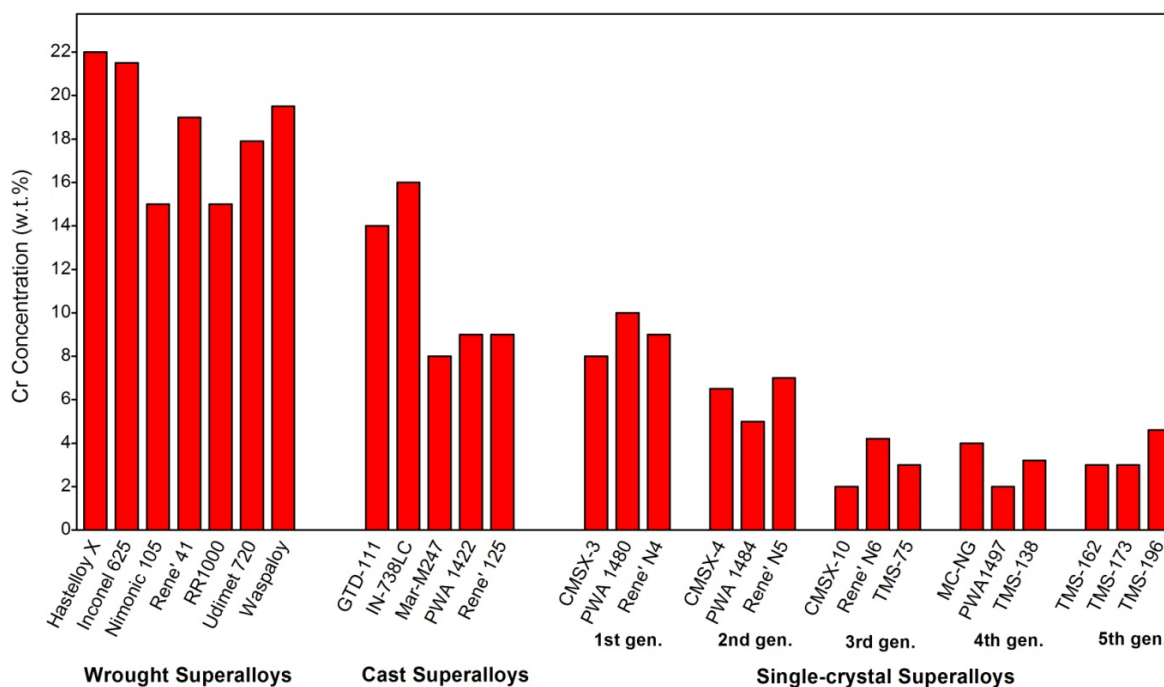


Figure 1.3 Overview of Cr concentration in some typical nickel-base superalloys

Figure 1.4 provides some insight into the effect of composition evolution on the oxidation performance of some typical single-crystal superalloys. The first-generation superalloy exhibits a fairly constant weight over the tested period, which represents good oxidation behaviour as a protective oxide scale is formed and the integrity of the scale is maintained. With decreasing Cr content, the second- and third-generation superalloys show a modest weight loss due to the formation and spallation of unfavourable fast-growing oxides. The oxidation performance is also complicated by the addition of rhenium (Re) and ruthenium (Ru). For example, Fig. 1.4 clearly shows that one of the fourth-generation single-crystal superalloys (TMS-138), which contains the same level of Cr (3%) and similar other alloying elements as the third-generation (TMS-75) except the 2% Ru (see Table 1.1), exhibits a significantly severe weight loss over the earlier generations. This obvious difference reflects the unstable nature of the oxide layer formed on the fourth-generation superalloys and thus confirms its inferior oxidation performance.

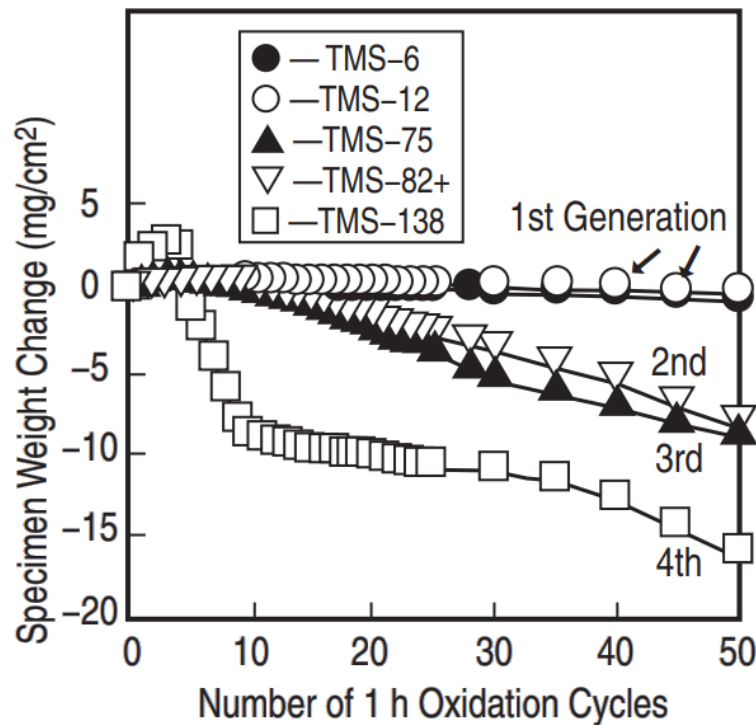


Figure 1.4 Oxidation performance of different generations of single-crystal superalloys (cyclic oxidation testing of 1h holding at 1100°C). Reprinted from Ref. [8] with permission of Springer Nature (Springer Nature Customer Service Centre GmbH).

Therefore, a contradiction exists in the development of superalloys for high-temperature applications, that is, the alloy composition that enhances creep strength at elevated temperature is usually at odds with the one that provides good oxidation performance. The common practice employed in the industry is to apply protective coatings on the mechanically optimized superalloys [1], so that the specifically designed coatings can tackle the oxidation attack while the underlying superalloys can satisfy the high-temperature mechanical requirements.

Three different types of coatings are used as protective coatings for superalloy applications, i.e., diffusion coatings, overlay coatings, and thermal barrier coatings. Diffusion coatings are aluminide-type (NiAl) coatings that are developed near the surface region of the nickel-base superalloys by diffusion and chemical reaction of an externally supplied Al with the Ni in the superalloys. The increased aluminum concentration in the aluminide coatings helps establish and maintain a protective alumina layer on the surface, and thus improves the oxidation performance of the superalloys. Diffusion aluminide coatings are also known for their

capability of mass production at relatively inexpensive costs, and the non-line-of-sight process to coat components with complex shapes. However, the ways diffusion coatings are produced lead to certain inherent drawbacks, such as degradation of the surface region of the superalloys, the dependence of coating performance on the substrate compositions, and fixed composition of the NiAl coatings that excludes the possibility of coating composition design to meet different application conditions.

Overlay coatings are developed to address the issues found in diffusion coatings. In contrast to diffusion aluminide coatings, overlay coatings are applied externally on the superalloy surface. Since the deposition of overlay coatings minimizes the modification of the superalloy substrate, the composition, microstructure, and mechanical properties of the superalloy substrate can be preserved as the designed characteristics. MCrAlY-type materials, where M stands for Ni and/or Co, have become the standard overlay coatings for gas turbines applications. The advantages of MCrAlY coatings, such as adaptable coating composition, flexible coating thickness, and independent coating performance from substrate nature, make it possible to optimize the composition and microstructure of the substrate and coating individually so that an optimum combination can be achieved to accommodate a wide variety of application conditions. MCrAlY coatings also have a high melting temperature and a low ductile-brittle transition temperature (DBTT) over diffusion coatings, which is desirable for high-temperature applications. The disadvantages of MCrAlY coatings, on the other hand, are the line-of-sight manufacturing process nature and the relatively high manufacturing process cost.

Another approach to protect the superalloy components from oxidation is the application of a thermal barrier coating (TBC) [9]. Conventionally, the TBC is a coating system that comprises two different layers of materials on the superalloy component surface. The outer layer is a low thermal conductivity ceramic topcoat that thermally insulates the underlying metallic components from the hot operating gases, allowing a primary temperature drop between the hot gases and the metallic components. Beneath the topcoat lies a dense metallic bond coat that is in direct contact with the superalloys and serves as an interconnecting bonding layer between the superalloys and the topcoat. Upon exposure to elevated temperatures, a third layer, the thermally grown oxide (TGO) forms at the topcoat/bond coat interface as a result of high-temperature oxidation of the metallic bond coat. As the ceramic topcoat is essentially oxygen

transparent [10], the bond coat and TGO layers in the TBC act as the physical barrier to prevent the intruding oxygen from reacting with the superalloys underneath. As such, diffusion aluminide coatings, or MCrAlY overlay coatings, are commonly employed as the bond coats in TBCs.

The primary use of TBCs, in conjunction with the development of sophisticated cooling technologies, is to reduce the surface temperature of the underlying superalloy components so they can survive further gas temperature increases. These technological solutions have enabled the pursuit of gas turbines with greater efficiency and performance at operating temperatures as high as 1600 - 1700°C, well above the melting temperature of the superalloys (~1300°C) [10-15]. Alternatively, the application of TBCs can help alleviate the severe conditions confronted by the bond coat owing to the temperature reduction (100°C to 300°C) through the low thermal conductivity ceramic topcoat [10]. As high-temperature oxidation is an ionic diffusion-controlled process and temperature has a profound influence on diffusion coefficient and diffusion rates [7], the reduction in temperature on the bond coat surface significantly lowers the transport rate of metallic cations and oxygen anions and thereby reduces the overall kinetics of oxidation.

Understanding the oxidation behaviour and mechanisms of bond coats at elevated temperatures is of prime importance in developing reliable and durable TBCs, since premature failures of TBCs, as a result of topcoat delamination and spallation, are directly related to the TGO growth characteristics and stress accumulations near the topcoat/TGO and TGO/bond coat interfaces. A continuous, uniform, dense, slow-growing, and chemically stable TGO layer at high temperatures is considered ideal and is believed to improve the oxidation performance of the bond coat by suppressing the diffusion of metallic elements and oxygen through the TGO layer; reducing the rates at which the underlying metallic components are oxidized. Aluminum oxide, specifically α -Al₂O₃, is well known for its high melting temperature, excellent stability at high temperatures, slow growth rate and low oxygen diffusivity, which satisfies most of the requirements for an ideal TGO scale. As such, bond coats are specifically designed and engineered to contain a considerable amount of aluminum in the composition so that selective oxidation of aluminum in the form of α -Al₂O₃ can be promoted in preference to other oxides such as NiO, CoO, Cr₂O₃ or spinel-type oxides. Therefore, the primary purpose of the bond

coat is to ensure the formation and maintenance of a continuous and uniform α -Al₂O₃ TGO scale.

Various factors can have a profound influence on the growth and integrity of the TGO scale, such as (i) the composition and microstructure of the coating and the substrate [16-18], (ii) the porosity level, oxide content, and surface finishing of the as-prepared coatings [19-24], and (iii) the conditions of the operating environment [25, 26]. As different manufacturing processes can affect the microstructure, surface finishing, and sometimes composition (due to in-process oxidation), the resultant coatings may have significantly different oxidation performances [25, 27, 28]. Therefore, for a specific combination of coating-substrate system, manufacturing process and exposure condition, the oxidation behaviour of the coatings must be characterized individually.

MCrAlY coatings are typically manufactured by traditional thermal spray processes such as air plasma spray (APS) and high-velocity oxygen-fuel (HVOF) due to their competitive cost and capability of depositing a wide range of materials in comparison with alternative manufacturing processes such as electron beam physical vapour deposition (EB-PVD). In thermal spray processes, feedstock materials initially in the form of powder are melted or partially melted by means of a plasma jet, electric arc or combustion flame and accelerated through a nozzle to achieve the desired particle velocity. The molten droplets, or semi-molten particles, are accelerated to high velocities then flatten with characteristic splat morphology upon impact on the substrate. These splats adhere, agglomerate, and rapidly solidify to produce a coating.

Since high temperatures and fast cooling rates are involved in thermal spray processes, several undesirable features are inevitably present in the coatings. Firstly, in-flight oxidation of the feedstock materials due to the high process temperature introduces oxide stringers in the coatings and consequently leads to low cohesive strength and appreciable porosity levels. This oxidation problem occurs in processes such as air plasma spray (APS) and HVOF, where particles are exposed to a high-temperature and oxygen-rich atmosphere, but it can be effectively resolved by controlling the process environment in some processes, such as low-pressure plasma spray (LPPS) and vacuum plasma spray (VPS). However, this largely increases cost due to the complication of the equipment and operation in these processes and

is only used for applications where the cost can be justified. Secondly, contraction of the deposited splats upon solidification introduces tensile residual stresses to the coatings and increases the level of porosity and the probability of cracks initiation/propagation. Thirdly, melting and solidification of the feedstock materials promote grain growth in the coatings, which can have adverse effects on certain applications when fine grains or even nano-grains are required. It has been demonstrated that the presence of these microstructural features (oxides inclusion, porosities, cracks, and coarse grains) can significantly reduce the oxidation performance of the protective coatings; therefore, it is necessary to minimize and ideally eliminate the defects through refinement of the process parameters and development of innovative techniques. As the defects are directly associated with the elevated temperature, reducing the process temperature is thus critical and appealing to produce coatings with improved performance.

Cold gas dynamic spray (simply cold spray or CS) is the newest member of the thermal spray process family and a supplement to the traditional thermal spray processes. It features low particle temperatures and high particle impact velocities and has been well developed in terms of process, equipment, and applications during the past two decades. As opposed to thermal energy used in thermal spray processes, CS employs kinetic energy to produce coatings. The absence of excessive heating in CS minimizes in-process powder oxidation and hence reduces the oxide inclusion in the coatings, and the high-velocity impact induces severe plastic deformation that results in dense coating microstructure with typically compressive residual stresses [29, 30]. These coating characteristics are beneficial to the performance of MCrAlY coatings, making CS a promising technique for manufacturing MCrAlY coatings used either as stand-alone overlay coatings or as the bond coats for TBC applications [31-33].

1.2 Motivation and General Objectives

The research presented in the thesis is part of an ongoing project at the uOttawa Cold Spray Research Laboratory that focuses on developing low-cost/high-performance MCrAlY coatings by means of the cold spray (CS) technique. Previous studies have demonstrated that MCrAlY coatings can be successfully deposited by the CS technique and that the CS coatings could potentially outperform their counterparts produced by traditional thermal spray processes, such

as air plasma spray (APS), high velocity oxygen fuel (HVOF), and low-pressure plasma spray (LPPS) [24, 31-40]. Most of these studies used helium as the process gas due to its favourable thermophysical properties that lead to high gas velocities, high particle impact velocities and deposition efficiencies (DE) [41-44]. However, helium is a non-renewable sensitive resource that is costly and not always readily available, and commercial helium recovery systems constitute a major capital investment and still require helium supply as the helium recovery process is not 100%. As such, most aerospace companies do not allow the use of helium in their production facility due to potential shortages and price fluctuations. There is an economical and strategic need to explore CS deposition of MCrAlY coatings using renewable and cost-effective gases such as nitrogen.

CS is a highly material-dependent coating deposition technique [45]. The feedstock powder and substrate material combination can greatly affect the powder deposition behaviour and resulting coating characteristics [46]. Studies on CS MCrAlY coatings mainly involved CoNiCrAlYs [31-33, 35, 38, 39, 47, 48] and NiCoCrAlYs [49-52]. MCrAlY+X (X can be Ta, Re, Si, or Hf) coatings have rarely been produced by CS [24, 34, 40], although they have been widely investigated using other spray processes due to their excellent high-temperature oxidation performance [53-55]. Furthermore, although single-crystal nickel-base superalloys have gained wide applications in turbine blades due to their superior thermomechanical properties [2], the substrates used in CS MCrAlY coatings studies are mostly polycrystalline nickel-base superalloys, such as IN738 [24, 32, 34, 36], IN718 [37, 38], and IN625 [33, 39]. The effects of CS particle bombardment on the microstructure of single-crystal superalloys as well as the effect of this substrate material on the CS deposition of MCrAlY+X coatings are unknown.

The general objective of the thesis research is **to characterize CS deposition on a single-crystal nickel-base superalloy (CMSX-4) and to develop low-cost NiCoCrAlTaY coatings with improved coating properties and performance using the CS technique**. To achieve this objective, the following specific studies will be performed:

- 1) Use cost-effective nitrogen gas instead of helium to reduce the process gas cost. Examine the effects of different substrate materials and preparation, powder feedstock variation on the CS deposition of NiCoCrAlTaY coatings.

- 2) Explore recycling of the feedstock powder to overcome increasing powder waste and costs associated with low deposition efficiency when nitrogen is used.
- 3) Develop nanocrystalline MCrAlY coatings to improve coating performance. Explore in-situ CS production of such coatings directly from conventional powders to simplify the conventional two-step approach, where a powder nanocrystallization process is needed prior to coating deposition.
- 4) Evaluate the isothermal oxidation performance of the CS nanocrystalline NiCoCrAlTaY coatings deposited on the CMSX-4 single-crystal superalloy substrate.
- 5) Investigate the influence of processing sequences, i.e., varying the relative order of CS coating deposition and heat treatments required for the CMSX-4 single-crystal superalloy, on the CS NiCoCrAlTaY coating characteristics and oxidation performance.

1.3 Outline of the Thesis

The thesis is structured into eight chapters. A summary of each chapter is briefly described here.

Chapter 1 presents general information on the background of the thesis topic. The development of nickel-base superalloys for critical gas turbine components is reviewed in terms of processing, microstructural, and compositional evolutions. The need for protective coatings on the superalloys is rationalized. Different types of protective coatings as well as several factors that affect their oxidation performance are summarized. This is followed by a brief description of the motivation and general objectives of the thesis research.

Literature relevant to the thesis research is reviewed in Chapter 2. Fundamentals regarding the oxidation process and the desirable oxidation performance are first introduced, followed by the justification of MCrAlY materials and a description of the growth and failure mechanism of the protective scale. The effects of some performance-controlling factors for MCrAlY coatings are explained based on available literature. Overview of the CS process as well as gas dynamics principles and bonding mechanisms pertinent to cold spray technique are also included.

Chapter 3 outlines the specific studies carried out in the thesis. The motivation and objective

for each study are elaborated in this chapter. This chapter demonstrates the importance of the specific studies in satisfying the general objective of the thesis research.

Chapter 4 presents the experimental approach for coating preparation and examination. This includes a description of the feedstock materials employed, the procedures followed in the coating preparation, as well as the equipment and setups used for oxidation testing and materials characterization.

Chapter 5 provides the results obtained regarding coating preparation and characterization, powder recycling, and cost analysis of the CS process. Several factors affecting the coating deposition, such as gas nature, substrate material type and preparation, and feedstock powder variation, are investigated. A peer-reviewed journal article is included in this chapter to present the microstructures and properties of NiCoCrAlTaY coatings produced using nitrogen and helium as well as the CS process economics that considers the benefits of powder recycling.

Chapter 6 proposes a CS process that can produce in-situ nanocrystalline NiCoCrAlTaY coatings while using conventional commercial powders. The results are presented in the format of two peer-reviewed journal articles that have been published in the journal of Surface & Coatings Technology. The processing-structure-properties-performance relationship of CS MCrAlY coatings on single-crystal Ni-base superalloy substrates is examined, with the first article focusing on the process analysis and microstructure characterization while the second presenting the isothermal oxidation performance at 1100°C.

Chapter 7 explores different processing sequences of superalloy heat treatments and CS coating deposition. Effect of substrate conditions on the coating microstructure and properties are investigated, and coating characteristics after subsequent heat treatments are characterized. Short-term isothermal oxidation performance of the CS NiCoCrAlTaY coatings produced using different sequences are presented in this chapter.

Finally, Chapter 8 summarizes the findings obtained in the thesis research. Future work is suggested to further explore CS deposition of MCrAlY coatings and improve the performance of such coatings used in gas turbine applications.

Chapter 2 Literature Review

This chapter reviews the available literature that is relevant to the thesis topic. Fundamentals regarding the oxidation process and the desirable oxidation performance are introduced first, followed by the justification of the MCrAlY composition as the materials of choice for high-temperature oxidation resistance applications. Growth and failure mechanisms of the protective scale are reviewed as well as some factors that can greatly affect the performance of the MCrAlY coatings, including the exposure conditions under which the coatings are employed, the variations in the coating (e.g., composition, microstructure, surface finishing), and the manufacturing processes by which the coatings are prepared. Overview of the cold spray process, gas dynamics principles and bonding mechanisms pertinent to the cold spray technique are presented at the end of this chapter.

2.1 Fundamentals of Oxidation and Resistance

Most metallic materials are unstable at elevated temperatures, especially approaching their melting temperatures. Corrosion of these materials, such as oxidation, nitridation, carburization, sulfidation, and hot-corrosion, will inevitably occur over a wide range of conditions and the corrosion products cannot be avoided [56]. Technical solutions for metallic material applications in such conditions, therefore, focus on the rate control of the corrosion reactions to reduce the metal consumption.

To control the reaction rates, the corrosion products must be formed in such a way that they can act as a barrier between the metallic materials and the environment, impeding the transportation of the reactants and thus reducing the overall rates. Among all the corrosion types, only oxidation can promote sufficiently resistant scales as the diffusion barrier [56]. Therefore, the key answer to the corrosion resistance issues is the formation and maintenance of a protective oxidation scale so that an acceptably slow rate of corrosion reaction can be achieved.

Oxidation, which occurs in all environment of sufficiently high oxygen (O_2) partial pressure, can be simplified into the following general reaction,



where M stands for metal component and M_xO_y for the resultant oxide.

The initial formation of the oxide on the metal surface starts with the adsorption of oxygen molecules, which dissociate and react with the metal to form oxide nuclei. As the process proceeds, increasing surface areas are covered by the nuclei and eventually a continuous thin oxide scale is established on the surface. At this point, the physical barrier can be recognized between the metal and the gas, as schematically shown in Fig. 2.1.

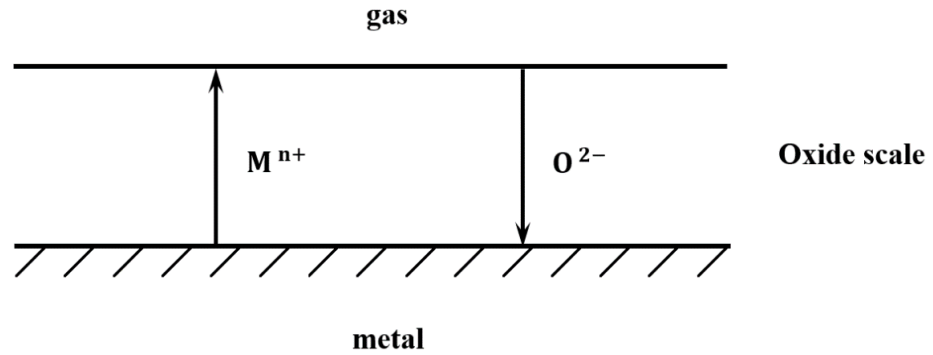


Figure 2.1 Schematic of a continuous oxide scale and diffusion of the reactants

Given that oxides are ionic in nature, ongoing oxidation reaction then requires the solid-state diffusion of either the metallic cation or oxygen anion through the scale to continue. For different types of oxide scales, the rates at which the diffusion and reaction proceed can be different. If the phase-boundary (gas/scale or scale/metal) reaction is the rate-determining step while diffusion through the scale is rapid and independent of the scale thickness, linear growth kinetics of the scale can be observed [56],

$$\frac{dX}{dt} = k'_l \quad \text{or} \quad X = k'_l t \quad (\text{Eq. 2.2})$$

where X is the scale thickness, k'_l is the linear rate constant, and t is the time. In contrast, if the oxidation rate is determined by the diffusion of the reactants through the dense scale, a parabolic oxidation kinetics results. According to Fick's first law for a steady-state diffusion, the diffusion flux (J) is proportional to the concentration gradient through the following

expression [7]

$$J = -D \frac{\Delta C}{X} \quad (\text{Eq. 2.3})$$

where D is diffusion coefficient, and $\Delta C/X$ is the concentration gradient through the scale. Assuming all the diffused species contribute to the growth of the scale, the flux can also be approximated by the rate of scale thickening and the oxide density (ρ_{ox}),

$$J = \rho_{ox} \frac{dX}{dt} = -D \frac{\Delta C}{X} \quad (\text{Eq. 2.4})$$

Reorganizing equation 2.4 and replacing $-D \Delta C / \rho_{ox}$ by a constant k'_p yield the well-known parabolic growth kinetics of the dense scale,

$$\frac{dX}{dt} = \frac{k'_p}{X} \quad \text{or} \quad X^2 = 2k'_p t \quad (\text{Eq. 2.5})$$

where k'_p is referred to as the parabolic rate constant. Similarly, the rate laws (linear and parabolic) derived for thickness growth can also be expressed in the form of scale weight gain by oxidation.

$$\text{Linear:} \quad \frac{\Delta W}{A} = k''_l t \quad (\text{Eq. 2.6})$$

$$\text{Parabolic:} \quad \left(\frac{\Delta W}{A} \right)^2 = 2k''_p t \quad (\text{Eq. 2.7})$$

where $\Delta W/A$ is the weight gain per unit area, k''_l and k''_p are the respective rate constants. The two characteristic oxidation kinetics can be compared schematically in Fig. 2.2.

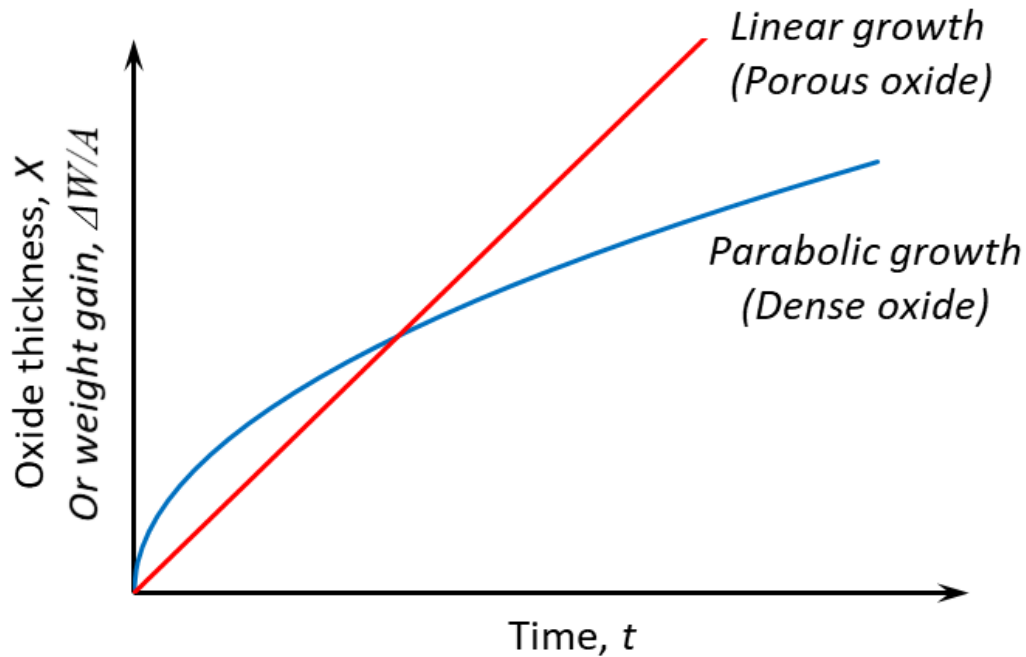


Figure 2.2 Schematic of linear and parabolic growth of oxide scales

Parabolic growth kinetics of a dense oxide is desirable. As the dense scale thickens, diffusion through the scale gradually slows down and the oxidation rate decreases accordingly. This also implies that the rate at which the metal is consumed diminishes with time. In contrast, the linear growth of a porous oxide results in a constant rate of metal consumption at all times.

In summary, dense oxides with low parabolic rate constants represent low metal consumption rates at elevated temperatures and are therefore preferred for oxidation resistance application. Figure 2.3 shows the parabolic rate constants over a range of temperatures for some typical oxides [57].

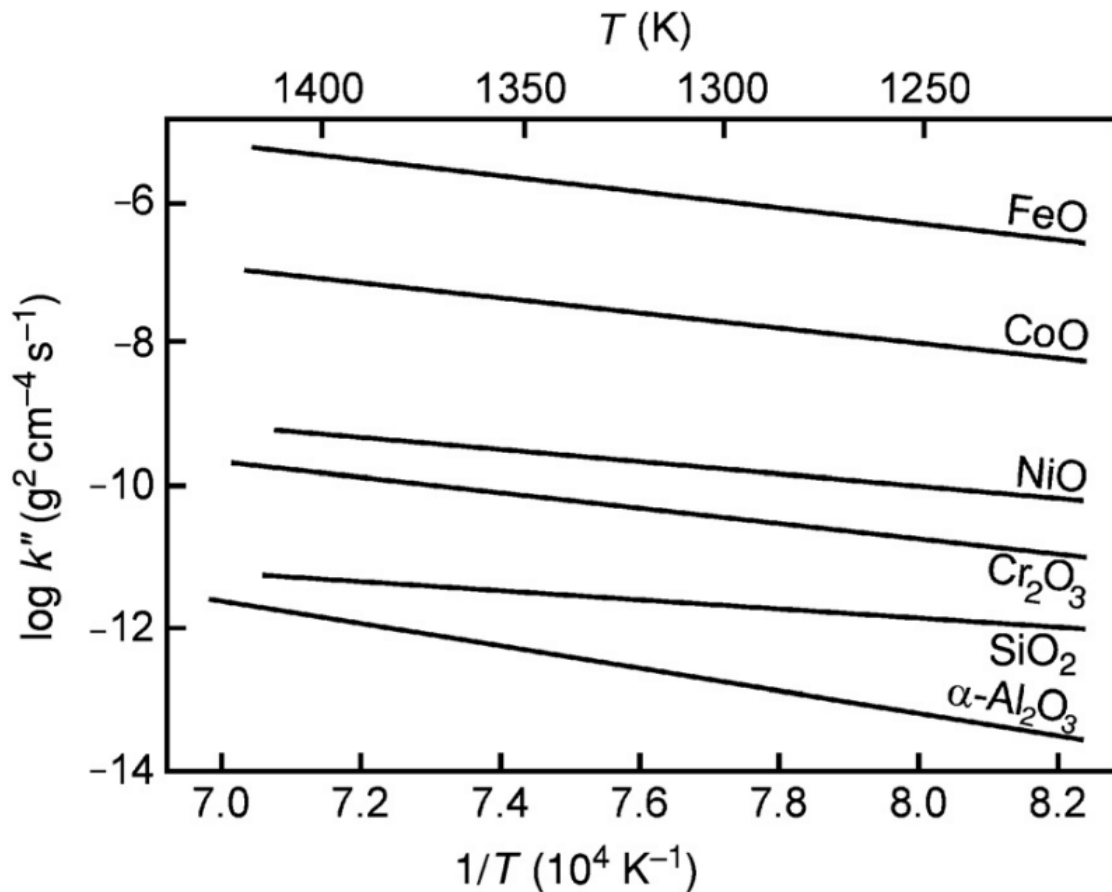


Figure 2.3 Order-of-magnitude parabolic rate constants for the growth of several oxides. Reproduced from [57] with permission of Cambridge University Press through PLSclear.

Alumina (especially $\alpha\text{-Al}_2\text{O}_3$), silica (SiO_2), and chromia (Cr_2O_3) exhibit the lowest parabolic rate constants among other oxides. They have attracted extensive technical attention as protective scales on high-temperature oxidation-resistant materials. At temperatures above 850°C to 900°C , Cr_2O_3 may form the volatile species, CrO_3 , limiting the long-term application of Cr-containing alloys at high temperatures [58]. Although SiO_2 is thermodynamically very stable in oxygen-rich environments at high temperatures, severe susceptibility of the oxide to mechanical failure and the formation of the volatile SiO in environments of low oxygen partial pressure also restrict the SiO_2 -based applications [58]. This relative stability of the three oxides in terms of thermodynamics and kinetics can also be seen in Fig. 2.4, where some typical oxides are placed on a map of scale growth rates versus the thermodynamic stability [59].

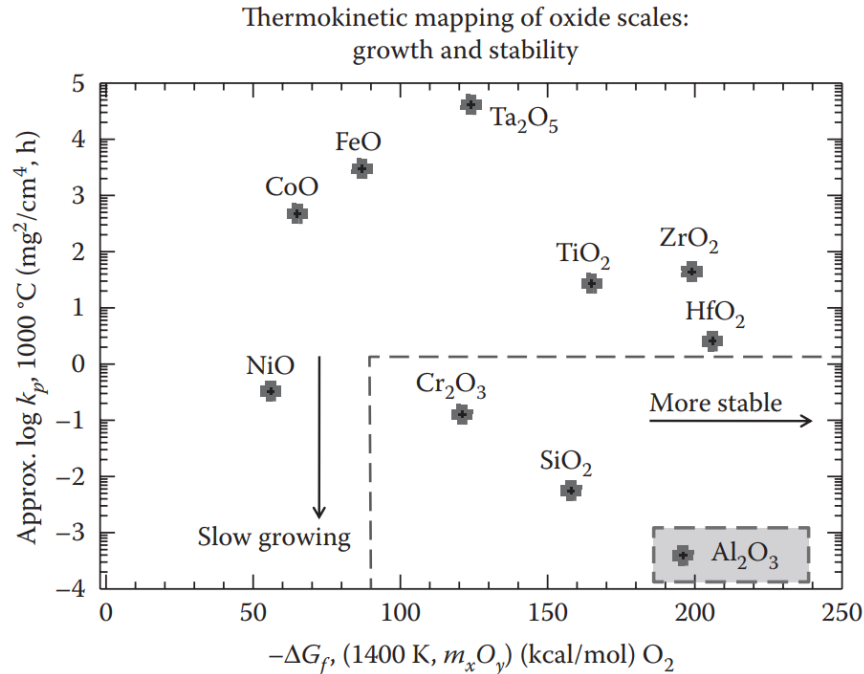


Figure 2.4 Thermokinetic map of various oxide scales showing parabolic rate versus free energy of formation. Optimum performance for stable slow-growing scales in lower right. Republished from Ref. [59] with permission of Taylor & Francis Group LLC - Books; permission conveyed through Copyright Clearance Center, Inc.

It is clear from Figs. 2.3 and 2.4 that the α -Al₂O₃ scale is not only the slowest growing oxide but also among the most thermodynamically stable ones, explaining why long-term high-temperature applications are predominantly based on Al₂O₃-forming oxidation-resistant materials.

To promote and maintain the slow-growing α -Al₂O₃ scale rather than other unfavourable oxides, a sufficient concentration of aluminum must be present in the materials, enabling a continuous Al supply during application. Increasing the Al concentration to the level that imparts oxidation resistance to the materials, however, usually results in non-optimal mechanical properties at high temperatures. To tackle this issue, Al-rich coatings are generally applied on high-temperature structural materials so that they can be designed and developed separately in terms of composition, microstructure, and mechanical properties. MCrAlY overlay coatings, where M stands for Ni and/or Co, are commonly employed for this purpose and will be introduced in the next section.

2.2 MCrAlY Materials Justification

The simplest Al_2O_3 -forming systems would be the binary M-Al alloys (M is, Ni, Co, or Fe), which were introduced as diffusion coatings for oxidation resistance application in the 1910s [60] and have been applied to gas turbine components since the 1940s [61]. The inherent drawbacks of the diffusion coatings, such as brittleness of the NiAl intermetallic phase and dependence of composition and microstructure on the underlying substrates, limit the possibility of tailoring the coatings to different applications. Further investment and exploitation of the coating technologies in the 1960s led to the development of the MCrAlY overlay coatings [60]. MCrAlY coatings were derived from the binary M-Al systems and usually contain chromium (Cr), yttrium (Y) and sometimes hafnium (Hf), silicon (Si), rhenium (Re), tantalum (Ta), etc. The influence of each alloying element on the coating microstructure, properties, and oxidation performance is briefly reviewed in the following section.

2.2.1 Addition of Chromium

A significant amount of chromium, as much as 31 wt.%, is present in the MCrAlY materials [62]. It has been found that the addition of chromium to the binary M-Al systems can significantly promote the formation and maintenance of the $\alpha\text{-Al}_2\text{O}_3$ scale, as shown schematically in Fig. 2.5 using the notional ternary diagrams [59].

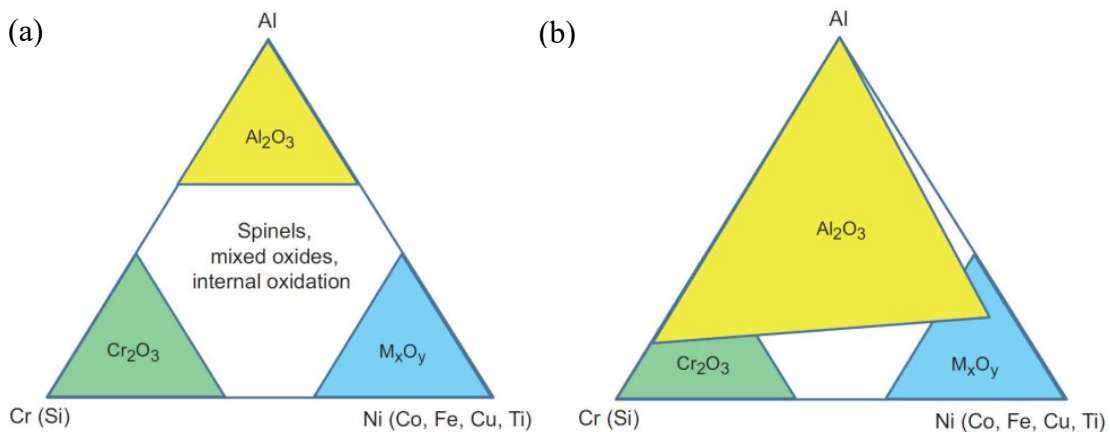


Figure 2.5 Notional ternary diagrams showing the influence of chromium addition on the scale make-up: (a) symmetric, idealized; (b) asymmetric, real. Republished from Ref. [59] with permission of Taylor & Francis Group LLC - Books; permission conveyed through Copyright Clearance Center, Inc.

Here, an enlarged field of Al_2O_3 oxide is realized when adding chromium to the alloy (Fig. 2.5b) in contrast to the idealized single oxide fields near the corresponding corners of the single elements in Fig. 2.5a with the assumption that all components behave individually and similarly (Fig. 2.5a). The diagrams also imply the capability of establishing the Al_2O_3 scale at considerably low Al concentration with the help of Cr addition. The mechanism by which chromium enhances the Al_2O_3 formation is well accepted as a general principle, the third-element effect [63]: the third element with an oxygen affinity between the two existing elements can effectively promote the establishment of the protective scale at reduced levels of the oxide-forming element in the alloy. The third element Cr is believed to act as an oxygen getter and to minimize internal oxidation of Al, allowing the outward diffusion of Al from the bulk to develop a continuous scale on the surface.

2.2.2 Addition of Reactive Elements

There are several effects, possibly separately, at play when a small amount of reactive elements (usually around 0.5 wt.%) is added to the M-Cr-Al systems, such as improvement in scale adhesion, decrease in oxidation rate and modification of scale microstructure.

Compressive residual stresses can arise in the scale due to the mismatch of thermal expansion coefficients between the coating and the oxide. The stresses maximized at ambient temperature can be sufficient to cause cracking and spalling for weakly bonded scales [64, 65]. The addition of reactive elements, typically yttrium (Y), has been demonstrated to improve the scale adhesion and alleviate the spallation issues. One of the mechanisms that have been proposed is the prevention of sulphur (S) segregation. Sulphur is a detrimental element to the oxidation performance even at extremely low levels, e.g., 1.5 parts per million weight (ppmw), as shown in Fig. 2.6 [66].

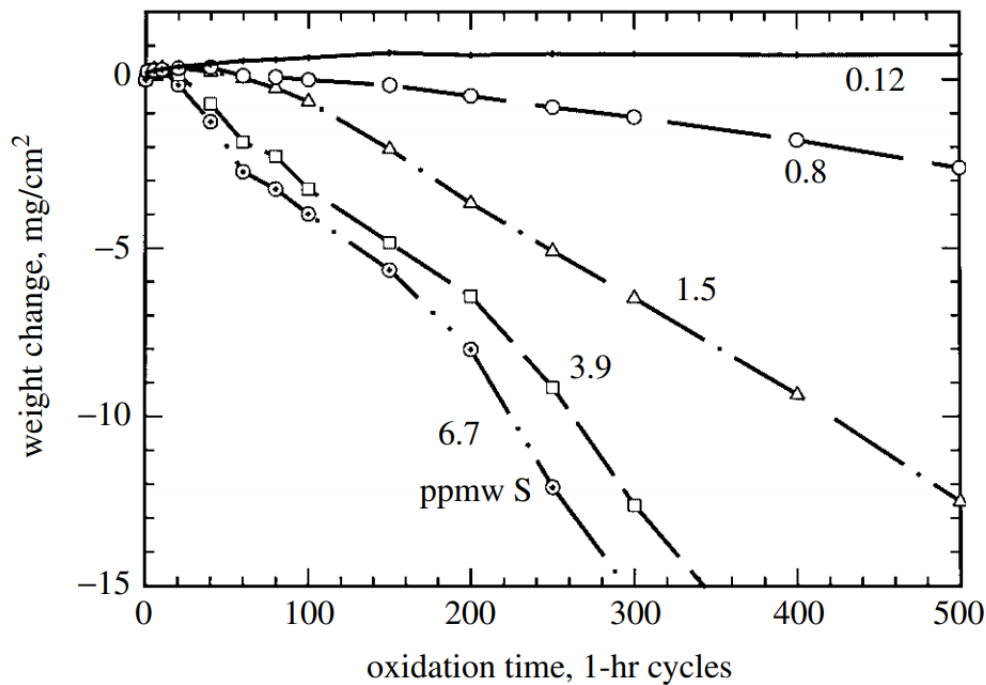


Figure 2.6 Effect of sulfur content on the oxidation performance of alloy PWA1480. Reproduced from Ref. [66] with permission of John Wiley and Sons.

The presence of sulphur, possibly chlorine and phosphorus as well, can segregate to the metal-scale interface and weaken the interfacial bond strength [67-69]. With increasing S contents, the oxidation performance of a first-generation single-crystal superalloy PWA1480 significantly deteriorates. Yttrium is a strong sulphide former and can capture the free sulphur in the form of stable refractory sulphide when present in the M-Cr-Al materials [70].

In addition to the perspective of sulphur segregation, the improvement of scale adhesion by yttrium addition has also been elucidated based on chemical bonding and mechanical pegging. Anderson et al. [71] reported that the alumina scale could be bonded very firmly to the yttrium aggregated at the surface of the bulk materials, leading to increased interfacial bond strength. Some studies [72-75] observed the internal formation of yttrium oxides with elongated shapes at the metal-scale interface and attributed the increased scale adhesion to the mechanical pegging or keying of these yttrium oxides.

Reactive elements have also been found to affect the overall oxidation rate, although not significantly. During early stages of oxidation, oxides of the reactive elements may act as sites

of preferential nucleation of the protective oxide and facilitate the transformation of transient alumina (e.g., γ - Al_2O_3 , θ - Al_2O_3) to α - Al_2O_3 [76], but it seems this effect depends largely on the amount of yttrium addition. When small amounts of yttrium are present, the grain growth of the metastable Al_2O_3 is hampered and heterogeneous nucleation of α - Al_2O_3 proceeds, resulting in accelerated phase transformation. However, the transition may be inhibited upon increasing the yttrium concentration to some critical values [68]. Once the protective α - Al_2O_3 scale is established, reactive elements seem to play an important role in the transport behaviour of oxygen and aluminum through the alumina scale. Details of the transport mechanism in the α - Al_2O_3 scale as well as the effect of reactive elements will be provided in section 2.3.1.

Microstructure and morphology of the alumina scale developed on M-Cr-Al-Y systems may also differ from those on materials without reactive elements addition. Scale with columnar grain and finer grain sizes were reported with the addition of yttrium [77], probably because of the yttrium effect on the transport processes in the scale. As outward transport of Al^{3+} ions is suppressed and inward transport of O^{2-} is promoted by the presence of yttrium oxide in the scale, the formation of new oxide primarily occurs at the metal-scale interface rather than within the bulk scale. Compressive growth stresses are therefore prevented, and lateral growth of the scale is avoided, leading to less convoluted scale morphology and smoother metal-scale interface in comparison with yttrium free scales [78].

Other reactive elements such as lanthanum (La) and cerium (Ce) are found to have a similar effect as yttrium in terms of improving scale adhesion and oxidation performance, although they may be slightly more detrimental to ductility at high temperature compared with yttrium [54, 79, 80]. Improved oxidation performance was also reported for MCrAlY systems with the addition of hafnium (Hf), silicon (Si), and rhenium (Re) [53-55].

2.2.3 Variations of MCrAlY systems

A variety of MCrAlY compositions exists due to the different alloying elements and various concentrations of each element. The performance of these coatings depends not only on the specific composition but also on their microstructure as well as the environment in which they are tested. However, several general trends have been recognized.

NiCrAlY coatings are excellent materials for high-temperature oxidation resistance

applications but they are susceptible to hot corrosion; CoCrAlY systems perform well in hot corrosion environments but need improvement on the ductility [81]. A compromise between these two systems yields the NiCo- and CoNi-based MCrAlY compositions, which have balanced oxidation and hot-corrosion resistance with NiCoCrAlY focusing on the oxidation performance and CoNiCrAlY on the hot-corrosion. For severe hot-corrosion application, MCrAlY with higher chromium is employed. Figure 2.7 presents a convenient way to compare these MCrAlY systems schematically [82].

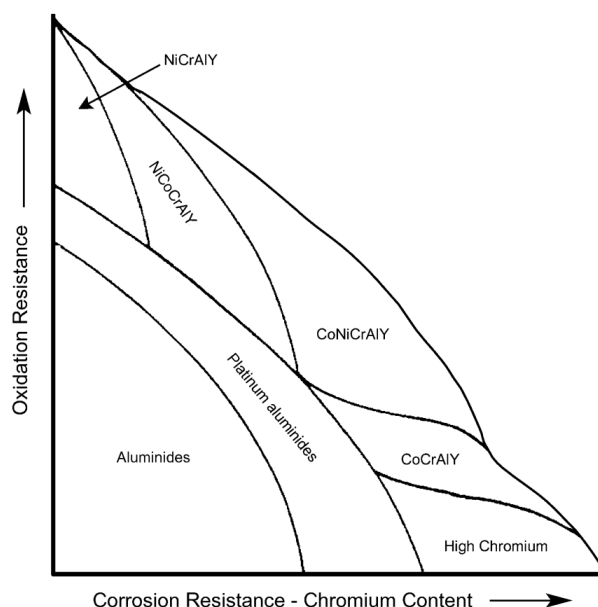


Figure 2.7 Optimum coating compositions in relation to oxidation and hot-corrosion resistance. Reprinted from [82] with permission from Elsevier.

2.3 Scale Growth and Failure Mechanism

Simplified descriptions of oxide formation and growth characteristics were introduced in section 2.1. The real process of scale growth in MCrAlY coatings, however, is much more complicated. Understanding of the process inevitably involves questions such as which of the reactant species (metallic cation or oxygen anion) are predominant in the transport process, which paths (oxide lattices or grain boundaries) do these species preferably take, and what are the effects of the alloying elements, particularly the reactive elements. This section provides an overview of the findings on the studies of scale growth and failure mechanism.

2.3.1 Transport Mechanism of Oxide Growth

Once the protective $\alpha\text{-Al}_2\text{O}_3$ scale is established, the rate of oxide growth is controlled by the transport of the reactants (Al^{3+} and O^{2-}) through the scale. Extensive research has been carried out in determining the transport species and transport paths during alumina growth, and different experimental approaches have been used to study the transport process, such as inert marker, oxygen isotope tracers.

Inert marker, as the name suggests, is a layer of metallic marker (e.g., platinum or gold) that are placed on the surface of the MCrAlY materials prior to oxidation and are stable (inert) under the oxidation condition. The transport direction or transport species can thus be concluded by examining the location of the inert marker after oxidation. If the marker is found at the scale-gas interface, it implies inward diffusion of oxygen occurs and new oxides are formed below the marker. On the contrary, outward diffusion of aluminum leads to the formation of new oxides on top of the inert marker, resulting in an intermediate position of the marker between the metal and scale. Several studies [83, 84] employed this method and concluded that the predominant transport mechanism is the inward oxygen diffusion, although outward transport of aluminum may provide appreciable contributions in some cases. These results, however, may not be appropriate for interpreting the transport processes involved in high-temperature oxidation because they only confirm that oxygen, instead of aluminum, is the main transport species through the inert marker, not necessarily the oxide scale. In the case that the marker flows along with the newly-formed oxide rather than sticking to it, as observed/suggested by [85], the actual transport mechanism through the alumina scale is not conclusive since either inward diffusion of oxygen or outward diffusion of aluminum through the scale is possible.

Detailed studies of the transport process during alumina growth have been performed using oxygen isotopic tracers [86, 87]. This method usually involves two-stages oxidation, first in an environment of $^{16}\text{O}_2$ to establish a layer of alumina and then in $^{18}\text{O}_2$ to investigate the diffusion process. If ^{18}O ions are located below the previously formed alumina, inward diffusion of oxygen can be concluded. Conversely, outward aluminum diffusion can be confirmed if the ^{18}O tracer is found on top of the initial alumina. A combination of the two transport modes would result in the distribution of ^{18}O ions within the scale. The theory is reasonably simple;

however, the results from these isotopic studies somehow lead to confusion. Some researchers [86] identified inward oxygen diffusion as the primary transport mechanism, while others reporting that either outward aluminum diffusion predominates [87], or a concurrent diffusion of aluminum and oxygen occurs [88]. Stott [89] pointed out that the potential formation of transition alumina phases (e.g., γ - Al_2O_3 , θ - Al_2O_3) may play a role in these misleading isotopic studies. It is likely that γ - Al_2O_3 and θ - Al_2O_3 grow by outward diffusion of aluminum, but inward oxygen diffusion dominates for α - Al_2O_3 growth.

Isotopic tracers (^{18}O and ^{26}Al) have also been used to quantify the diffusion coefficients of oxygen and aluminum in the Al_2O_3 scale. The bulk diffusivity data, summarized by Heuer et al [90] from available literature, are presented in Fig. 2.8.

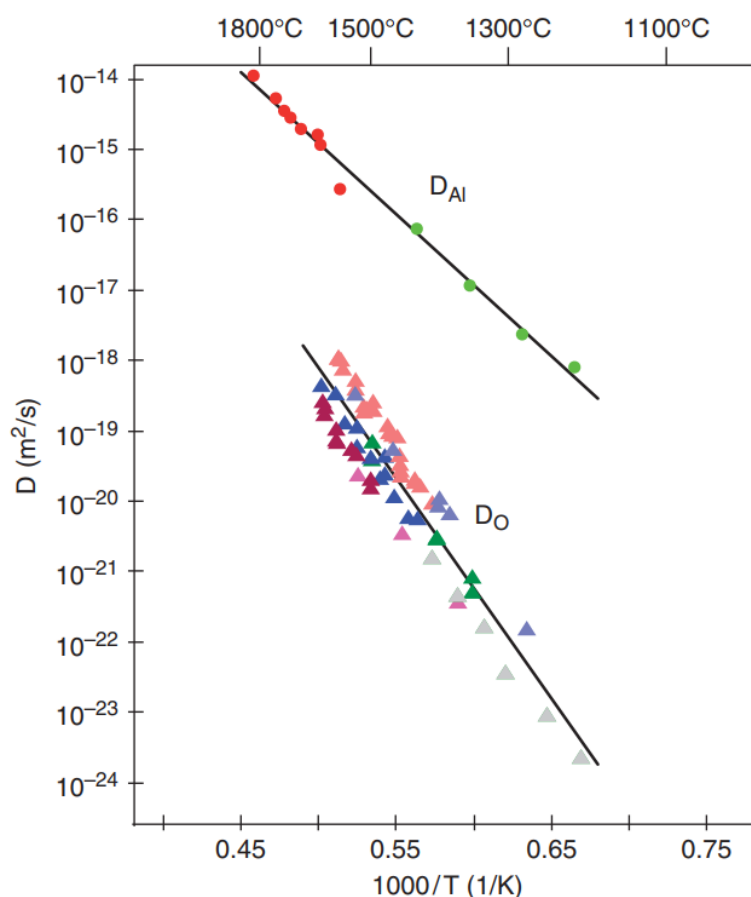


Figure 2.8 Bulk diffusivity data for oxygen and aluminum diffusion in Al_2O_3 . Adapted from [90] with permission of John Wiley and Sons.

Apparently, the lattice diffusion of aluminum is much faster than that of oxygen in the scale. If only lattice diffusion is involved during alumina growth, the predominant transport species would simply be the outward transport of aluminum. However, the rates at which alumina thicken during oxidation experiments were generally several orders of magnitude larger than the rate calculated from the lattice diffusion of aluminum [79]. This implies that the growth of the alumina scale must be controlled by some forms of short-circuit diffusion, e.g., via grain boundaries or dislocation networks, rather than the lattice diffusion based on the point defect mechanism. The contribution of grain-boundary diffusion was confirmed by existing literature [91, 92], when comparing the self-diffusion coefficients of oxygen in both single crystal and polycrystalline oxides.

The enhanced grain-boundary diffusion was also confirmed recently by Abbasi et al [93] using a high-resolution time-of-flight secondary ion mass spectrometer (TOF-SIMS). Evidence of ^{18}O tracers was clearly shown at the grain boundaries as well as at the metal-scale and scale-gas interfaces after the two-stage oxidation (first in $^{16}\text{O}_2$ then in $^{18}\text{O}_2$), indicating a concurrent diffusion of both aluminum and oxygen.

As mentioned earlier in section 2.2.2, the presence of reactive elements even at a low concentration may have a profound effect on the transport mechanism in the alumina scale. A generally accepted mechanism suggests that reactive elements and their oxides segregate at the alumina grain boundaries, resulting in a distorted grain-boundary structure with a reduced concentration of mobile point defects [94]. Outward diffusion of aluminum is therefore suppressed or eliminated, which prevents the formation of new alumina within the existing scale and allows the inward diffusion of oxygen to reach and react at the metal-scale interface. A similar model based on dynamic segregation was proposed by Pint [95]. The reactive elements in this model are considered to be mobile rather than stagnant, moving slowly along the grain boundaries of the scale from the metal-scale interface to the scale-gas interface, as schematically shown in Fig. 2.9. The outward aluminum transport is therefore blocked along the grain boundaries due to the large ionic radii of the reactive elements, similar to the explanation provided in the “stagnant segregation” model.

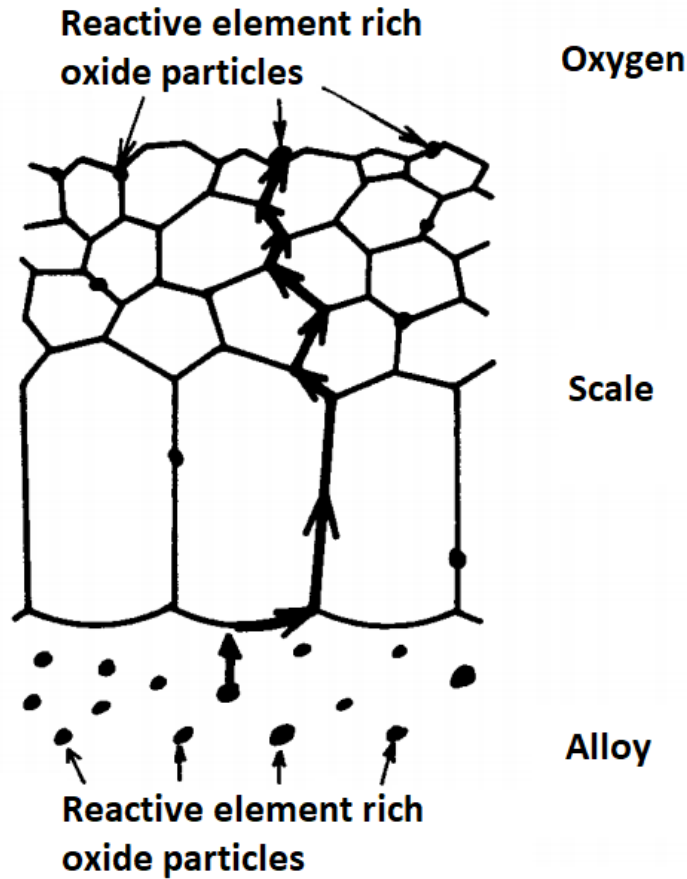


Figure 2.9 Schematic diagram showing the outward diffusion of reactive elements along grain boundaries of an α - Al_2O_3 scale. Adapted from [95] with permission of Springer Nature (Springer Nature Customer Service Centre GmbH).

As opposed to the “site blocking” mechanism, Heuer, et al. [90] demonstrated that the effect of reactive elements addition on the transport mechanism may be attributed to the change in the electronic structure of the α - Al_2O_3 , which reduces the injection of aluminum vacancy into the scale and promotes a predominantly inward oxygen diffusion and scale growth.

In summary, high-temperature oxidation of Al_2O_3 -forming materials is a very complex process, which includes many complicating factors, such as the alloy composition, temperature, oxygen partial pressure, and concentration of the reactive elements. Although it is well accepted that diffusion of the oxidation reactants (Al^{3+} or O^{2-}) chiefly occurs along with some forms of short-circuit paths, e.g., grain boundaries, the actual transport species would depend on the combined effect of the aforementioned factors.

2.3.2 Failure Mechanism

Maintenance of the protective scale is equally important as the initial establishment of the scale in the preferred form of $\alpha\text{-Al}_2\text{O}_3$, not only because the integrity of the $\alpha\text{-Al}_2\text{O}_3$ scale can effectively suppress the rate of the ongoing oxidation, but also because the scale morphology can significantly affect the stress distribution in the scale. The growth of the $\alpha\text{-Al}_2\text{O}_3$ scale is a dynamic process, in which the composition and microstructure of the scale and underlying coating are continuously evolving. Under certain circumstances, the thermally grown oxide (TGO) scale may contain oxides other than the $\alpha\text{-Al}_2\text{O}_3$, such as mixed oxides of NiO, CoO and Cr_2O_3 and spinel-type oxides $(\text{Ni, Co})(\text{Al, Cr})_2\text{O}_4$. These oxides are characterized as porous and fast-growing and should therefore be avoided or delayed from being formed for oxidation resistance applications. Generally, failure of the protective scale is considered to occur either (i) chemically when substantial amounts of fast-growing oxides are formed or (ii) mechanically when excessive spallation of the scale is realized.

Figure 2.10 schematically illustrates the process of chemical failure of the protective scale resulting from prolonged oxidation of the MCrAlY coatings.

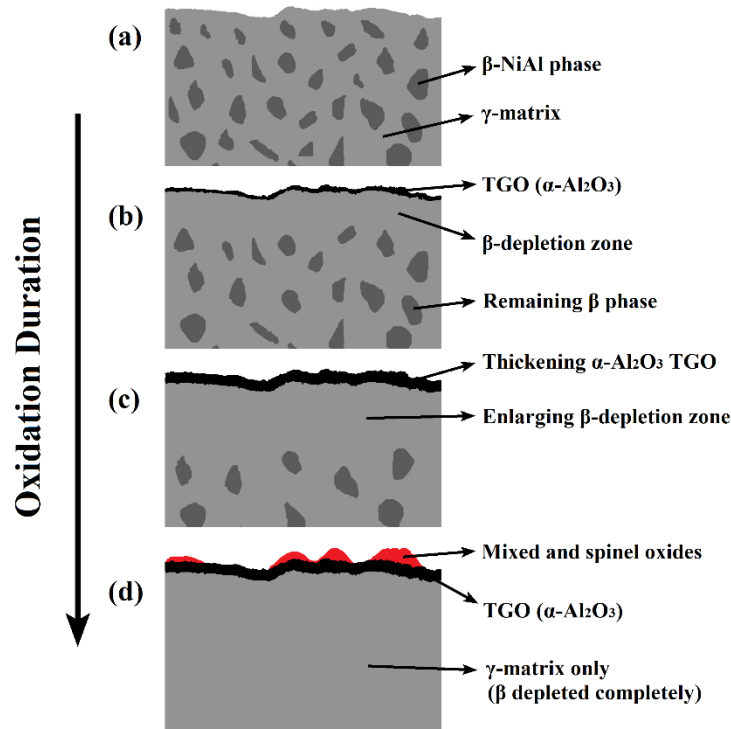


Figure 2.10 Schematic diagram showing the chemical failure of the protective scales

As-deposited MCrAlY coatings are typically composed of two phases: an aluminum-rich β -NiAl phase that is randomly dispersed in a γ - (Ni, Co) solid solution phase (Fig. 2.10a). A sufficient concentration of aluminum is usually alloyed in the MCrAlY coatings to promote the formation and maintenance of the protective layer. As such, a thermally grown oxide (TGO) scale in the form of α -Al₂O₃ typically develops on the MCrAlY surface when exposed to elevated temperatures (Fig. 2.10b). The formation and growth of the α -Al₂O₃ TGO scale consume the aluminum in the coating, resulting in a region of low-Al concentration in the γ phase near the coating surface. Given that the β phase is aluminum-rich, a gradient of Al concentration is established between the low-Al surface region and the adjacent Al-rich β phase, providing a driving force for Al to escape the lattice of the β phase and to diffuse towards the surface to replenish the Al concentration. For this reason, the β phase is often described as an aluminum reservoir, and the effectiveness of MCrAlY coatings is usually discussed based on the availability of this phase.

The continuous Al supply ensures the unremitting formation of the protective α -Al₂O₃ but inevitably induces the β -to- γ phase transformation, resulting in a β -depletion zone near the coating surface (Fig. 2.10b). With longer oxidation time, the α -Al₂O₃ TGO scale thickens and progressively consumes the Al transported from the coating, leading to an enlarging β depletion towards the center of the coating (Fig. 2.10c). Eventually, the β phase could be completely depleted from the coating, representing a situation of Al deficiency for maintaining the α -Al₂O₃ growth (Fig. 2.10d). The appearance of the mixed and spinel oxides on top of the α -Al₂O₃ scale is generally considered as the onset of the chemical failure of the protective scale (Fig. 2.10d). Alternatively, the fast-growing oxides may emerge even when an appreciable amount of β phase is still present in the coating. This is usually the case when the rate at which Al is supplied from the β phase becomes slower than the rate at which Al is consumed by the surface oxidation. The broadening β depletion increases the distance for Al to diffuse through and thus impedes the rate of Al supply, resulting in an Al concentration lower than the critical value and favouring the formation of the fast-growing oxides.

In practice, the protective α -Al₂O₃ TGO scale is often subjected to mechanical stresses, e.g., externally applied stresses, oxide growth stresses, and thermal residual stresses induced by the mismatch of the thermal expansion coefficients between the coating and the TGO scale. These

stresses may be tensile, compressive, shear, or multiaxial stresses in nature [96] and, when exceeding certain material- and geometry-depend critical values, may lead to premature mechanical failure of the protective TGO scale before the chemical failure of the scale occurs.

Tensile stresses may also be present in the TGO scale during phase transformation of transient aluminas to the stable α -Al₂O₃ owing to the accompanied volume contraction (e.g., 14.3% for γ -Al₂O₃ to α -Al₂O₃ transformation [79, 97]) and during heating periods of the metal-scale system as a result of differences in thermal expansion coefficients of the coating and the scale. The processes of cracking and spallation initiation in the protective scale caused by tensile stresses are schematically presented in Fig. 2.11.

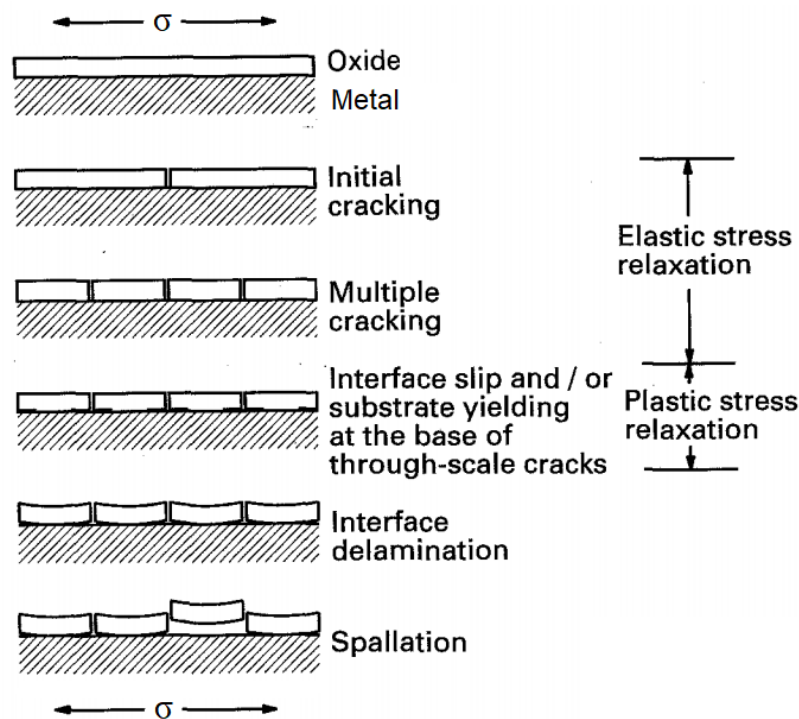


Figure 2.11 Schematic of cracking and spallation initiation in the protective scale under tensile stresses. Reprinted from Ref. [98] with permission of Springer Nature (Springer Nature Customer Service Centre GmbH).

Given the presence of defects (voids, pores, etc.) in the scale, through-scale cracks can progressively develop in the vicinity of these defects due to high stress concentration at these sites [99]. Stress relaxation in the form of scale and metal deformation is merely elastic at this stage, however, plastic stress relaxation, such as interface slip and/or substrate yielding at the

base of the cracks, may take place beyond this point depending on the adhesion of the scale and the properties of the metallic materials. The development of interfacial sliding may produce shear fracture at the oxide-metal interface and eventually lead to scale delamination and subsequent spallation [99].

Premature failure of the protective scale under tension is generally not of great concern for high-temperature oxidation resistance applications, primarily because of the self-healing effect involved in the scale cracking process during oxidation. As through-scale cracks develop in the scale, easy access of oxygen is regained via the open path, leading to accelerated oxidation kinetics than that is observed in crack-free scales (typically parabolic). If the oxide growth rate within the crack is faster than the rate at which the crack surfaces move apart, the crack is spontaneously closed and thus considered as self-healed. Schütze [100] regarded the combination of the scale cracking and healing as "pseudo-plasticity", and concluded that large apparent strains are allowed to build up in the scale by means of pseudo-plasticity at low strain rates. As such, it is possible that scales with greater deformation are macroscopically intact although the scale may have cracked several times [100]. A prerequisite for pseudo-plasticity is to maintain a sufficiently low strain rate and an adequate concentration of the elements forming the protective scale [100].

In contrast, protective scales can be very susceptible to compressive stresses, which may result in excessive scale spallation particularly under thermal cycling conditions. Aside from external stresses, compressive stresses in the scale are mainly derived from cooling the scale-metal combination from elevated temperatures owing to the different coefficients of thermal expansion, but may also originate from the formation of new $\alpha\text{-Al}_2\text{O}_3$ oxides at the grain boundaries of the existing scale due to counter-diffusion of the oxidation reactants in the scale. Convolutional scale morphology is usually observed for scales under compression and localized scale thickening may be present in the form of ridges and protrusions extending inward and/or outward [79]. These features of the scales contribute to the complex stress situation in the scale and at the scale-metal interface, allowing potential crack initiation and subsequent scale fracture at the sites of stress concentration. Depending on the relative strength of the oxide and the interfacial adhesion, scale spallation may proceed in one of two possible routes [101], as shown schematically in Fig. 2.12.

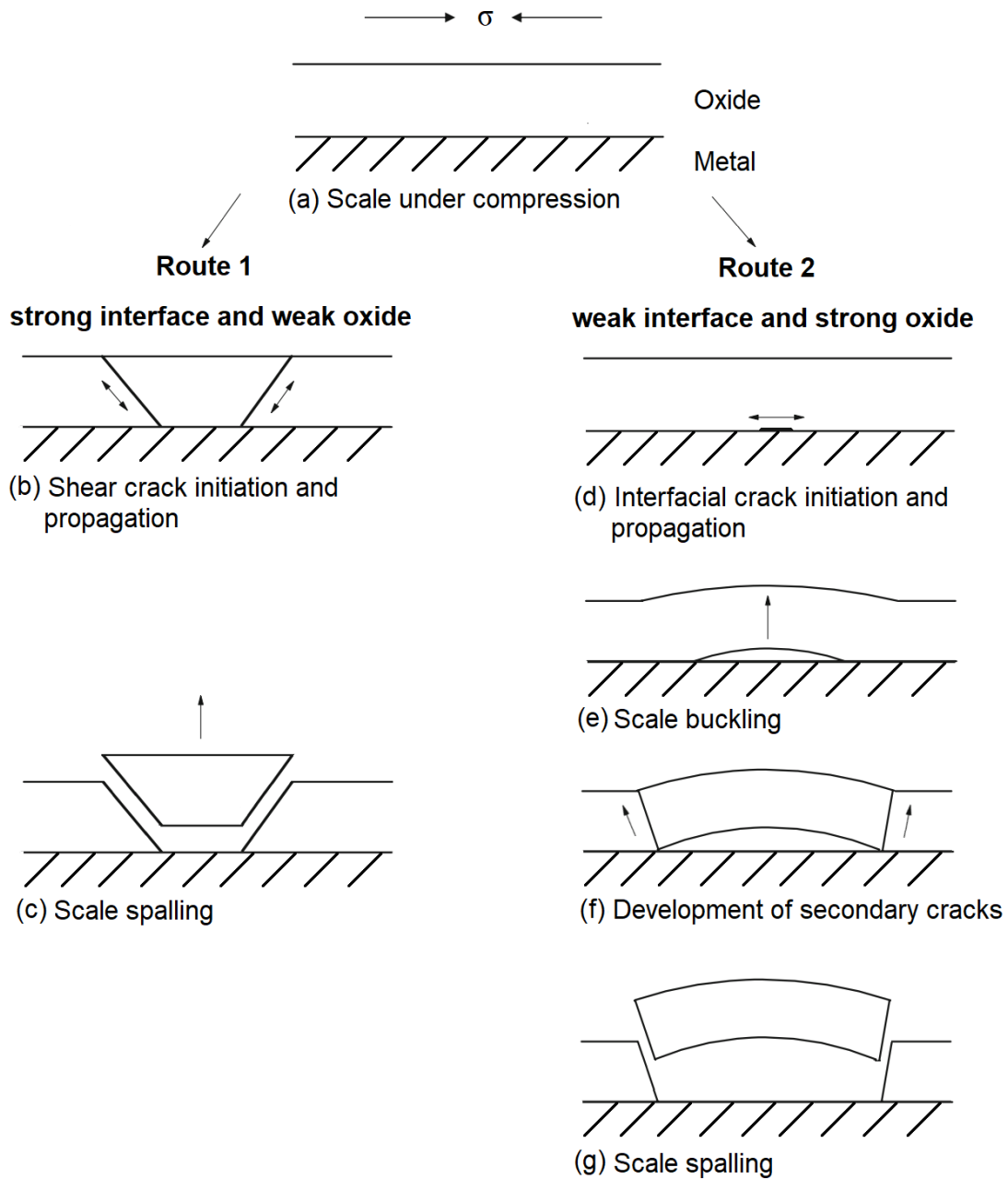


Figure 2.12 Schematic of two possible routes leading to crack initiation and scale spallation for protective scales under compression. Adapted from Refs. [101] and [102] with permissions from Elsevier and Springer Nature (Springer Nature Customer Service Centre GmbH), respectively.

For a weak oxide scale with strong adhesion (route 1), the presence of compressive stresses in the scale will be partially relaxed by the formation of inclined shear cracks at pre-existing defects within the scale [101]. Propagation of the shear cracks through the scale produces an oxide block that is still attached to the interface. As the compressive stresses increase (e.g., with further decreasing temperatures), scale spalling will ultimately occur because of the so-called wedging effect of the adjacent oxides, which forces the oxide block to slide upwards along the surfaces of the shear cracks [99] and to lose contact with the interface. Route 2, on the contrary, represents the situation where the scale-metal interface is weaker than the oxide scale itself. Crack(s) will therefore first develop at sites of defects along with the scale-metal interface when conditions are met. De-cohesion of the scale accompanies the crack initiation and propagation and leads to scale buckling because of stress relaxation. The integrity of the scale will eventually be compromised by the development of secondary tensile cracks at the maximum curvature of the buckled scale and through the scale subsequently, resulting in the spallation of the buckled scale [101].

Routes 1 and 2 differ in the sequence of through-scale crack development and scale-metal interface de-cohesion. In route 1, through-scale cracks develop first followed by the separation of the scale-metal interface, whereas interface de-cohesion occurs before the crack propagation through the scale in route 2. In both cases, the interfacial strength is seen to play a vital role in the scale spallation process and is therefore the most critical factor for improving the spallation resistance of the protective scale. To have an interfacial bond sufficiently strong to resist spallation, it is important to create a strong initial bond at the scale-metal interface and to maintain the bond for a prolonged time during service [10]. A strong initial bond can be achieved by ensuring the growth of α -Al₂O₃ scale in preference to other transient oxides (γ -Al₂O₃, θ -Al₂O₃, etc.) at the initial stages of oxidation and by minimizing the sites of defects at the interface. To maintain a strong bond, the interfacial segregation of detrimental elements, such as sulphur (S), must be prevented in the course of high-temperature exposure. A reasonably low bulk S content (below 1 part per million by weight or 1 ppmw) and the addition of reactive elements (e.g., Y, Zr, Hf) in the coating/substrate are effective ways to prevent the segregation [103].

2.4 Factors Affecting the Oxidation Performance

Previous sections described somewhat simplified fundamentals regarding the process of high-temperature oxidation as well as the mechanisms of the attainable oxidation resistance. However, many complicating factors exist and may have a significant impact on the oxidation process and the behaviour of the protective scales. The present section aims at focusing on the high-temperature oxidation of the MCrAlY coatings and reviewing the pertinent factors deemed of great importance.

2.4.1 Exposure Conditions

The conditions to which the MCrAlY overlay coatings are exposed have the most direct impact on their oxidation behaviour, as they can significantly alter the initial formation of the oxide scale, the transport processes of the reactants, and the severity of the scale spallation, etc. Some important parameters of the exposure conditions are the exposure temperature, the partial pressure of oxygen and the level of water vapour.

Since oxidation performance of MCrAlY coatings relies on the diffusion and chemical reaction of aluminum and oxygen ions (see section 2.1) to form the protective alumina, the effect of the testing temperature can be easily appreciated due to the profound influence of temperature on the diffusion coefficients and the kinetics of the chemical reactions. To be specific, the thickness of the protective scale increases as the temperature rises, while the lifetime of MCrAlY coatings may decrease considerably as a result of accelerated aluminum consumption and severe scale spallation [104]. Another temperature effect on the oxidation behaviour of MCrAlY coatings is the formation of the less protective transition aluminas at low temperatures. Several researchers have observed the presence of θ -Al₂O₃, δ -Al₂O₃, γ -Al₂O₃ when oxidizing MCrAl alloys in the range of 900°C-1000°C [105], and similar results have been confirmed for MCrAlY coatings [106]. While the transition aluminas may persist for an extended duration at low temperatures, they were found to eventually transform to the more stable form of α -Al₂O₃ at 1000°C [107]. The transition aluminas may also be present in the early stages at high temperatures (e.g., 1100°C to 1300°C), however, the duration of their existence before transformation to α -Al₂O₃ is much shorter [108]. As the growth rates of the various aluminas are likely to be different [109], the formation of the transition phases at low

temperatures or in the early stages of high-temperature oxidation inevitably affects the overall oxidation performance of the MCrAlY coatings.

The availability of oxygen, usually represented by the partial pressure of oxygen, affects the inward diffusion of oxygen and the subsequent oxidation reaction. Low oxygen partial pressure not only decreases the rate at which the oxidation process proceeds, but, more importantly, promotes the formation of a continuous and uniform α -Al₂O₃ scale on the coating surface [110, 111]. Owing to these beneficial effects, MCrAlY coatings are frequently subjected to pre-oxidation treatment in an environment of low oxygen partial pressure prior to long-term oxidation evaluation. The establishment of the protective α -Al₂O₃ layer during pre-oxidation can effectively suppress the ongoing oxidation rate, thus improving the lifetime of the coating during long-term oxidation [112, 113].

The presence of water vapour in the environment can also influence the oxidation behaviour of the MCrAlY coatings [114-116]. It appears that water vapour may have a greater effect on the initial stages of oxidation and affect the stability of the transition aluminas rather than the transport processes in the protective α -alumina layer once it is established [115]. This was also confirmed by Sullivan and Mumm [116] when investigating the oxidation behaviour of CoNiCrAlY coating in an atmosphere containing water vapour (30 vol.% H₂O and 10 vol.% O₂) at 1125°C. Complete surface coverage of spinel oxides was observed after only 5 hours of high-temperature holding, resembling a situation of long-term spinel growth in an Al-depleted MCrAlY coating. They suggested that the facilitating water vapour condition may extend the existence of the transient aluminas that are developed during the ramping stage and may enhance the growth of the spinel oxides by permitting the diffusion of spinel-forming cations to the surface.

2.4.2 Coating Characteristics

Under given exposure conditions, the characteristics of the MCrAlY coatings, such as composition, microstructure, and surface finish, may intrinsically result in different oxidation behaviour.

The necessity of the elements in MCrAlY coatings has been discussed previously in section 2.2, in which general mechanisms are provided regarding the effect of the comprising elements

on the coating's oxidation behaviour. In addition, variations in the concentration of the elements (particularly aluminum) may also play a critical role. Brandl, *et al.* [16] compared the oxidation behaviour of two MCrAlY coatings with different Al concentrations (8 wt.% and 12 wt. %). Despite a similar oxidation rate found for the two coatings at an early stage of oxidation (6 h), the spallation behaviour of the scale was considerably different for long-term exposure. Severe scale spallation was observed for the low Al coating after oxidation at 1050°C for 4000h, whereas the scale on the high Al specimen was uniform without spallation. The significance of the Al concentration has also been concluded by Pace, *et al.* [117] when examining two MCrAlY coatings with different Al contents (10 wt. % and 13 wt. %). MCrAlY coatings with different nickel and cobalt compositions were studied by Seo, *et al.* [17]. Differences in the scale constituents, growth kinetics, and element distribution in the inter-diffusion zone at the substrate/coating interface were characterized. One surprising result in their study is that the Co-based coatings outperformed the nickel-based ones under the examined condition (1000°C in air). This is inconsistent with the consensus that Ni-based coatings are more resistant to the oxidizing environment. The difference in the microstructure of the as-deposited coatings, such as voids and oxide inclusion, may possibly explain the contradicting results in their study.

Additional concern on the effect of coating composition actually originates from the substrate. Since MCrAlY coatings are relatively thin (50-250µm), elements from the substrate can diffuse into the coating and eventually reach the coating/scale interface, particularly at high temperatures and after prolonged exposure. If the substrate contains certain elements such as titanium and sulphur, which are well known to be detrimental to the scale adhesion, degradation of the coating's performance can occur [118].

The microstructure of the as-prepared coatings (e.g., grain size, oxide content, and porosity) can greatly influence the process of Al diffusion in the coating, and correspondingly influence the overall oxidation behaviour of the coatings. The performance of MCrAlY coatings with nanocrystalline grains has been characterized by Ajdelsztajn *et al.* [119], Tang *et al.* [120], and Wang [121]. Superior oxidation behaviour of the nanocrystalline coatings was observed because of the increased number of grain boundaries and the enhanced Al diffusion along the grain boundaries. The increased grain boundaries provide more sites for oxide nucleation,

allowing for a faster establishment of a uniform and continuous protective scale, while the enhanced diffusion rates facilitate the Al supply for the scale growth and maintain the scale in the preferred form of α -Al₂O₃. Conversely, the presence of oxides and porosity in the coatings can hinder Al diffusion, resulting in the formation of other undesirable mixed and/or spinel oxides on the coating surface, and thus are detrimental for the coating performance [19].

The oxidation behaviour of the MCrAlY coatings can also be influenced by the surface roughness of the coatings. Comparative studies on the oxidation behaviour of coatings with different surface treatments (e.g., grinding, polishing, and shot peening) have been carried out by several studies [23, 24, 36, 122]. A rough surface may considerably complicate the situation of scale formation and growth, resulting in different oxide types and scale morphologies in the convex and concave areas. The convex surface areas are generally more susceptible to the depletion of the critical elements (e.g., Al and Y) than the concave areas due to the high surface-to-volume ratio. The depletion of Al at the convex location promotes the local formation of non-protective spinel oxides, while loss of Y excludes the potential benefit from the pegging effect of the yttrium oxides.

2.4.3 Manufacturing Processes

MCrAlY coatings are typically manufactured by thermal spray techniques, such as air plasma spray (APS), vacuum plasma spray (VPS), low-pressure plasma spray (LPPS), and high velocity oxygen fuel (HVOF). The inherent differences associated with the processes provide an indirect but comprehensive effect on the oxidation behaviour of the coatings, as they can produce coatings with various characteristics, namely composition, microstructure, and surface finish. While each of the coating characteristics may be at play as discussed in the previous section, the net effect on coating's performance when combining these factors may sometimes lead to contradicting conclusions. For example, Scrivani *et al.* [123] compared the microstructure of MCrAlY coatings prepared by VPS and HVOF. Porosity and oxide content were found lower in VPS coating than in HVOF coating, suggesting a better oxidation behaviour for the VPS coatings. In contrast, Brandl *et al.* [25] concluded that the oxidation rate of HVOF coatings was considerably lower than that of the VPS coatings after conducting an oxidation experiment at 950 and 1050°C for different periods. The slow oxidation rate of the HVOF coatings was rationalized by the presence of finely distributed α -Al₂O₃ particles in the

as-sprayed coating, which was thought to hinder the grain boundary diffusion of the elements in the coating. However, Tang *et al.* [19] observed that in-process oxidation in the HVOF process can promote the formation of undesirable spinel-type oxides during high temperature exposure at 1000°C. Comparative studies of different thermal spray technique have also been carried out by other researchers [124, 125]. Unanimously, APS coatings were found to exhibit inferior oxidation behaviour when compared to VPS and HVOF coatings, predominantly due to the porous microstructure, high oxide inclusion, and rough coating surface of the APS coatings. The results from these studies manifest that MCrAlY coatings with low porosity and oxide content would be preferable for the oxidation resistance application.

To this end, the cold spray technique, which is characterized by low process temperature and high particle impact velocity, has been explored as an alternative manufacturing process for MCrAlY coatings during the past two decades. Favourable coating characteristics, i.e., minimal levels of porosity and oxide inclusion in the as-deposited coating, can be achieved by a proper processing parameters selection and would be beneficial to the coating's oxidation behaviour. The performance of such coatings has been compared to coatings manufactured by previously mentioned thermal spray techniques. Richer *et al* [31] characterized the microstructural evolution of the MCrAlY coatings prepared by cold spray, HVOF and APS processes and evaluated their isothermal oxidation behaviour at 1000°C. Results show that the cold sprayed and HVOF coatings significantly outperformed the APS coatings due to the dense coating microstructure with low oxide inclusion. Similar conclusions have also been reached by Chen *et al.* [33], in which thermal barrier coatings with MCrAlY bond coats instead of free-standing MCrAlY coatings were subjected to thermal cycling at 1050°C. Although the cold sprayed coatings in these studies have marginally greater TGO growth rates than the HVOF coatings, the authors implied that cold sprayed coatings could probably surpass the performance of the HVOF coatings by optimizing the spray parameters to minimize the porosity level and the initial oxide content in the as-deposited coatings. As such, understanding the cold spray process as well as identifying the major influencing parameters are critical to fully exploit the potential of the technique. The next section will deal with these aspects.

2.5 Cold Gas Dynamic Spray

Cold gas dynamic spray (CGDS or simply cold spray) is a high strain-rate solid-state material deposition process, in which feedstock powder (usually 1 to 50 μm in diameter) is introduced to a supersonic gas stream and then accelerated to high velocity (200 m/s to 1200 m/s [126]). Upon impact with a substrate, the powder particles and the substrate both experience plastic deformations that result in particle-substrate bonding and subsequent coating formation. Overview of the cold spray process as well as gas dynamic principles and bonding mechanisms relevant to the cold spray technique are provided in this section.

2.5.1 Process Overview

The modern cold spray was originally developed by a group of Russian scientists in the mid-1980s [127, 128]. Further research on the process development and components refinement by the group lead to their first US patent for the technology in 1994 [127]. Since then, a growing number of journal articles [41-43, 45, 128-138], related patents [139] and academic books [29, 30, 140, 141] have been published. With the extensive interests from academia and industry, many in-house cold spray systems, as well as more advanced commercial systems, have been developed throughout the years [139, 142-144]. A typical cold spray system is schematically shown in Fig. 2.13.

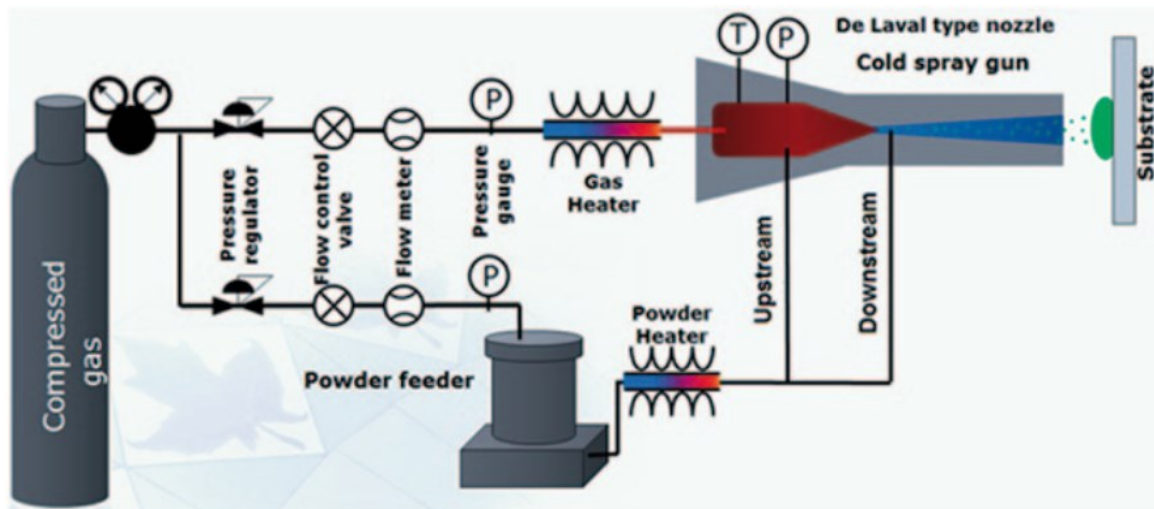


Figure 2.13 Schematic diagram of a typical cold spray system. Republished from [29] with permission of Springer; permission conveyed through Copyright Clearance Center, Inc.

A high-pressure gas source (typically nitrogen or helium) is used to produce the two gas flows for the cold spray process: a primary (or processing gas) flow for particle acceleration and a secondary (or carrying gas) flow for powder feeding. The primary gas flow is usually heated by means of an electric gas heater before entering a converging-diverging (also known as de-Laval) nozzle, where the pressurized gas expands and accelerates at the cost of gas pressure and gas temperature. For a sufficient pressure difference between the gas source and the ambient, a supersonic gas stream can be achieved in the diverging section of the nozzle. Such a situation can be schematically represented in Fig. 2.14, in which the pressure and temperature of the gas gradually decrease in the de-Laval nozzle while gas velocity increases from subsonic in the converging section (where Mach number $M < 1$) to sonic at the nozzle throat ($M = 1$) and finally to supersonic in the diverging section ($M > 1$). The gas velocity at a specific location within the nozzle is a function of gas nature, gas stagnation properties (pressure, temperature), and the nozzle geometry.

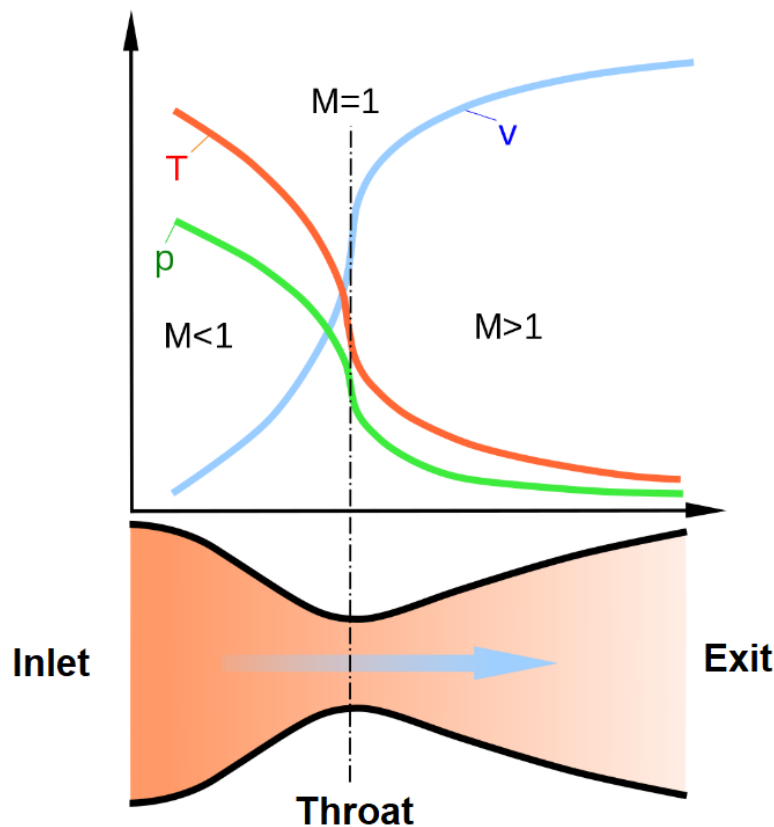


Figure 2.14 Schematic showing the evolution of pressure (p), temperature (T) and velocity (v) of a gas flowing through a de-Laval nozzle. Adapted from [145].

The feedstock powder, carried by the secondary gas flow (see Fig. 2.13), can be injected into the primary flow either axially in the converging section of the nozzle or laterally through a sidewall port on the diverging section of the nozzle. Axial powder injection leads to higher particle temperature that facilitates the coating deposition, but requires high powder feeding pressure and may result in powder oxidation and nozzle clogging (particularly at the throat). In contrast, the pressure needed for lateral powder injection is significantly lowered due to the rapidly reduced pressure of the primary gas after the nozzle throat. Throat clogging is avoided by lateral injection and powder oxidation is minimized because of the low gas temperature in the diverging section. However, low particle temperature associated with the lateral injection may affect the deposition of hard materials. In such a case, a compromise can be made by preheating the powder prior to lateral injection (as shown in Fig. 2.13). The powder temperature, even heated in the converging section or preheated by an external heater, is always maintained below its melting temperature. The particles, therefore, remain in the solid form throughout the entire process of feeding and acceleration, rendering the process “cold” as opposed to conventional thermal spray processes, in which particles are completely or partially melted upon impact with a substrate [45].

The inherent nature of cold spray, i.e., particles of low temperatures (relative to the melting temperature) impacting the substrate at high velocities, produces many unique features for the resulting coating. For example, the high-velocity impact causes severe plastic deformation of the powder and the substrate, resulting in good coating-substrate adhesion, dense coating microstructure, and compressive residual stresses in the coatings. Meanwhile, the absence of significant powder heating minimizes the in-process powder oxidation, allowing little or no oxide inclusions in the coating. The shrinking-induced porosity and tensile stresses that are usually observed in thermal processes are mostly avoided in cold spray given the non-melted condition of the powder. Low particle temperature also makes it possible for the deposition of temperature- and oxidation-sensitive materials.

The characteristic cold spray process also has its limitations. As plastic deformation of the powder and the substrate is a prerequisite for coating adhesion and formation, the application of the cold spray technique is inevitably limited to materials with plasticity potential, such as metals, alloys, polymers, and their mixtures. Brittle materials, such as ceramics, can only be

deposited for limited thicknesses or must be combined with a ductile binder. The other major limitation of cold spray is its relatively high gas consumption, which can be costly, especially when helium is used. As such, it may be necessary to recycle the helium gas, replace it with other cost-effective gases, or restrict the gas consumption via nozzle design and spray parameters adjustments.

In summary, the cold spray technique relies on the high-velocity impact of the particles with the substrate to form the coating. Since the particles obtain their kinetic energies from the gas stream in the diverging nozzle section, accelerating the gas to sufficiently high speeds through the de-Laval nozzle is, therefore, an essential step to assure enough momentum transfer and achieve high particle velocity. To better understand the process of gas and powder acceleration and clarify the influence of some critical parameters, relevant gas dynamic principles in the cold spray process are briefly reviewed in the following section.

2.5.2 Gas Dynamic Principles

As mentioned in the previous section, cold spray utilizes a converging-diverging (de-Laval) nozzle to accelerate the processing gas to supersonic velocities. It has been demonstrated [41, 44, 146] that the flow behaviour in this process can be treated as a one-dimensional, steady-state isentropic flow. Moreover, since helium or nitrogen are typically used in cold spray, it is reasonable to consider the gas as an ideal gas with constant specific heats. As such, this section reviews the gas dynamic principles pertinent to an isentropic flow of an ideal gas. Fox and McDonald's Introduction to Fluid Mechanics [147] is consulted and relevant equations are presented to justify the configuration of the converging-diverging (de-Laval) nozzle and to discuss the different flow behaviour in the nozzle as the stagnation properties of the gas change.

For an ideal gas going through a nozzle of varying cross-section area, the following equation can be derived from the consideration of continuity equation and momentum equation based on the assumption of an isentropic flow.

$$(M^2 - 1) \frac{du}{u} = \frac{dA}{A} \quad (Eq. 2.8)$$

where u is the velocity of the gas flow, A is the cross-section area of the nozzle, and M is the

Mach number of the flow, which is defined as the ratio of the flow velocity to the speed of sound c , or $M = u/c$. Equation 2.8 offers some insights into how changes in the flow velocity du are related to the changes in the nozzle area dA under the influence of the Mach number. Since the flow can be either subsonic ($M < 1$), sonic ($M = 1$) or supersonic ($M > 1$), three different situations can be realized.

- For subsonic flow ($M < 1$), the term $(M^2 - 1)$ in equation 2.8 is negative. This means the changes in flow velocity inversely depend on the changes in the nozzle area, i.e., a decreasing nozzle area ($dA < 0$) is required to accelerate the flow ($du > 0$).
- For flow at supersonic speed ($M > 1$), the term $(M^2 - 1)$ is positive and the exact opposite situation to the subsonic flow is expected. That is, the changes in flow velocity and nozzle area are of the same sign, implying that an increasing cross-section area ($dA > 0$) would correspondingly lead to an increasing flow velocity ($du > 0$).
- In the case of $M = 1$ where the flow travels at a definite speed (the sonic speed), there is simply no changes in velocity ($du = 0$) and the term $(M^2 - 1)$ also equals zero. According to equation 2.8, the only possible way to maintain the sonic flow is to keep the cross-section area of the nozzle constant ($dA = 0$). For a nozzle of varying sectional area, in contrast, the flow of sonic speed would only exist as a transient condition.

As such, equation 2.8 can also be consulted to select the nozzle geometry for specific applications. In cold spray, a gas flow (helium or nitrogen) of adequate supersonic speeds is desirable to propel the particles. To accelerate the gas from stagnation to supersonic speeds, a converging nozzle is firstly needed in the subsonic regime to accelerate the gas to sonic speed at the minimum cross-section area (known as the throat), and a diverging nozzle is then required to further accelerate the gas in the supersonic regime. This converging-diverging nozzle configuration and the changes of gas velocity through the nozzle are better represented in Fig. 2.15.

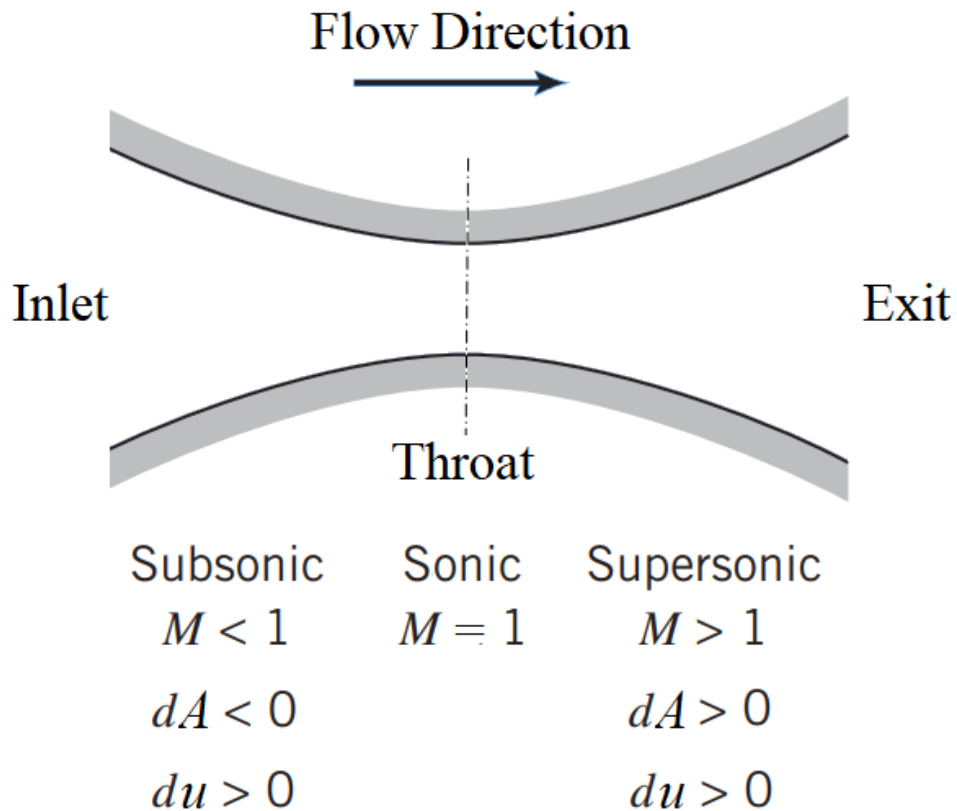


Figure 2.15 Subsonic to supersonic flow through a converging-diverging nozzle. Adapted from [147] with permission of John Wiley & Sons - Books; permission conveyed through Copyright Clearance Center, Inc.

The configuration of the converging-diverging nozzle in Fig. 2.15 satisfies the geometric requirements for continuous gas acceleration. To initiate a gas flow, a pressure difference between the nozzle inlet and exit must be provided. Moreover, as the pressure difference varies, the flow behaviour in the converging-diverging nozzle also evolves accordingly. The different flow characteristics are shown in Fig. 2.16, in which the varying pressure difference is achieved by gradually reducing the back pressure (P_B) where the flow discharges while keeping the stagnation pressure (P_0) constant at the nozzle inlet.

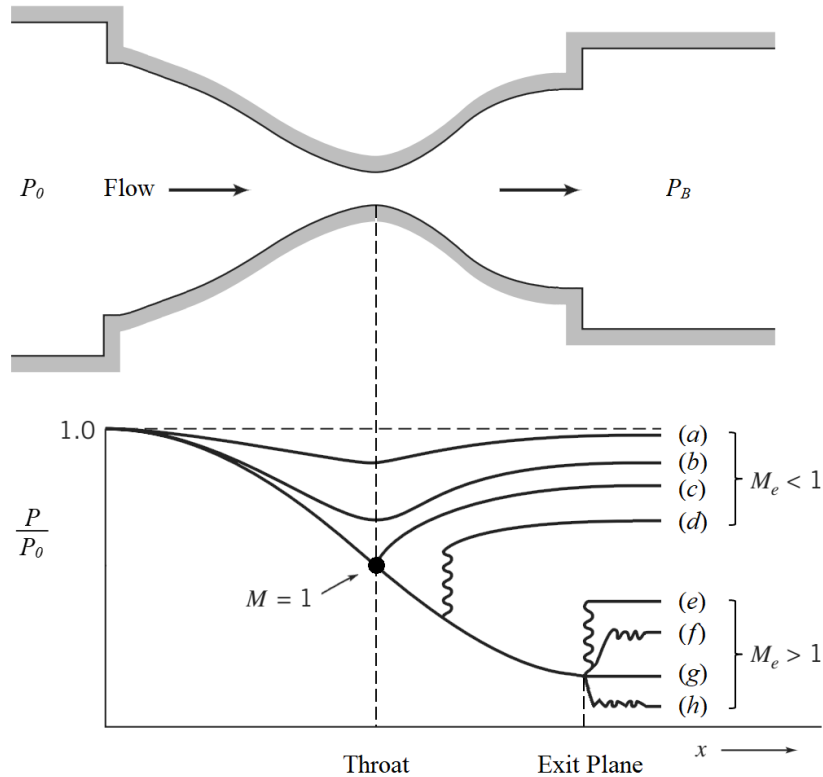


Figure 2.16 Flow characteristics in a converging-diverging nozzle for varying back pressure. Adapted from [147] with permission of John Wiley & Sons - Books; permission conveyed through Copyright Clearance Center, Inc.

The previous examination of equation 2.8 concluded that a converging nozzle will accelerate a subsonic flow ($M < 1$) whereas a diverging nozzle will decelerate a subsonic flow but accelerate a supersonic flow ($M > 1$). With this in mind, the flow behaviour in the converging-diverging nozzle (Fig. 2.16) can be qualitatively described as follows.

- When the back pressure P_B is slightly reduced from the stagnation pressure P_0 , as in case (a), the established pressure difference will simultaneously generate a flow through the nozzle. The flow will first accelerate in the converging section with decreasing flow pressure, reaching a maximum velocity and minimum pressure at the throat, and then decelerate in the diverging section as the flow pressure recovers to the back pressure $P_{B(a)}$. As there is only a limited pressure difference, the complete flow is therefore maintained in the subsonic regime throughout the nozzle.

- Lowering the back pressure further will correspondingly increase the flow velocity and decrease the flow pressure everywhere in the nozzle. However, insufficient pressure difference, as in case (b), will result in similar subsonic flow characteristics as the one in case (a).
- In case (c), the back pressure is finally lowered to sufficiently accelerate the flow to sonic speed ($M = 1$) at the throat, however, $P_B(c)$ is not low enough to cause any supersonic flow in the diverging section. Instead, the flow reverts to subsonic after the throat and decelerates as pressure gradually adjusts to the back pressure.
- Subsequently reducing the back pressure below $P_B(c)$ will lead to essentially the same flow behaviour in the converging section as in case (c). The characteristic of the flow in the diverging section, in contrast, will depend on the actual pressure difference. Case (d) represents a situation in which the pressure difference is adequate to accelerate the flow even after the nozzle throat where the flow is sonic ($M = 1$), leading to a region of supersonic flow in the diverging section. Since the back pressure $P_B(d)$ is too high for this region of supersonic flow, the flow is abruptly decelerated to subsonic speed by a normal shock within the diverging section while the pressure suddenly increases and adapts to the back pressure. The subsonic flow then decelerates through the rest of the diverging section and leaves the nozzle at a pressure equal to the back pressure.
- As the back pressure is further decreased, the region of the supersonic flow will be extended, and the location of the normal shock will be shifted toward the nozzle exit until it occurs at the exit plane as in case (e). At this condition, the pressure difference is sufficient to continuously accelerate the flow, resulting in the supersonic flow throughout the entire diverging section. Further attempts at lowering the back pressure will not modify the flow behaviour in the converging-diverging nozzle, and thus the flow properties in the nozzle are independent of the varying back pressure. However, the flow features outside the nozzle may be distinctly different as the back pressure varies. Three typical conditions are represented in cases (f), (g) and (h).
- Case (f) is characterized by higher back pressure than the flow pressure at the nozzle exit. To coordinate this pressure difference, the flow leaving the nozzle will suffer a series of oblique shocks which decelerates the flow and increase the flow pressure. This type of flow condition is said to be over-expanded since the flow is expanded to

pressure lower than the back pressure.

- In case (g), the back pressure is exactly the same as the nozzle exit pressure. The flow outside the nozzle will therefore keep travelling at supersonic speeds without experience of any shocks. As it is desirable for the flow to be accelerated without any interruption, the nozzle operating at the given pressure difference is said to be working under design conditions.
- If the back pressure is further lowered, as in case (h), below the design condition, oblique expansion waves will occur in the flow outside the nozzle as the flow leaving the nozzle seeks to accommodate the back pressure. The flow under this condition is said to be underexpanded because additional expansion occurs outside the converging-diverging nozzle.

It is worth noting that cases (a) to (d) are identified with a subsonic flow at the nozzle exit ($M_e < 1$), while supersonic flows are accomplished and sustained to the exit plane ($M_e > 1$) for cases (e) to (h). Since normal or oblique shocks are detrimental for gas acceleration such as in cases (d), (e) and (f), the ideal conditions for the cold spray process would be either the design condition as in case (g) or underexpanded condition as in case (h) to achieve high gas velocity. A proper nozzle geometry and suitable spray parameters are critical for the cold spray process to avoid these shocks and operate under desirable conditions.

The nozzle used in the cold spray process can be designed by considering the following equation that is derived from the one-dimensional isentropic flow:

$$\frac{A}{A^*} = \frac{1}{M} \left[\left(\frac{2}{\gamma + 1} \right) \left(1 + \frac{\gamma - 1}{2} M^2 \right) \right]^{\frac{\gamma + 1}{2(\gamma - 1)}} \quad (Eq. 2.9)$$

where A^* is the cross-section area of the nozzle throat, and γ is the specific heat ratio of the gas (c_p/c_v). Equation 2.9 indicates that the area ratio of a selected nozzle can be related to the local Mach number when the gas type (and thus γ) is known. For example, given the desired Mach number at the nozzle exit, the nozzle can then be designed accordingly from the calculated area ratio of A_e/A^* , where A_e is the cross-section area of the nozzle exit.

Another perspective to examine equation 2.9 is that there exists a maximum Mach number for a known gas flow, as defined by the equation, for a specific nozzle cross-section with an area ratio of A/A^* . An adequate pressure difference is required to reach the prescribed maximum Mach number, as depicted in Fig. 2.16, where an identical flow behaviour in the converging-diverging nozzle is observed as the back pressure is sufficiently reduced such as in the cases (e) to (h). This identical flow indicates that the possible maximum Mach number for any selected nozzle plane is reached and will not be increased for any further back-pressure drop.

The limit on the Mach number of the flow by the nozzle geometry, however, does not necessarily mean the flow velocity at a specific nozzle plane is also restricted. Recall the definition of Mach number $M = u/c$ and given that the speed of sound c in an ideal gas undergoing an isentropic process is a function of specific heat ratio (γ), specific gas constant (R_s), and local temperature (T) according to the following equation,

$$c = \sqrt{\gamma R_s T} \quad (Eq. 2.10)$$

the flow velocity u can then be expressed in terms of the local Mach number and speed of sound,

$$u = Mc = M\sqrt{\gamma R_s T} \quad (Eq. 2.11)$$

As such, the flow velocity can still vary with the local speed of sound even if the local Mach number is fixed, and gases with a higher speed of sound are preferred for the cold spray process to achieve high flow velocity. Table 2.1 shows the speed of sound for several common gases under standard ambient temperature (25 °C) and pressure (100 kPa). Helium, as it is seen in the table, has a substantially high speed of sound due to its low molar mass (high specific gas constant) and monatomic nature (high specific heat ratio), and would be advantageous to use for cold spray. However, dramatic increases in cost and limited availability discourage its wide application in the industry. Nitrogen, in contrast, is much cheaper, readily available, and relatively inert, making it the most common gas used in the cold spray process.

Table 2.1 Speed of sound for several common gases under standard ambient condition (25 °C, 100 kPa)

Gas	Speed of Sound
Carbon dioxide	269 m/s
Argon	322 m/s
Air	346 m/s
Nitrogen	351 m/s
Helium	1016 m/s

Another important result from Equations 2.10 and 2.11 is that the speed of sound and the flow velocity depend exclusively on the local temperature of a known gas type (i.e., γ and R_s are known). A higher local temperature therefore will be favourable for accomplishing a higher flow velocity. For an isentropic expansion of an ideal gas through a converging-diverging nozzle, the properties of the flow (P , T) at any given point in the nozzle can be related to the stagnation properties (P_0 , T_0) at the nozzle inlet via the local Mach number:

$$\frac{T_0}{T} = 1 + \frac{\gamma - 1}{2} M^2 \quad (\text{Eq. 2.12})$$

$$\frac{P_0}{P} = \left(1 + \frac{\gamma - 1}{2} M^2 \right)^{\frac{\gamma}{\gamma - 1}} \quad (\text{Eq. 2.13})$$

These equations indicate a directly proportional relationship between the stagnation properties and the flow properties in the nozzle, as the right side of the equations yields a positive value. Equation 2.12, therefore, implies that a higher stagnation temperature will lead to a higher flow temperature, which in turn will increase the local speed of sound and the local flow velocity as suggested by equation 2.11. This explains why gases employed in the cold spray process are purposely pre-heated to a desired stagnation temperature to achieve a high flow velocity, e.g., at the nozzle exit.

The same trend also applies to the flow pressure as it is seen in equation 2.13, i.e., a higher stagnation pressure will result in a higher flow pressure everywhere in the nozzle. Moreover, the equation also shows that an appropriate pressure ratio (P_0/P) is needed to accelerate the flow to a specific Mach number. Considering the nozzle exit plane, for example, the Mach number for a supersonic flow is set by the nozzle geometry (A_e/A^*) according to equation 2.9. If the atmospheric pressure is taken as the back pressure, as in most cases of cold spray applications, the minimum stagnation pressure that is required to achieve a flow of design or underexpanded condition (i.e., the exit pressure is equal to or higher than the back pressure, as discussed in Fig. 2.16) can then be determined from equation 2.13.

Given the ease of measurement and regulation in practice, spray parameters such as pressure and temperature for a specific cold spray application are usually specified in terms of the stagnation properties of the gas flow. Equations 2.12 and 2.13 thus provide a convenient way of utilizing the stagnation properties to predict and control the flow properties at a specific location within the nozzle.

As mentioned in the previous section, one intrinsic limitation for the cold spray technique is the high operating cost resulted from the large gas consumption, especially when helium is used. It is valuable at this point to identify the major factors that can affect the mass flow rate of the gas, so that possible ways to reduce the operating cost can be recognized. The mass flow rate in the nozzle can be estimated from any nozzle section due to mass conservation, as shown in the following equation:

$$\dot{m} = \rho u A \quad (\text{Eq. 2.14})$$

where ρ , u , A are the density, velocity, and the area of the flow at the nozzle section. For a choked flow where $M = 1$ is reached at the nozzle throat, the maximum mass flow rate can be conveniently calculated at the throat using the ideal gas law and equations 2.11, 2.12, and 2.13:

$$\dot{m} = \rho^* u^* A^* = P_0 A^* \sqrt{\frac{\gamma}{R_s T_0} \left(\frac{2}{\gamma + 1} \right)^{\frac{\gamma+1}{\gamma-1}}} \quad (\text{Eq. 2.15})$$

Equation 2.15 shows that for a given gas (γ and R_s), the maximum flow rate in a choked

nozzle is only a function of the nozzle throat area (A^*) and the stagnation properties (P_0 , T_0). It is therefore viable to directly restrict the mass flow rate by employing a nozzle with a reduced throat area and/or using a lower stagnation pressure. Heating the gas to a higher stagnation temperature also contributes to the reduction of the mass flow rate, but to a lesser extent (due to the square root dependence) than the adjustment of the stagnation pressure and the throat area.

One concern with lowering the stagnation pressure is that it correspondingly decreases the flow pressure everywhere in the nozzle, as seen in equation 2.13. This may lead to over-expanded flow condition when the flow pressure in the nozzle is lower than the back pressure (which is usually atmospheric pressure for cold spray process), resulting in unfavourable oblique shocks outside the nozzle, or even normal shock in the nozzle if the stagnation pressure is reduced below a critical pressure P_0^c . Normal shock is stronger and more detrimental than oblique shocks for particle acceleration because of a larger decrease in flow velocity, greater loss in stagnation pressure, higher increase in entropy, etc. across the shock. It is, therefore, necessary to maintain the stagnation pressure above the critical pressure (P_0^c) such that the occurrence of the normal shock can be avoided while keeping the gas consumption at a reasonable level. This critical stagnation pressure can be calculated by considering the special case in which the normal shock occurs exactly at the nozzle exit, as it is shown in case (e) of Fig. 2.16. Under this situation, the pressure before the normal shock is the critical exit pressure P_e^c to be calculated while the pressure after the shock is the back pressure P_b . They are related in the following expression,

$$\frac{P_b}{P_e^c} = \frac{2\gamma}{\gamma + 1} M_e^2 - \frac{\gamma - 1}{\gamma + 1} \quad (Eq. 2.16)$$

where M_e is the Mach number of the flow at the nozzle exit, as determined by the area ratio (A_e/A^*) for isentropic expansion according to equation 2.9. Assuming atmospheric pressure for P_b , the critical exit pressure P_e^c can be calculated from equation 2.16 and the critical stagnation pressure P_0^c can then be found accordingly through equation 2.13. Cold spray process operating at a stagnation pressure lower than the critical value will move the normal shock inside the diverging section, whereas a stagnation pressure above the critical value will eliminate the normal shock but create oblique shocks outside the nozzle. Further increasing the

stagnation pressure will decrease the strength of the oblique shock and will eventually reach the design flow condition (absence of any shock) for the specific nozzle, however, higher stagnation pressure may result in a high level of gas consumption. As such, a trade-off must be made between high gas velocity outside the nozzle (as a result of weak shocks) and low mass flow rate by selecting an appropriate stagnation pressure.

With the developed understanding of the gas flow in the converging-diverging nozzle, accelerating the powder particles in the high-velocity gas flow can now be considered, and the influence of gas and particle properties on the particle velocity can be discussed. The particles in the flow are subjected to a drag force (F_D) that can be written as,

$$F_D = \frac{1}{2} C_D A_p \rho (u - u_p)^2 \quad (Eq. 2.17)$$

where C_D is the drag coefficient, A_p is the frontal area of the particle, ρ is the density of the flow, u and u_p are the velocity of the gas and the particle, respectively. This drag force acts on the particle surface, propelling the particle to high velocities toward the nozzle exit. Since the flow density and the relative velocity ($u - u_p$) are constantly changing as the gas expands, the drag force, as a result, also varies correspondingly. When introducing Newton's second law to equation 2.17, the instantaneous acceleration (a_p) of the particle can be derived,

$$a_p = \frac{F_D}{m_p} = \frac{1}{2} C_D \frac{A_p}{V_p} \frac{\rho}{\rho_p} (u - u_p)^2 \quad (Eq. 2.18)$$

where subscript p is used to represent the properties of the particle, i.e., m_p , V_p , ρ_p are the mass, volume, and density of the particle. Equation 2.18 indicates that the particle acceleration positively depends on the drag coefficient (C_D), the flow density (ρ), and the relative velocity of the flow and the particle ($u - u_p$), but is inversely related to the particle size (as a result of A_p/V_p) and the particle density (ρ_p). Since the flow density and velocity are interrelated in the nozzle, i.e., density decreases continuously as the gas expands, the overall influence of flow density and velocity is not very clear in equation 2.18. To clarify how the flow properties affect the particle acceleration, the ideal gas law and equation 2.11 can be incorporated into 2.18, yielding the particle acceleration in the following expression,

$$a_p = \frac{1}{2} C_D \left(\frac{A_p}{V_p \rho_p} \right) (\gamma P) \left(M - \frac{u_p}{\sqrt{\gamma R_s T}} \right)^2 \quad (Eq. 2.19)$$

The equation, therefore, confirms that the acceleration of the particle is closely related to the local properties of the flow (Mach number, flow pressure and temperature) for a given gas. Since Mach numbers for isentropic flow are prescribed by the nozzle geometry according to equation 2.9, an increase in the stagnation properties (P_0 , T_0) directly raises the local flow properties given the existing proportional relationship shown in equations 2.12 and 2.13 and thus leads to a higher particle acceleration according to equation 2.19. To accelerate the particles in a given nozzle with a finite length, it is always favourable to utilize higher stagnation properties. However, safety and gas consumption concerns inevitably impose restrictions on the allowable stagnation properties, limiting the maximum attainable particle velocity.

For fixed gas stagnation properties, the particle acceleration can also be increased, according to equation 2.19, by modifying the nozzle geometry (i.e., adjusting the area ratio, A/A^*) to yield a higher Mach number. However, increasing the Mach number results in decreasing local flow properties (equations 2.12 and 2.13), which partially cancel out the benefit of the Mach number increase. Hence, there exists an optimal Mach number (and optimal nozzle geometry) that provide the maximum particle acceleration for a fixed set of gas and particle properties [41]. If the particle velocities achieved are not satisfactory, a longer nozzle can always be used to extend the duration of the particle acceleration in the flow and thus obtain higher particle velocities. However, a boundary layer thickness, which develops along the internal walls of the nozzle, may affect the flow behaviour especially when the nozzle is long, and thus needs to be considered when increasing the nozzle length.

Alternatively, reducing the particle size and/or particle density can also contribute to higher particle velocities as a result of the increasing acceleration indicated by equation 2.19. However, the particles, especially the small and light ones, are subjected to the bow shock that is generated in the vicinity of the substrate when the supersonic gas flow impinges on the substrate [148]. As the particle size and particle density decrease, there comes a point when the particle velocity can be significantly reduced across the shock. The detrimental effect of

the bow shock is strongly dependent on the flow Mach number before the shock; therefore, it is recommended that the design exit Mach number for typical cold spray nozzles should be limited to 2 - 3, based on the type and size of the particles used, to reduce the loss of the particle velocity across the shock and the influence of bow shock on the coating deposition [148].

Achieving high particle velocity at impact is of prime importance for cold spray technique. The particle impact velocity determines the amount of kinetic energy available for particle deformation and ultimately dictates whether the particle would adhere to the substrate or simply deflect and bounce off. The following section will focus on the impact of the high-velocity particle on the substrate and illustrate the potential bonding mechanisms.

2.5.3 Particle Impact and Bonding

When the high-velocity particle impacts the substrate, the particle and the substrate both experience certain amounts of elastic and plastic deformation. Given the high impact velocity (500m/s for example) and the small particle size (5 to 50 μm), the time scale within which the deformation occurs is extremely short (approximately 10 to 100 ns, based on calculations of the particle diameter divided by the impact velocity). As such, the heat generated during the high strain-rate deformation does not have time to transfer evenly through the particle and the substrate, making it an essentially adiabatic condition in the deformation region. The heat dissipation in the localized deformation region at the interface of the particle and the substrate may induce significant rises in the local temperature (potentially reaching the melting temperature of the materials) and lead to thermal softening of the materials, which lowers the shear strength of the materials and facilitates further particle deformation in the region. This phenomenon is generally referred to as adiabatic shear instability and has been demonstrated by several studies [131, 149-151].

Assadi *et al.* [131] modelled the impact of a single copper particle on a copper substrate using finite element analysis (FEA). They observed that thermal softening of the materials due to adiabatic heating has a dominant influence on the characteristics of the particle deformation. Figure 2.17 shows the simulation results of the strain and flow stress distribution along the particle radial path for two impact velocities.

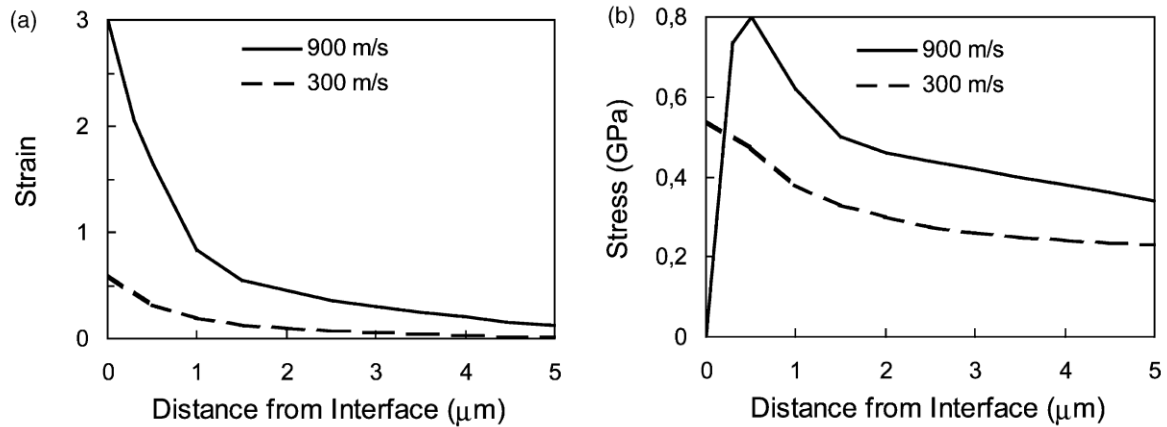


Figure 2.17 Calculated profiles of (a) plastic strain and (b) flow stress along the particle radial path for two impact velocities. Reprinted from Ref. [131] with permission from Elsevier.

The plastic strain near the interface for the high impact velocity (900 m/s) greatly exceeds that of the low velocity (300 m/s). Correspondingly, a significantly reduced flow stress (approaching zero at the interface) is observed, implying the occurrence of thermal softening as well as adiabatic shear instability in the region. Further investigation by the authors reveals that the threshold impact velocity for the beginning of the adiabatic shear instability is likely in the range of 550 m/s to 580 m/s, above which particle deformation mechanism may change from plastic to viscous flow near the particle/substrate interface due to adiabatic shear instability. These findings have also been confirmed by Grujicic *et al.* [149] with similar simulations for extended combinations of particles and substrates. The critical particle impact velocities for different particle/substrate systems obtained from the simulations agreed well with the ones calculated from the one-dimensional analysis of adiabatic shear localization, thus validating the mechanism of the adiabatic shear instability.

Adiabatic shear instability at the particle/substrate interface is believed to be critical for the bonding of the particle to the substrate. One of the bonding mechanisms proposed by some researchers [152] is based on the mechanical interlocking of the deformed particle and substrate. Under conditions that result in adiabatic shear instability, an out-flowing jet of the particle and/or the substrate is usually observed at the edge of the contact zone as a result of the extensive plastic deformation. The jet can subsequently develop into rollups and vortices

at the interface [152], as shown in Fig. 2.18. The formation of these features mechanically anchors the two materials together and creates interfacial bonding. Mechanical bonding can also be improved by artificially introducing the anchoring sites to the substrate surface before coating deposition. Grit blasting [153] and pulsed water jet technique [154], for example, can be used for this purpose.

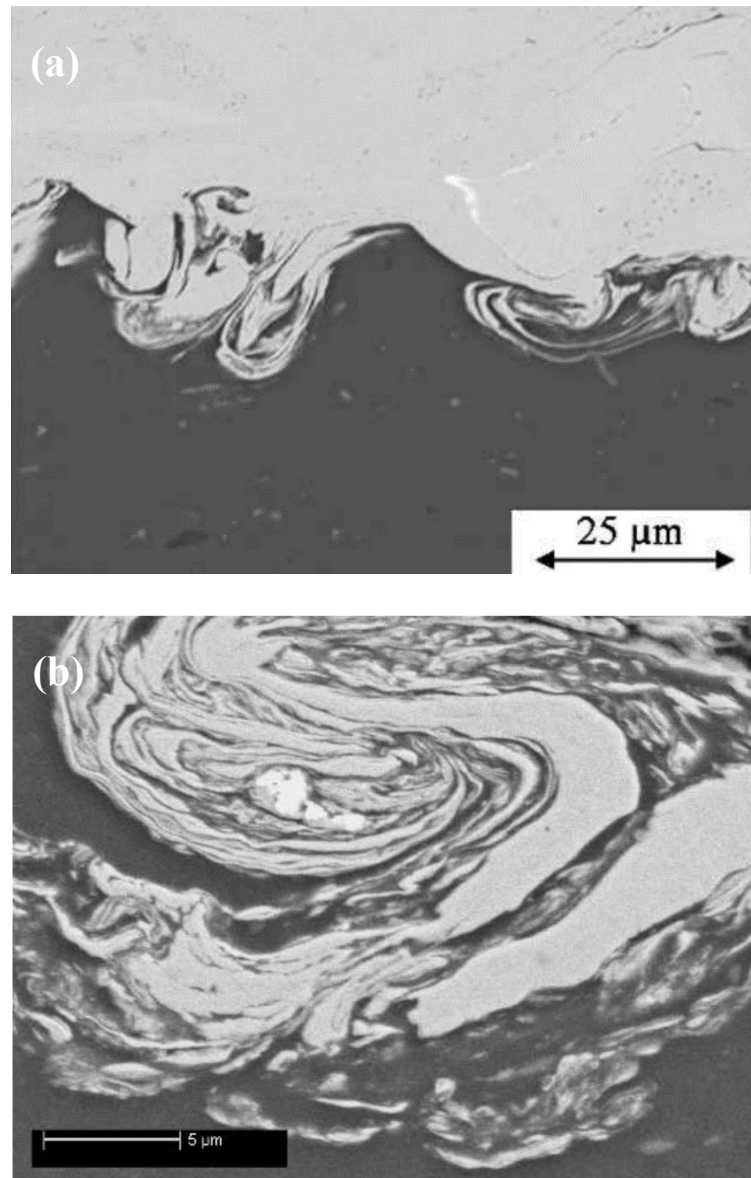


Figure 2.18 SEM images showing the rollups and the vortices at the interface of (a) Cu on Al6061 substrate (b) Ni on Al substrate. Reprinted from Refs. [155] and [142], respectively, with permission of Springer Nature (Springer Nature Customer Service Centre GmbH).

Another bonding mechanism for the cold sprayed particles is metallurgical bonding. It is proposed [129, 156, 157] that the extensive plastic deformation experienced by the particles and the substrate can effectively disrupt the native oxide film on the materials, exposing fresh and clean surfaces between the two materials. Metallurgical bonding can thus occur at sites where adequate local contact pressure acts on the two surfaces with intimate contact. The out-flowing jet is also considered beneficial for the formation of the metallurgical bonding, as it flushes out the fragments of the native oxides residing at the contact surfaces of the particle and the substrate, and thus increases the exposure of the fresh surfaces for potential bonding to occur [158].

Although the actual mechanisms differ, the mechanical and metallurgical bonding both rely on the prerequisite of sufficient plastic deformation of the particle and the substrate. As such, factors that affect the extent of the plastic deformation, such as the nature of the particle and the substrate, the impact velocity and impact temperatures of the materials, contribute largely to the type and strength of the bonding. In addition, the topology of the substrate prior to particle impact is also seen to play an important role in determining the percentage of the specific bonding type [151].

Chapter 3 Research Objectives

The general objective of the thesis research is **to characterize CS deposition on a single-crystal nickel-base superalloy (CMSX-4) and to develop low-cost NiCoCrAlTaY coatings with improved coating properties and performance using the CS technique**. As part of an ongoing project at the uOttawa Cold Spray Research Laboratory, it is worth noting the focus of the present research and the differences in comparison with studies previously carried out by colleagues in the research group [159, 160].

Firstly, this research utilizes a commercially available CS system, which provides several major upgrades to the in-house CS system used in previous studies, such as a commercial nozzle assembly made of tungsten carbide and cobalt (WC-Co), an integrated powder-preheating unit, and improved pressure and temperature controls. Secondly, a NiCoCrAlTaY powder, as opposed to CoNiCrAlY powders in previous studies [159, 160], is used as the feedstock material for CS coating deposition. Increasing the concentration of nickel in the composition is considered beneficial for mechanical strength and oxidation performance at high temperatures [161]. The addition of 4 wt. % tantalum (Ta) in the powder is believed to reduce the refractory elements (Ta, W, Re) diffusion to the coatings at elevated temperatures [162]. These composition modifications are expected to improve the oxidation performance of the CS NiCoCrAlTaY coatings. Thirdly, a single-crystal nickel-base superalloy (CMSX-4), instead of aluminum alloy 6061 in the previous studies [159, 160], is used as the substrate to closely resemble the components in real gas turbine applications. The materials combination of the feedstock powder and the substrate as well as their interactions during the CS deposition would be more relevant to the actual applications, and the oxidation performance of the MCrAlY coatings with the substrate (instead of standalone coatings) would be more representative. Finally, **the present research aims at replacing expensive helium with nitrogen as the processing gas for CS coating deposition**. This would significantly reduce the gas cost and potentially make the CS process more economical.

The upgraded CS system and nozzle assembly, different feedstock materials, and the use of nitrogen instead of helium represent significant changes in experimental conditions. Consequently, the results obtained in previous studies can not be directly transferred to the

present research in terms of CS deposition behaviour, coating microstructure, properties, and performance. Several studies, as outlined in the following sections, will need to be performed to fulfill the general research objective.

3.1 Deposition of NiCoCrAlTaY Coatings by Cold Spray Using Nitrogen

It is necessary to first verify whether it is feasible to produce NiCoCrAlTaY coatings using the available CS system, given all the changes in the feedstock materials and process gas from previous studies. Different CS spray parameters (gas temperature and pressure, powder preheating temperature, powder feed rate, traverse speed, etc.) are explored to identify the major factors affecting the coating microstructure and properties. The criteria for CS parameters selection are based on achieving dense and well-adhered NiCoCrAlTaY coatings. Furthermore, three materials, namely, aluminum alloy 6061, Inconel alloy 625 polycrystalline nickel-base superalloy, and CMSX-4 single-crystal nickel-base superalloy, are used as the substrates to investigate the effect of substrate materials on CS deposition of NiCoCrAlTaY coatings. Grit blasting is performed on the substrates, while one set of the CMSX-4 substrates is ground to study the effect of substrate surface preparation. In addition, NiCoCrAlTaY powders from different production batches are used to examine the effect of powder variation on the CS deposition and resulting coating characteristics.

3.2 Powder Recycling and Process Economics

Given the fundamental difference in thermophysical properties (e.g., heat capacity ratio, specific gas constant) [41], gas velocities are significantly lower when using nitrogen versus when using helium. This in turn limits powder acceleration in the gas stream, resulting in lower particle impact velocities when nitrogen is used. As such, a low deposition efficiency (DE) is expected for CS deposition of MCrAlY coatings using nitrogen, as MCrAlYs have relatively high strength that requires high particle velocities for deposition [130, 163]. This means that a large portion of the impacting particles would bounce off without adhering to the substrate. These non-deposited powder particles are typically a waste product and can significantly increase the production cost of the CS MCrAlY coatings, despite great gas cost saving by replacing helium with nitrogen. It would be economical and ecological to collect and re-use

these non-deposited powder particles.

To this end, the objective of this study is **to explore the feasibility of powder recycling** and compare the characteristics of the recycled powder, e.g., morphology, hardness, particle-size distribution, and microstructure, to that of the as-received feedstock powder. The possibility of utilizing the recycled powder for CS deposition will be verified and the coatings prepared from the powders (as-received and recycled) will be characterized. This study also aims at **developing a cost model that considers the benefit of powder recycling**. Using this cost model, the process economics of CS MCrAlY coatings using nitrogen, with and without the powder recycling, will be analyzed and compared to a similar process employing helium as the process gas.

3.3 Production of In-situ Nanocrystalline MCrAlY Coatings by Cold Spray

Nanocrystalline MCrAlY coatings have been demonstrated to significantly improve oxidation performance due to reduced coating grain size and increased grain boundaries that promote the formation and adhesion of a protective α -Al₂O₃ scale [121, 164]. Conventional methods typically used for manufacturing nanocrystalline MCrAlY coatings can be categorized into two distinct approaches: “bottom-up” and “top-down” [165, 166]. The bottom-up approach, e.g., physical vapour deposition (PVD), involves building coating structures atom by atom or molecule by molecule to assemble nanoscale clusters into bulk material and usually has low deposition rates [167]. The top-down method generally requires a powder nanocrystallization process (such as cryomilling) prior to thermal spray coating deposition using the nanocrystalline powder [166]. This two-step approach not only complicates the fabrication processes, increasing the processing time and costs, but may also introduce undesirable contaminants (due to powder interactions with the milling media during cryomilling [119, 120, 168]) and oxides (due to powder oxidation during subsequent thermal spray process [19]) that potentially degrade the performance of the specifically designed MCrAlY coatings.

In this study, **the production of in-situ nanocrystalline NiCoCrAlTaY coatings is explored** using the CS technique with conventional powders. As a solid-state coating technique involving high velocity impacts and severe plastic deformation, CS is widely reported as inducing in-situ grain refinement during coating deposition [169-172], a prominent feature that

is unattainable using traditional thermal spray processes where the feedstock powder is molten. However, the degree of CS-induced grain refinement or the resulting grain sizes are highly sensitive to the local plastic strain level. Richer, *et al.* [35] and Borchers, *et al.* [50] observed that nanosized grains were present at the particle contact regions within the CS MCrAlY coatings where severe plastic deformation occurred, while the grain sizes were noticeably coarser within the particles due to lack of sufficient plastic deformation. In light of these studies, it can be anticipated that extended particle deformation could likely result in a more uniform grain structure, and in-situ nanocrystalline coatings may be potentially produced using solely the CS technique.

The present study focuses on promoting particle deformation via enhanced in-process particle impingements. The coating process was first analyzed using single-splat and interrupted spray tests, in which varying amounts of powder particles are sprayed over the substrates. This provides insights into the particle-substrate and particle-particle interactions during the CS coating process under the proposed spray conditions. The CS NiCoCrAlTaY coatings, CMSX-4 substrates, and their interfacial features are then characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). These results can answer whether the CS process can be used to produce in-situ nanocrystalline NiCoCrAlTaY coatings, as well as reveal the effect of CS deposition on the microstructure of CMSX-4 single-crystal superalloy.

3.4 Isothermal Oxidation Evaluation

Examination of the relevant literature has suggested that the most critical prerequisite for the performance of MCrAlY coatings is the formation and growth of a thermally grown oxide (TGO) scale in the form of α -Al₂O₃. Particularly, it is desirable for the α -Al₂O₃ scale to develop rapidly at the beginning but grow slowly afterward. Upon high-temperature exposure, a rapidly developed α -Al₂O₃ scale can effectively prevent the formation of other unfavourable oxides (e.g., NiO, Cr₂O₃, spinel oxides), protecting the underlying coatings from excessive oxidation. Once the continuous and uniform α -Al₂O₃ TGO is formed, a slowly growing scale can reduce the rate at which aluminum in the coating is consumed and minimize the stress accumulation within the TGO scale that eventually causes scale delamination and spallation. CS

nanocrystalline MCrAlY coatings are expected to favour a rapid TGO formation due to the presence of large grain boundaries that may act as α -Al₂O₃ nucleation sites.

This study focuses on the isothermal oxidation evaluation of the CS nanocrystalline NiCoCrAlTaY coatings. Short-term oxidation tests (e.g., 1h, 2h, 5h) are carried out to characterize whether the protective α -Al₂O₃ TGO scale is established during the early oxidation stages. By performing prolonged isothermal oxidation, the evolution of the microstructure, composition, and phase constituents in the CS NiCoCrAlTaY coatings and the TGO scale can be examined. TGO growth kinetics can then be characterized by plotting the TGO thickness as a function of the oxidation duration. These results from isothermal oxidation tests will help to determine if the CS nanocrystalline NiCoCrAlTaY coatings are capable of sustaining the α -Al₂O₃ TGO growth and preventing the formation of unfavourable oxides.

3.5 Processing Adjustment

To achieve the designed properties and optimum performance, three-step heat treatments are generally required for nickel-base superalloys [2, 173]. A solution heat treatment (SHT) is first performed to homogenize the microstructure and to avoid any elemental segregation. This is followed by primary ageing (PA) to develop the cuboidal γ/γ' microstructure. Finally, secondary ageing (SA) is carried out to further promote finer γ' precipitates in the γ phase.

This study **explores the CS deposition of NiCoCrAlTaY coatings on the CMSX-4 single-crystal superalloy substrates under three different conditions**; that is, the CMSX-4 substrates undergo the heat treatments of SHT, SHT + PA, and SHT + PA + SA, respectively, as shown in Fig. 3.1.

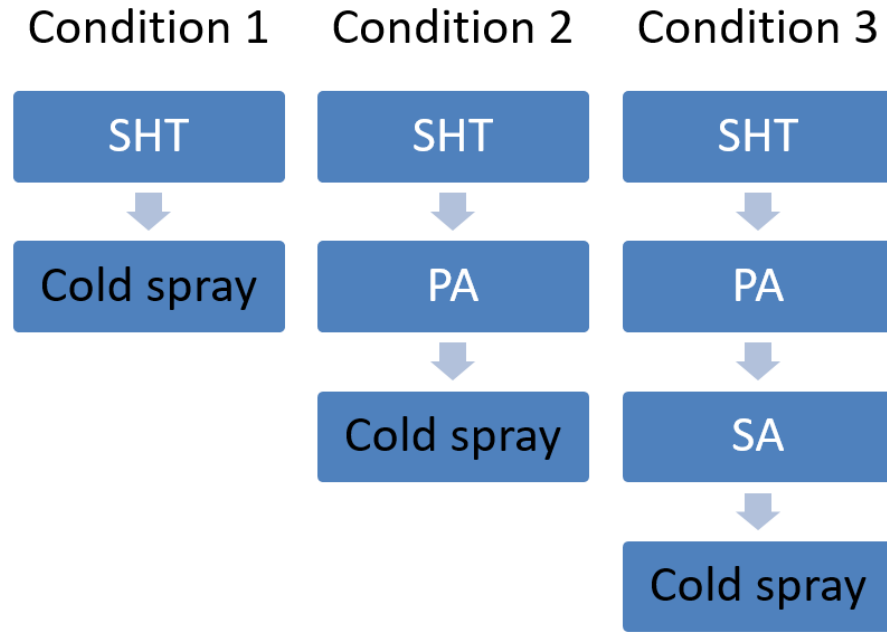


Figure 3.1 Flowchart showing the CMSX-4 superalloy substrate conditions prior to CS deposition

The first objective of the study is to examine the effect of the superalloy substrate conditions on the CS deposition behaviour and resulting coating characteristics. Coating microstructure, thickness, porosity, hardness, and coating-substrate interface are characterized and compared among the as-deposited NiCoCrAlTaY coatings produced on CMSX-4 substrates of different conditions.

Since the required heat treatments are not fully completed for the first two CMSX-4 substrates, i.e., Conditions #1 and #2 in Fig. 3.1, subsequent ageing steps are needed to develop the desired microstructure and properties: PA and SA for Condition #1; SA for Condition #2. These heat treatments are performed on the coated substrates after the CS coating deposition. This results in different processing sequences due to the changes in relative order of the CS deposition with respect to the superalloy heat treatments, as shown in Fig. 3.2.

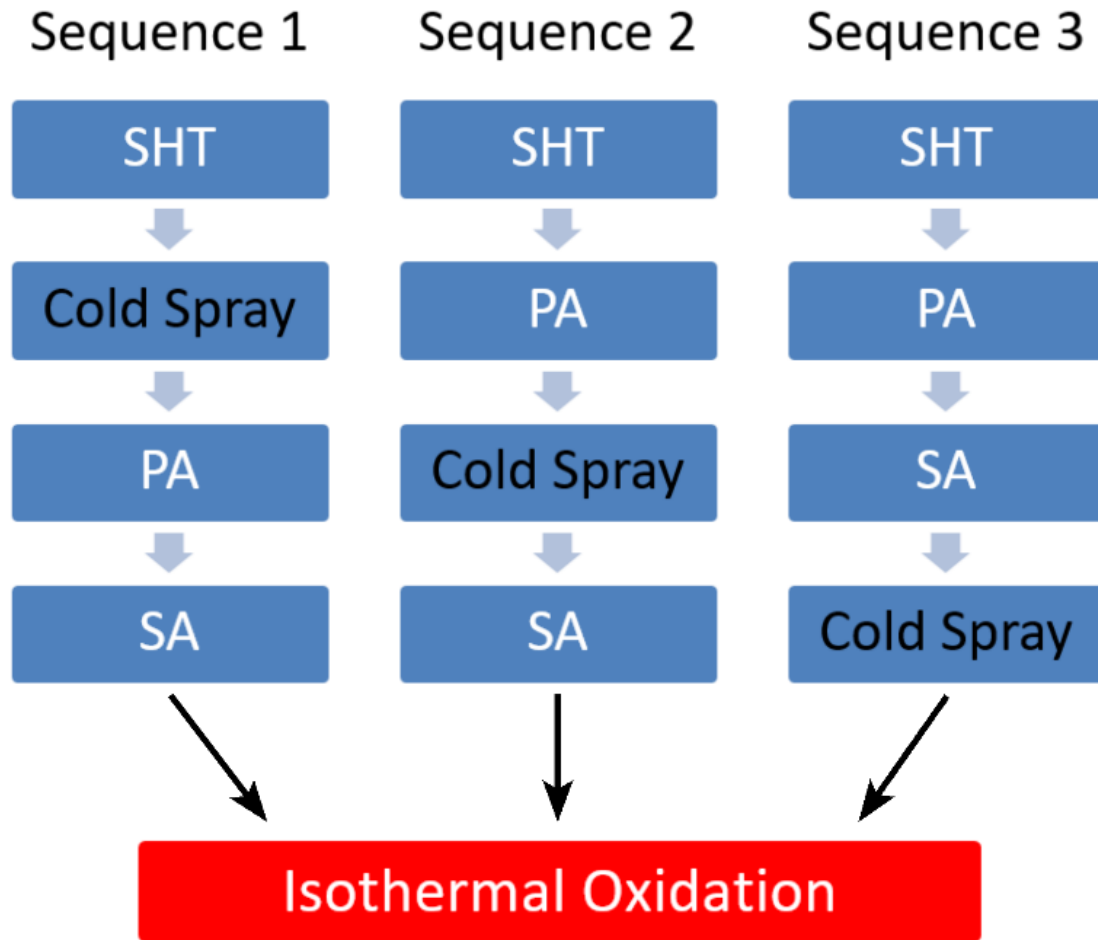


Figure 3.2 Flowchart showing different sequences of superalloy heat treatments and CS deposition

Therefore, the second objective of the study is to **investigate the influence of different processing sequences on the performance of CS NiCoCrAlTaY coatings under isothermal oxidation conditions at 1100°C for 2 hours**. The microstructures of the CMSX-4 substrates and CS NiCoCrAlTaY coatings following different processing sequences are characterized after each heat treatment as well as after the isothermal oxidation test. It has been demonstrated that pre-oxidation treatment of MCrAlY coatings is beneficial to their subsequent oxidation performance [112, 113, 174]. This study also examines whether a similar effect can be achieved by performing the superalloy ageing (PA and/or SA) on the CS NiCoCrAlTaY coatings.

Chapter 4 Methodology

In this chapter, a detailed description of the experimental approach employed for the research project is provided. This includes procedures followed and equipment used in the process of deposition, evaluation, and characterization of the coatings.

4.1 Feedstock Powder

The feedstock powder used for CS coating deposition is a gas-atomized NiCoCrAlTaY powder that is commercially available under the name of Amdry 997 (Oerlikon Metco, Westbury, USA). The powder's nominal composition is given in Table 4.1.

Table 4.1 Nominal composition of the Amdry 997 powder and CMSX-4 superalloy substrate (wt. %)

	Ni	Co	Cr	Al	Ta	Y	W	Re	Ti	Others
Amdry 997	43.9	23.0	20.0	8.5	4.0	0.6	-	-	-	-
CMSX-4	61.7	9.0	6.5	5.6	6.5	-	6.0	3.0	1.0	Mo 0.6 Hf 0.1

The presence of a significant amount of Ni and Co in the Amdry 997 powder provides an excellent balance of high-temperature oxidation and hot corrosion resistance. The concentrations of other alloying elements, such as chromium (Cr), aluminum (Al), and yttrium (Y), are similar to that in other common MCrAlY powders except for tantalum (Ta), which accounts for 4.0 wt. % in the NiCoCrAlTaY powder. The alloying of Ta to MCrAlY is believed to improve the oxidation performance of the NiCoCrAlTaY coatings at high temperatures, possibly due to reduced refractory elements (e.g., Ta, W, Re) diffusion from the substrate into the coating [162]. As such, the Amdry 997 powder is selected to develop low-cost/high-performance MCrAlY coatings using the CS technique.

The morphology and microstructure of the as-received NiCoCrAlTaY powder are shown in Figure 4.1.

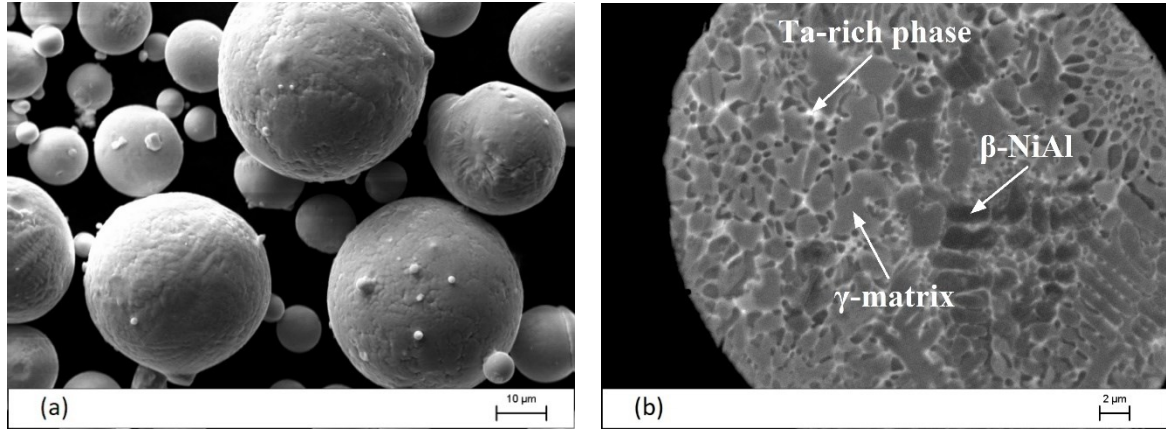


Figure 4.1 (a) Morphology and (b) microstructure of the NiCoCrAlTaY powder

The powder is spherical and consists of three phases: a face-centred cubic (FCC) nickel-based solid solution γ phase (light grey matrix), a body-centred cubic (BCC) Al-rich β -NiAl phase (dark grey), and a Ta-segregated phase (white). The particle size distribution of the NiCoCrAlTaY powder was characterized using a laser diffraction instrument (Microtrac S3500, Nikkiso, Japan) with the results shown in Fig. 4.2.

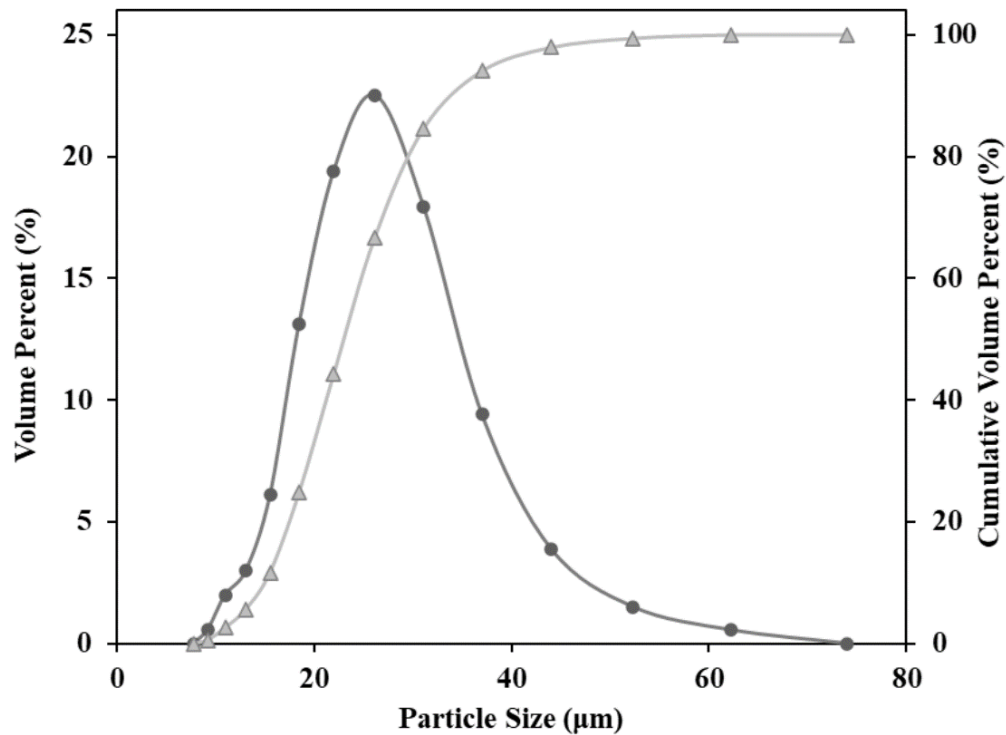


Figure 4.2 Particle size distribution of the NiCoCrAlTaY powder

The mean particle sizes based on volume (MV), number of particles (MN), and area (MA), and the particle sizes (D10, D50, D90) corresponding to the 10th, 50th, 90th percentile of the cumulative volume are summarized in Table 4.2. The particle size distribution results confirm that more than 90% of the Amdry 997 powder falls in the range of 5-50 μm , which is suitable for CS coating deposition.

Table 4.2 Mean and percentile particle sizes for the NiCoCrAlTaY powder

Mean Particle Size (μm)			Percentile Particle Size (μm)		
MV	MN	MA	D10	D50	D90
23.91	16.91	21.47	15.02	23.00	33.77

4.2 Substrate and Preparation

A second-generation single-crystal nickel-base superalloy (CMSX-4, Cannon Muskegon Corporation, Muskegon, USA) is used as the substrate for CS NiCoCrAlTaY coating deposition. The nominal composition of the CMSX-4 superalloy is listed in Table 4.1 for a direct comparison with the feedstock NiCoCrAlTaY powder. The cast CMSX-4 was received in the form of a $\varnothing 16 \text{ mm} \times 170 \text{ mm}$ cylindrical bar, which was then sliced into multiple disks of $\varnothing 16 \text{ mm} \times 3 \text{ mm}$ by electrical discharge machining (EDM) at the University of Ottawa. The as-received CMSX-4 bar and the disks after EDM cutting are shown in Fig. 4.3.

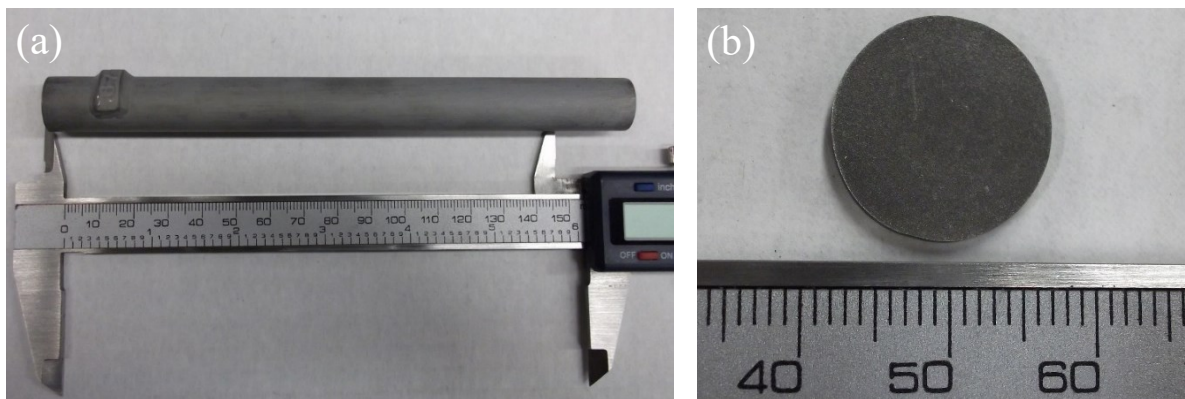


Figure 4.3 (a) As-received CMSX-4 bar and (b) CMSX-4 disk after EDM cutting

The CMSX-4 superalloy was received in the SHT condition, which was processed at the Alcoa Howmet Research Center (Whitehall, USA). The primary ageing (PA) and secondary ageing (SA) were performed at the University of Ottawa using a laboratory furnace (Lindberg/Blue M™, Thermo Scientific™). Details of the heat treatment conditions are summarized in Table 4.3.

Table 4.3 Heat treatment conditions for the superalloy substrate and MCrAlY coatings

Name	Temperature	Time	Environment	Cooling
SHT	1310 °C	7 h	Argon	GFQ
PA	1140 °C	6 h	Air	AC
SA	870 °C	20 h	Air	AC

Note: GFQ - gas fan quenching, AC - air cooling

In addition to the CMSX-4 superalloy substrates, aluminum alloy 6061 and Inconel alloy 625 polycrystalline nickel-base superalloy substrates were also used in some experiments during the preliminary investigation of CS coating deposition. All substrate surfaces were treated using a grit blasting unit (Princess Auto SKU: 8140709) prior to the CS coating deposition. An 80 mesh (0.178 mm) aluminum oxide (Opta Minerals Inc) was used as the abrasive, and an air pressure of 60 psi (414 kPa) was employed for the grit blasting. Moreover, the CMSX-4 disks were ground to examine the effect of surface preparation on the CS coating deposition and interfacial characteristics. Figure 4.4 shows the different substrate materials after grit blasting and grinding.

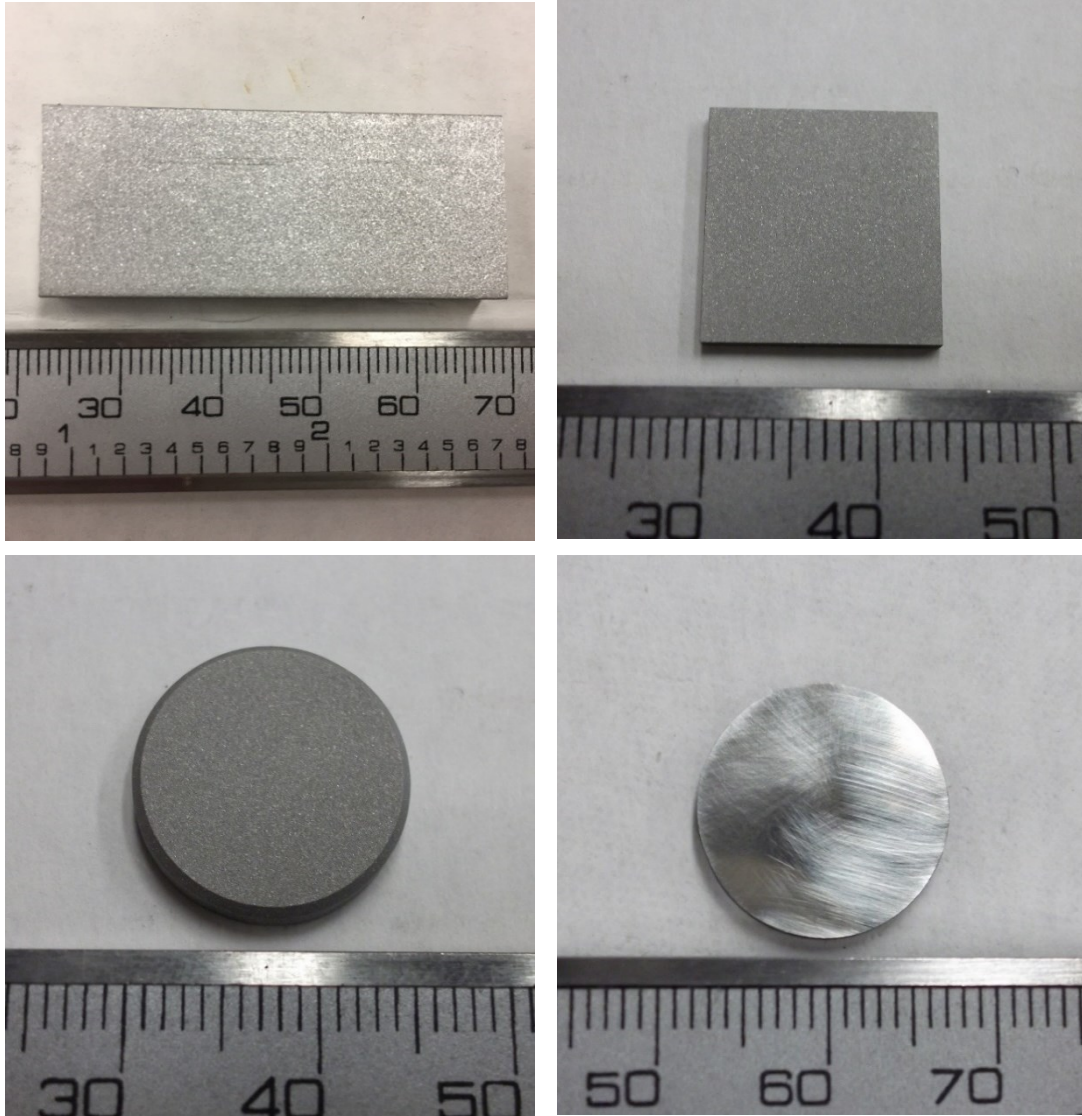


Figure 4.4 Grit blasted (a) Al6061, (b) IN625, (c) CMSX-4, and (d) ground CMSX-4 substrates

4.3 Cold Spray Deposition

The system used for coating deposition is a commercially available CS system (SST-EP Series, Centerline Technology (Winsor), Canada), which consists of an operation module, a spray chamber, a moveable spray gun, and a filtration system. Figure 4.5 shows an overview of the CS system and a close-up of the spray gun that comprises an automated X-Y robot, a gas heater, a nozzle assembly (UltiLife™, Centerline Technology (Winsor), Canada), and a powder pre-heating unit.

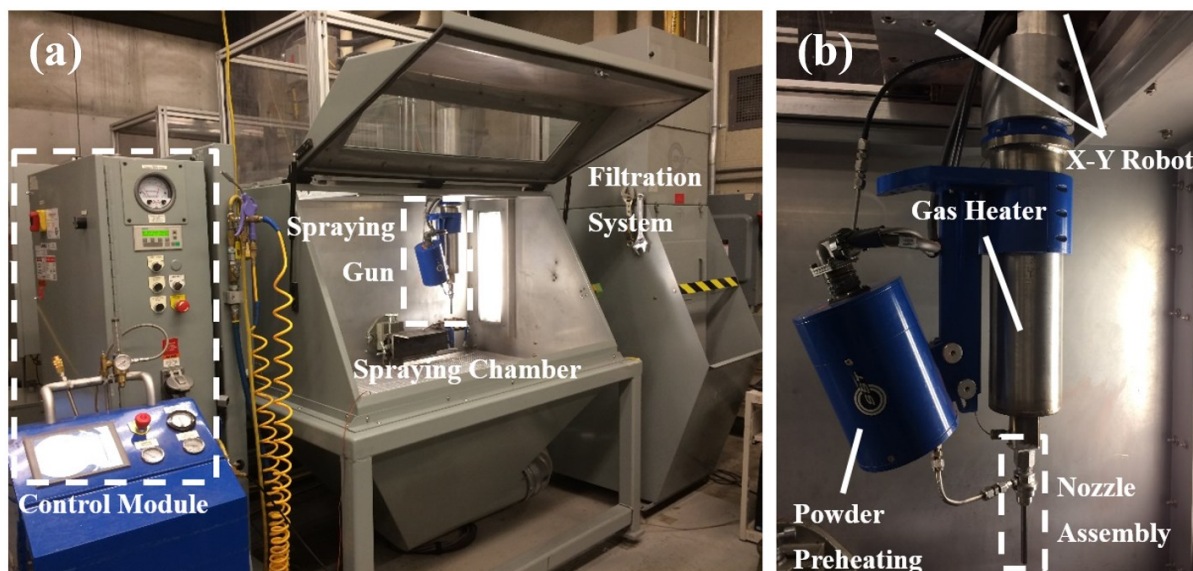


Figure 4.5 Overview of (a) the CS system and (b) the spray gun

The parameters regarding the stagnation pressure, gas temperature, and powder preheating temperature can be specified and regulated in the operation module. During an actual spray, a primary gas flow (nitrogen or helium) from a pre-assembled 11-bottle pressurized gas reservoir (or bottle pack) is guided to the spray gun, where the gas is heated by the gas heater before entering the converging-diverging nozzle. A secondary gas flow is used to entrain the feedstock powder that is fed via a commercial powder feeder (Model AT-1200, Thermach Inc., Appleton, USA). The powders, after reaching a modest temperature in the powder pre-heating unit, are then injected into the diverging section of the nozzle for acceleration. After impacting on the substrate in the spray chamber, a portion of the powders deposits on the substrate to form the coating while the remaining non-deposited powders are collected by the filtration system to avoid environmental contamination.

4.4 Oxidation Evaluation

Coated samples were subjected to isothermal oxidation at 1100°C in a furnace (Fig. 4.4) with static atmospheric air for predetermined oxidation durations up to 500 hours. Short-term oxidation of 1, 2 and 5 hours were carried out to study the oxidation behaviour of the coatings during the early stage of oxidation. The samples were loaded into the furnace once the temperature stabilized at 1100°C and removed from the furnace immediately after the

predetermined test durations to ensure the exact oxidation time. The samples were then air-cooled in the ambient environment to room temperature.

The oxidized samples were characterized after each duration in terms of microstructure, composition, and phase constituents. The TGO scale thicknesses were measured and used to derive the TGO growth kinetics.

4.5 Materials Characterization

Standard metallographic procedures, i.e., sample sectioning (Struers Secotom-10), mounting (Struers LaboPress-3), grinding and polishing (Struers TegraPol-31, TegraForce-5, and TegraDoser-5), were followed to prepare the coated samples for microstructural examination. Commercially available software and equipment are used for measurement and characterization, e.g., coating porosity and TGO thickness (Vision-Lite, Clemex, Canada), coating surface roughness (SRG-4000, Phase II Plus, USA), microhardness (Duramin-1, Struers, Denmark), and particle velocities at 15 mm from the nozzle exit (ColdSprayMeter, Tecnar Automation Ltd., St-Bruno, Canada).

Several characterization techniques were employed to characterize the microstructure, chemical composition, and phase constituents of the feedstock powder, substrates, as-deposited CS coatings, and oxidized samples after specified oxidation evaluation. Scanning electron microscopy (SEM) (EVO-MA10, Carl Zeiss, Germany) was used along with energy-dispersive X-ray spectrometry (EDS) (INCA-x-act, Oxford Instruments, UK) using a voltage of 15 kV. X-ray diffraction (XRD) analyses were carried out using a diffractometer with Cu K α radiation (X-Pert PW1830, PANalytical, Netherlands). A focused ion beam (FIB) workstation (GAIA 3, Tescan, Czech Republic) was employed to prepare samples at the coating/substrate interface. The FIB milling was performed using gallium ions with an energy of 30 keV and a probe current of 100 pA. Scanning transmission electron microscopy (STEM) (Talos F200X, FEI, USA) using a voltage of 200kV was used to investigate the coating and substrate microstructures as well as their interfacial bonding features at high magnification.

Chapter 5 Cold Spray Deposition of NiCoCrAlTaY Coatings Using Nitrogen

This chapter provides the experimental results, coating characterization, and process economics analysis with respect to the CS deposition of NiCoCrAlTaY coatings using nitrogen. The first part of the chapter presents the work that examines the effects of substrate materials, substrate surface preparation, and feedstock powder variations on the CS coating deposition. The second part of the chapter consists of the study that compares the characteristics and properties of the CS NiCoCrAlTaY coatings produced using nitrogen and helium, as well as analyzes the process economics of the two CS processes considering the benefit of powder recycling.

5.1 Coating Deposition

This section reports the results obtained at the early stages of the thesis research to explore the potential of using nitrogen as the process gas for the CS deposition of NiCoCrAlTaY coatings. Many preliminary works were performed to investigate the influences of CS spray parameters, such as gas temperature, gas pressure, powder preheating temperature, powder feed rate, nozzle stand-off distance, and nozzle traverse speed. These results were not included in the thesis due to a large amount of data and the trial-and-error nature of the work. By the end of these investigations, a set of CS spray parameters that can produce dense and well-adhered NiCoCrAlTaY coatings was determined and listed in Table 5.1.

Table 5.1 Parameters for CS deposition of NiCoCrAlTaY coatings using nitrogen

Stagnation Pressure (MPa)	Stagnation Temperature (°C)	Powder Preheating (°C)	Powder Feed Rate (g/min)	Stand-off Distance (mm)	Step Increment (mm)	Traverse Speed (mm/s)	Number of Passes
3.45	500	500	13.3 ± 0.3	15	1	5	1

Using these spray parameters, more experimental trials were carried out and several notable factors that affected the coating characteristics, namely substrate nature, substrate surface

preparation, and feedstock powder variation, were summarized below.

The effect of substrate nature on the CS deposition of NiCoCrAlTaY coatings was investigated by using three substrate materials, i.e., aluminum alloy 6061, Inconel alloy 625 polycrystalline nickel-base superalloy, and CMSX-4 single-crystal nickel-base superalloy. Figure 5.1 shows the cross-section SEM images of the NiCoCrAlTaY coatings deposited on these substrates.

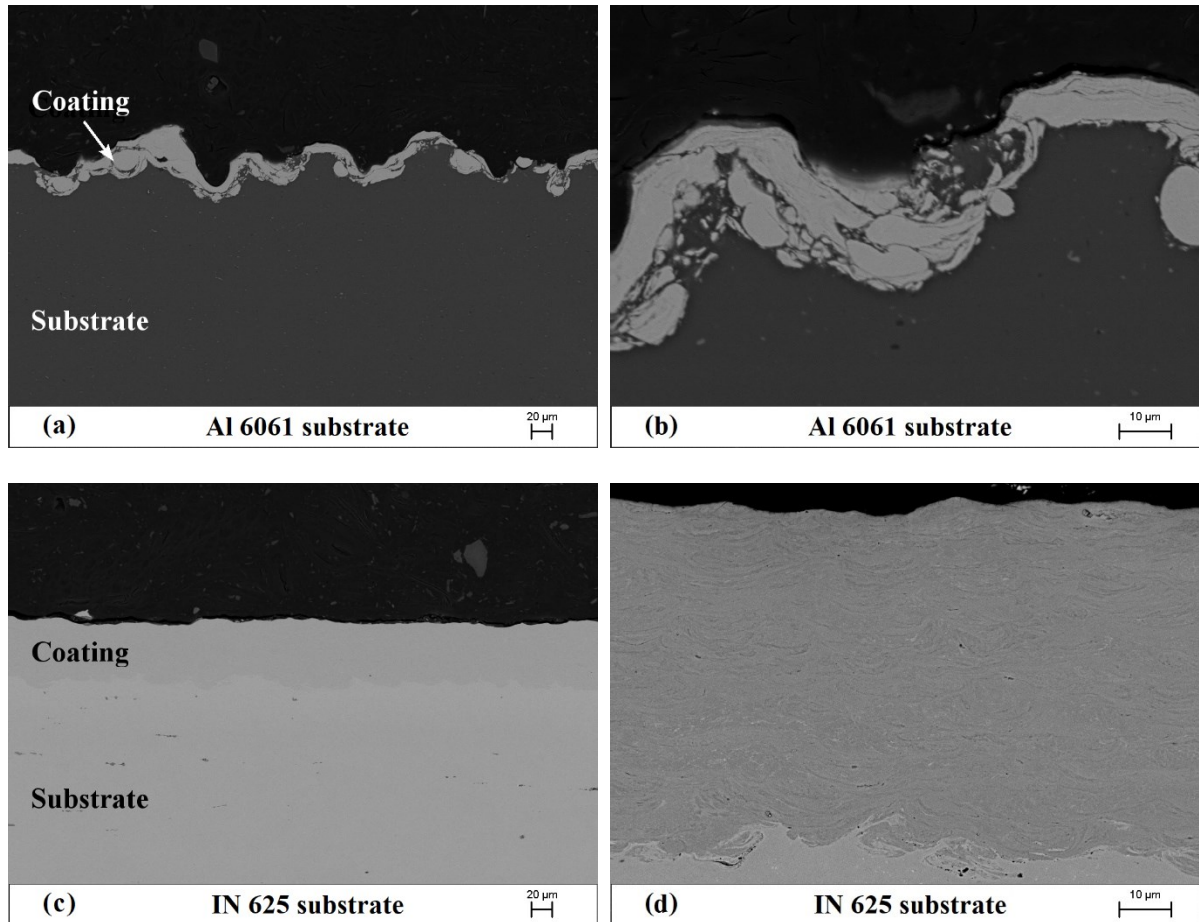


Figure 5.1 CS NiCoCrAlTaY coatings deposited on three substrate materials: (a, b) Aluminum alloy 6061, (c, d) Inconel alloy 625 polycrystalline nickel-base superalloy, and (e, f) CMSX-4 single-crystal nickel-base superalloy. (continued on the next page)

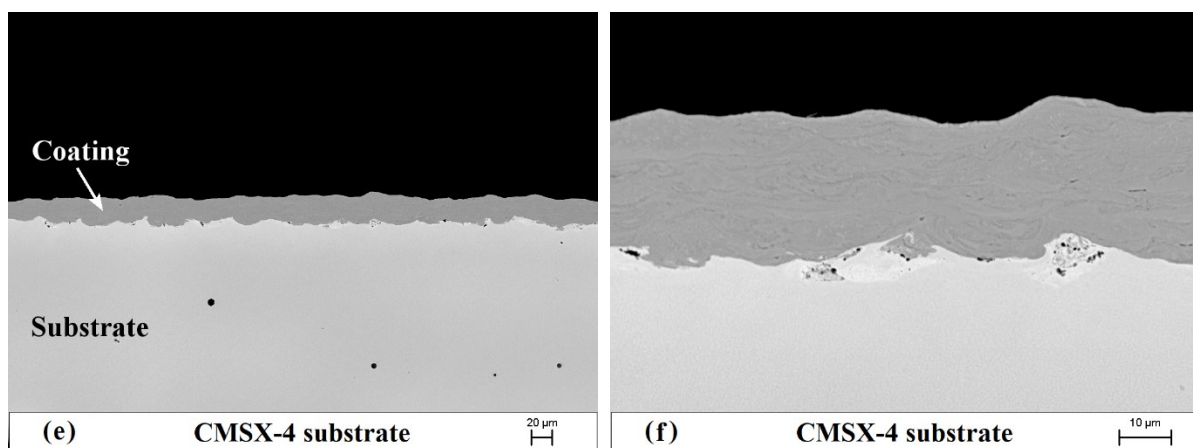


Figure 5.1 (continued) CS NiCoCrAlTaY coatings deposited on three substrate materials: (a, b) Aluminum alloy 6061, (c, d) Inconel alloy 625 polycrystalline nickel-base superalloy, and (e, f) CMSX-4 single-crystal nickel-base superalloy.

The CS deposition on the Al 6061 substrate barely resulted in NiCoCrAlTaY coatings. The deposits obtained (Figs. 5.1a and 5.1b) are non-uniform with rough surfaces: a few particles were able to adhere at some locations, whereas no particles were observed at other locations. Discontinuities can be seen within the deposited particles, indicating poor inter-particle cohesion. In contrast, the NiCoCrAlTaY coatings produced on the IN 625 (Figs. 5.1c and 5.1d) and CMSX-4 (Figs. 5.1e and 5.1f) substrates show a similar dense microstructure with a smoothened surface, despite a difference in coating thickness. The deposited particles leading to these dense coatings were highly deformed that individual particle boundaries were not discernible, implying a good coating cohesion. These different coating characteristics on the three substrate materials are attributed to the differences in the mechanical properties of the materials. Table 5.2 provides the microhardness values for the feedstock powder and the three substrate materials.

Table 5.2 Microhardness of feedstock NiCoCrAlTaY powder, Al 6061, IN 625, and CMSX-4 substrates (HV_{0.3})

NiCoCrAlTaY	Al 6061	IN 625	CMSX-4
337 ± 20	101 ± 3	248 ± 8	439 ± 11

Al 6061 is significantly softer than the feedstock NiCoCrAlTaY powder. Upon particle impacts, the Al 6061 substrate deformed readily, creating a convoluted substrate-coating interface (Fig. 5.1a). The lack of sufficient plastic deformation of impacting particles prevented the buildup of the NiCoCrAlTaY coatings. Higher particle impact velocities, e.g., by using elevated spray parameters or using helium, would be required to induce more particle deformation and promote coating deposition on Al 6061. IN 625 and CMSX-4 are considerably harder than Al 6061, with a hardness value closer to the feedstock NiCoCrAlTaY powder. This promoted plastic deformation of both the substrate and the powder following particle impacts, thus facilitating the coating buildup. The NiCoCrAlTaY coatings deposited on the CMSX-4 substrate are noticeably thinner than that on the IN 625 substrate. This reveals a relatively lower deposition efficiency (DE) on the CMSX-4 substrates due to its high mechanical strength. However, this effect of substrate materials on DE should not be lasting, as the coating deposition would involve only particle-particle interactions after a certain coating thickness. It has been demonstrated that thick NiCoCrAlTaY coatings of approximately 500 μm , as shown in Fig. 5.2, can be achieved on the CMSX-4 substrates by simply increasing the number of spray passes.

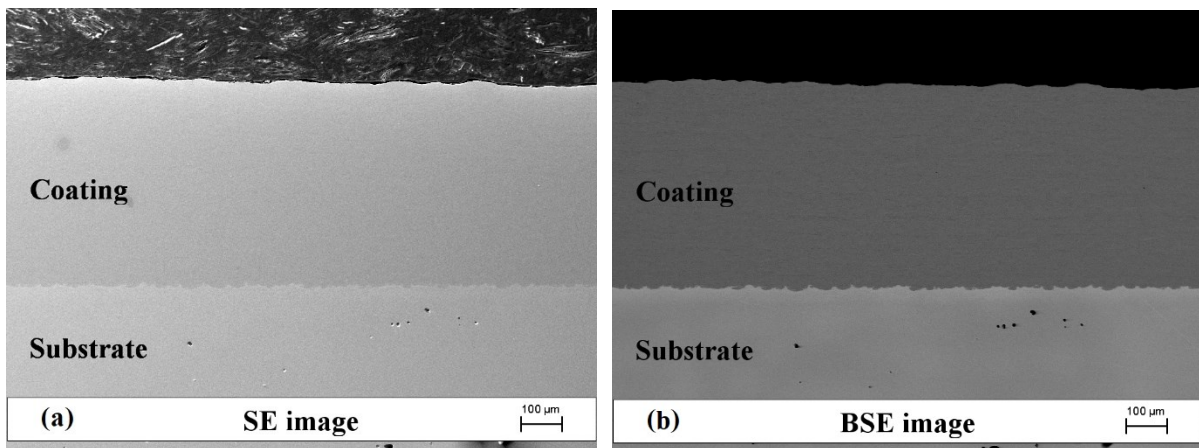


Figure 5.2 Thick NiCoCrAlTaY coating produced by CS using nitrogen on a CMSX-4 substrate: (a) secondary electron (SE) image, and (b) backscattered electron (BSE) image.

Although dense coating microstructures were achieved on the IN 625 and CMSX-4 substrates, grit-blasting treatment of the substrates prior to coating deposition is not ideal as grit residues were found at the substrate-coating interfaces (Figs. 5.1d and 5.1f). The embedment of grit

residues not only diminishes the local coating adhesion but also introduces contaminants into the materials that could result in unknown effects on the coating performance at high temperatures. To avoid the use of grit blasting, grinding was performed on the substrates and the resulting NiCoCrAlTaY coatings were compared with that deposited on the grit blasted substrate. Figure 5.3 shows the NiCoCrAlTaY coatings produced on the CMSX-4 substrates that were treated using the two surface preparation methods.

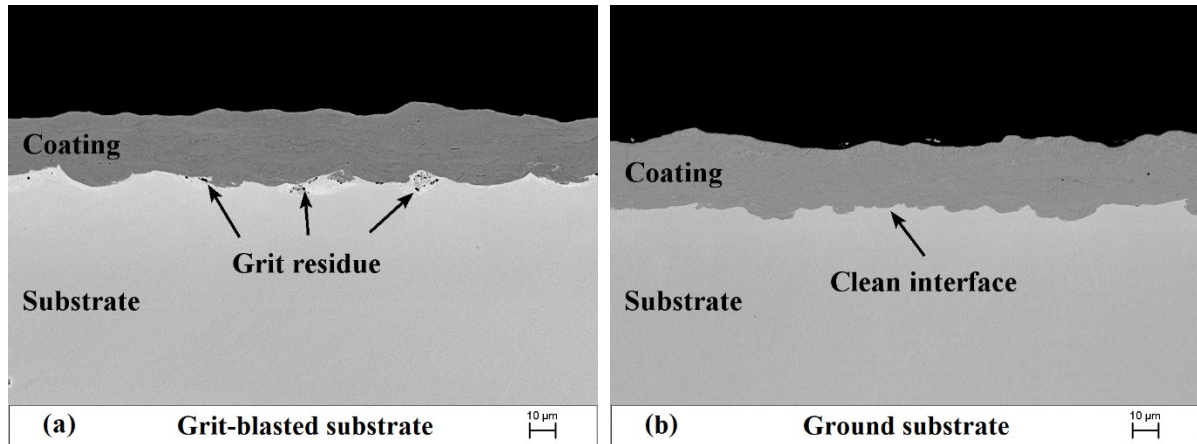


Figure 5.3 CS NiCoCrAlTaY coatings deposited on CMSX-4 substrates with different surface preparation: (a) grit blasting, and (b) grinding.

While the presence of grit residues is evident in the sample with the grit blasted substrate (Fig. 5.3a), the sample with the ground substrate (Fig. 5.3b) shows a clean interface with the absence of noticeable defects or contaminants. Interestingly, the coating-substrate interface of the ground substrate sample exhibits a similar undulation as that of the grit-blasted sample. This is attributed to the plastic deformation of the ground CMSX-4 substrate as a result of particle impingement and deposition. These results reveal that conventional grit blasting is not required prior to the CS deposition of NiCoCrAlTaY coatings on CMSX-4 substrates, as the particle-substrate interactions in the CS process essentially provide an in-situ grit blasting. As such, grit blasting of CMSX-4 substrates was not performed for subsequent coating deposition. Instead, substrate grinding was used to remove its surface oxidation that resulted from previous substrate processing, e.g., electrical discharge machining and heat treatment.

During preliminary experimental trials, it was also found that minor powder variations from different production batches can have a significant effect on the characteristics of the CS

NiCoCrAlTaY coatings. Figure 5.4 presents the morphology and microstructure of two NiCoCrAlTaY powders procured from different production batches (arbitrarily termed as batch X and batch Y).

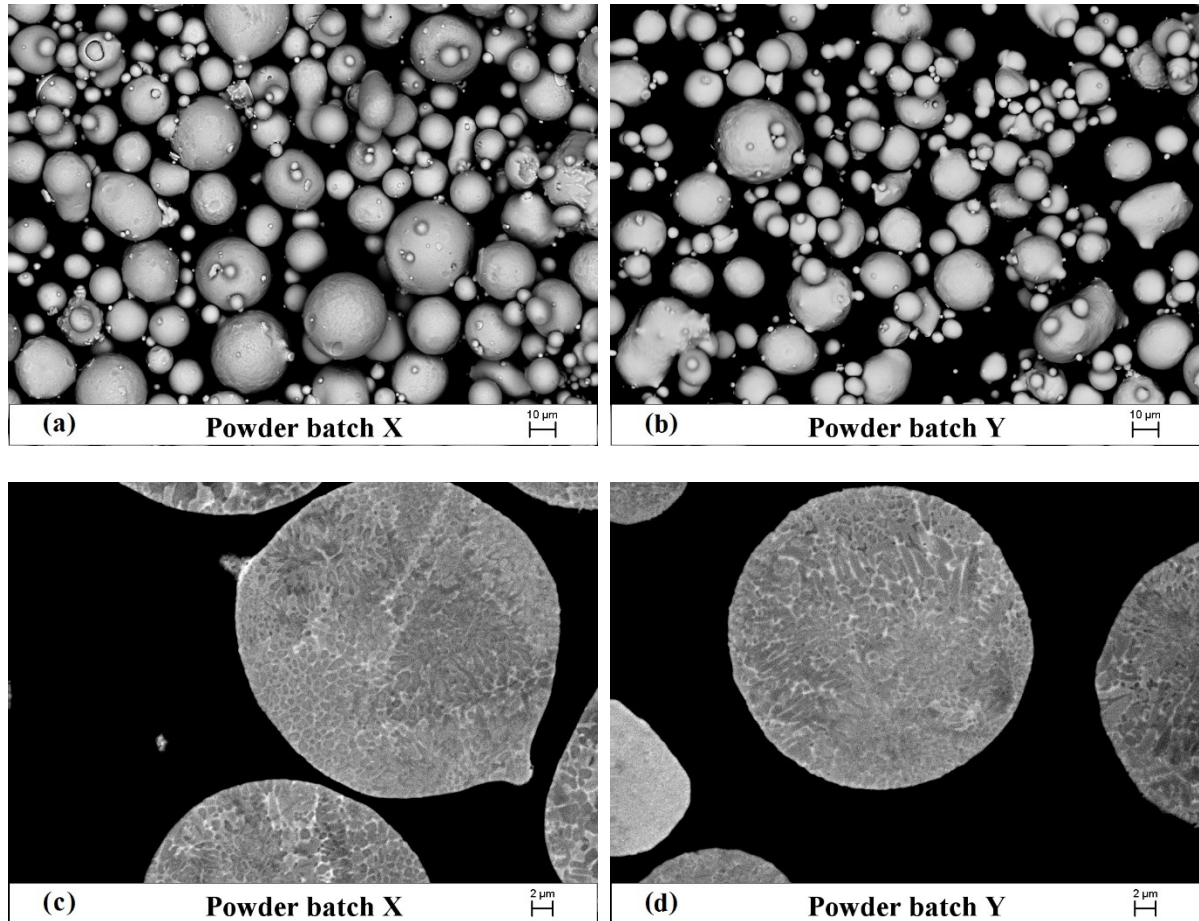


Figure 5.4 Morphology and microstructure of NiCoCrAlTaY powders from different production batches: (a, c) batch X and (b, d) batch Y.

The characteristics of the two NiCoCrAlTaY powders are similar in terms of the particle size distribution (as determined by a laser particle analyzer), chemical composition (as quantified by EDS), microstructure (as shown in the SEM image Figs. 5.4 c and d), and mechanical properties (as represented by microhardness). Yet, their CS deposition behaviour and the resulting coatings are significantly different. Figure 5.5 shows the surface morphology and microstructure of the CS NiCoCrAlTaY coatings produced from the two powders using the same spray parameters listed in Table 5.1.

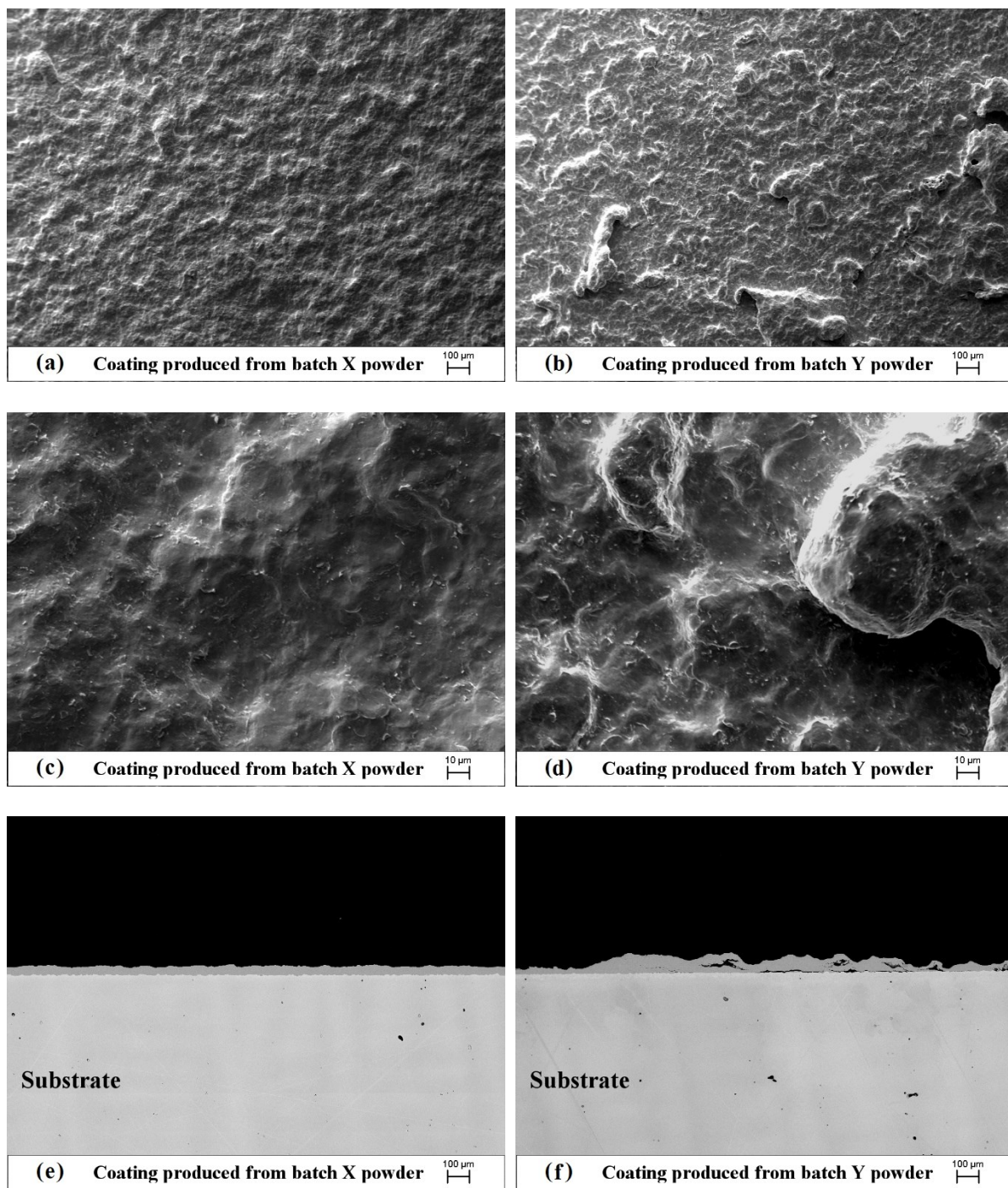


Figure 5.5 Topview and cross-section SEM images of CS NiCoCrAlTaY coatings produced from (a, c, e, g) batch X powder, and (b, d, f, h) batch Y powder. (continued on the next page)

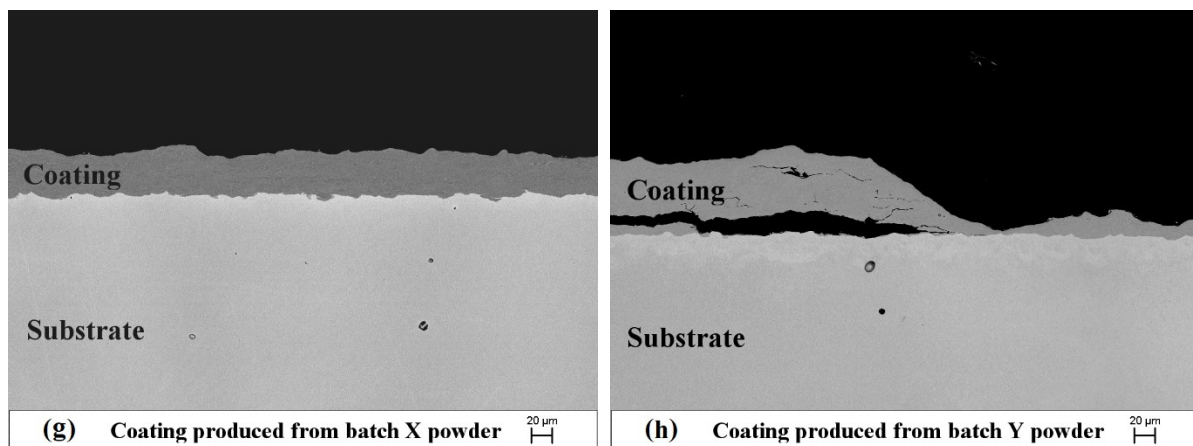


Figure 5.5 (continued) Topview and cross-section SEM images of CS NiCoCrAlTaY coatings produced from (a, c, e, g) batch X powder, and (b, d, f, h) batch Y powder.

The NiCoCrAlTaY coatings produced from the batch X powder show a relatively smooth surface finish (Figs. 5.5a and 5.5c) with the absence of large particle protrusions. In contrast, a rough surface with localized deposit flakes (Fig. 5.5b) and partially deformed particles (Fig. 5.5d) are observed on the NiCoCrAlTaY coatings produced from the batch Y powder. The coating microstructures reveal similar trends. Dense and adherent coatings were achieved from the batch X powder, whereas the coatings obtained from the batch Y powder exhibit evident defects both inside the coating and at the substrate-coating interface.

While the characteristics of the two powders were thought to be similar, it is suspected that some minor variations (e.g., oxide/oxygen content) may exist between the powders but were not detected by the characterization methods used. It is possible that the undesirable variations of the batch Y powder resulted in erratic particle deposition behaviour. This could explain the defects, delamination, and non-uniform thickness observed in the NiCoCrAlTaY coatings produced from the batch Y powder (Figs. 5.5f and 5.5 h). Through experimental trials, it was found that the CS deposition issues using batch Y powder can be overcome by tuning down the spray parameters. Figure 5.6 shows the NiCoCrAlTaY coatings prepared from the batch Y powder using a gas temperature of 400°C (instead of 500°C) and a powder preheating temperature of 400°C (instead of 500°C) while keeping the other spray parameters the same as that listed in Table 5.1.

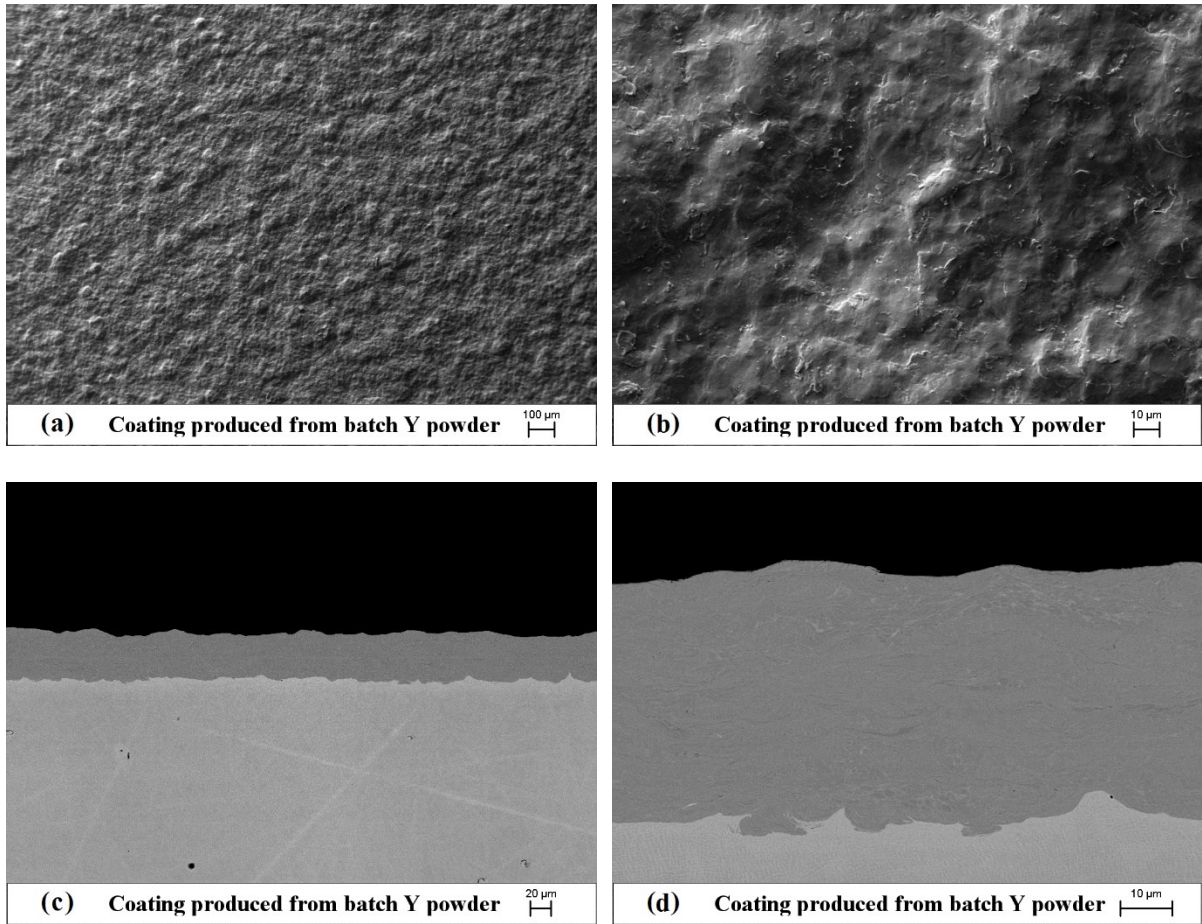


Figure 5.6 Topview and cross-section SEM images of CS NiCoCrAlTaY coatings produced from the batch Y powder using adjusted spray parameters ($T_{\text{gas}} = 400^{\circ}\text{C}$ and $T_{\text{powder}} = 400^{\circ}\text{C}$)

The coating characteristics produced from the batch Y powder under these adjusted CS conditions are similar to that of the NiCoCrAlTaY coatings produced from the batch X powder (Fig. 5.5): low surface roughness, dense microstructure, and good adhesion. The fact that a lower set of spray parameters yielded favourable coating characteristics implies that the relatively large particles were likely the culprit causing the previous deposition issues. Under the previous CS conditions, i.e., a gas temperature of 500°C and a powder preheating temperature of 500°C , some large particles probably just reached the required impact velocities for adhesion. However, the impact velocities were not sufficient to induce extensive plastic deformation, thus resulting in poor adhesion and cohesion in the vicinity of the adhered large particles. By tuning down the spray parameters, it is postulated that those large particles that

cause the deposition issues were not able to adhere due to a decrease in gas velocity and hence particle impact velocities. Instead, they acted as “shot balls” of large mass impinging on the substrate or previously adhered particles. This promoted plastic deformation contributing to the dense and adherent coatings without noticeable defects. Nevertheless, to ensure a reliable CS deposition process and achieve consistent coating quality, the best option would be to use the right powders for every CS operation. This would require strict quality control during powder production.

5.2 Coating Properties and Process Economics

The study in this section focuses on the characterization of the CS NiCoCrAlTaY coatings deposited on CMSX-4 single-crystal Ni-based superalloy substrates. Nitrogen and helium were used to produce the CS NiCoCrAlTaY coatings under similar spray conditions. The coating microstructures and properties were characterized and compared. Furthermore, recycling of the non-deposited powder was explored aiming at reducing the powder cost. The powder characteristics of the recycled powder were examined, and the feasibility of utilizing the recycled powder for CS deposition was verified. A general cost model that considers the benefits of powder recycling was proposed for the CS process. It was demonstrated that the use of nitrogen not only produced superior CS MCrAlY coatings but could also be potentially cost-competitive with the use of powder recycling.

These results are presented in the format of a peer-reviewed journal article that has been published in the Journal of Thermal Spray Technology. The article is entitled “Cold Spray MCrAlY Coatings on Single-Crystal Superalloy Using Nitrogen: Properties and Economics” (DOI: <https://doi.org/10.1007/s11666-020-01058-x>) [175] and is reprinted by permission from the copyright owner, Springer Nature (Springer Nature Customer Service Centre GmbH).



Cold Spray MCrAlY Coatings on Single-Crystal Superalloy Using Nitrogen: Properties and Economics

Deliang Leon Guo¹ · Daniel MacDonald¹ · Linrui Zhao² · Bertrand Jodoin¹

Submitted: 27 March 2020 / in revised form: 14 May 2020 / Published online: 11 June 2020
 © ASM International 2020

Abstract Cold spray (CS) has been proven a promising manufacturing process for the MCrAlY coatings deposition. In this study, NiCoCrAlTaY coatings were deposited on single-crystal nickel-based superalloy (CMSX-4) substrates using the CS technique. Nitrogen and moderate spray parameters were used, and the resulting MCrAlY coatings were compared to coatings sprayed using helium under similar spray conditions. It was found that, contrary to general expectation, favorable coating characteristics were achieved when nitrogen was used. This is attributed to low deposition efficiency under the studied spray conditions, resulting in significant particle impingement that promotes overall particle deformation in the coatings sprayed using nitrogen. However, low deposition efficiency may lead to elevated process cost, despite great gas cost savings by using nitrogen, due to significant increases in powder waste and cost. As such, recycling of the non-deposited powder was explored in an aim to reduce powder cost when using nitrogen. A general cost model that considers the benefits of powder recycling was proposed for the CS process. It was demonstrated that the use of nitrogen and powder recycling can be economical over CS using helium, while producing MCrAlY coatings with desirable properties that are potentially beneficial to the oxidation performance of the coatings.

Keywords cold spray · MCrAlY · single crystal · superalloy · process economics

List of symbols

A^*	Nozzle throat area (m ²)
C_{total}	Total cost (\$)
$C_{\text{total}}(\text{He})$	Total cost using helium (\$)
$C_{\text{total}}(\text{N}_2)$	Total cost using nitrogen (\$)
C_{powder}	Powder cost (\$)
C_{gas}	Gas cost (\$)
C_{Labor}	Labor cost (\$)
DE	Deposition efficiency
DE _{He}	Deposition efficiency using helium
DE _{N₂}	Deposition efficiency using nitrogen
$\$_{\text{gas}}$	Unit price of gas (\$/kg)
$\$_{\text{He}}$	Unit price of helium (\$/kg)
$\$_{\text{labor}}$	Labor rate (\$/s)
$\$_{\text{N}_2}$	Unit price of nitrogen (\$/kg)
$\$_{\text{powder}}$	Unit price of powder (\$/kg)
$\dot{F}_{\text{powder}}$	Powder feed rate (kg/s)
γ	Gas heat capacity ratio
$\dot{m}_{\text{gas}}$	Gas mass flow rate (kg/s)
$\dot{m}_{\text{He}}$	Gas mass flow rate using helium (kg/s)
$\dot{m}_{\text{N}_2}$	Gas mass flow rate using nitrogen (kg/s)
ω	Powder-to-gas mass loading ratio
ω_{He}	Powder-to-gas mass loading ratio for helium
ω_{N_2}	Powder-to-gas mass loading ratio for nitrogen
P_0	Stagnation pressure (Pa)
RE	Recycling efficiency of the non-deposited powder
$\dot{R}_{\text{powder}}$	Powder recycling rate (kg/s)
R_s	Specific gas constant [J/(kg·K)]
t	Spray time (s)
T_0	Stagnation temperature (°C)

✉ Deliang Leon Guo

¹ Cold Spray Research Laboratory, University of Ottawa, Ottawa, ON, Canada

² Aerospace Research Centre, National Research Council Canada, Ottawa, ON, Canada

Introduction

Cold gas dynamic spraying (CGDS), or simply cold spray (CS), is a well-developed and established coating technique (Ref 1–10) and additive manufacturing process (Ref 11–15). The “cold” nature of the technique, i.e., the use of kinetic energy as opposed to thermal energy for coating deposition, differentiates it from other spraying processes. In traditional thermal spray processes, an energy source (flame, electric arc, or plasma jet) is used to heat the feedstock material to a molten or semi-molten state prior to coating formation (Ref 16). In contrast, CS uses a supersonic gas stream to accelerate the feedstock powder to high impact velocities. The feedstock powder particles, remaining at temperatures well below their melting point, then produce coatings following their solid-state plastic deformation during impact onto a substrate (Ref 1). The absence of excessive heating in CS minimizes in-process feedstock oxidation and allows the use of oxidation and temperature sensitive materials. The severe plastic deformation experienced by the particles and substrates leads to adherent and dense coatings with typically compressive residual stresses (Ref 17, 18).

Given the advantages of CS, it has been explored as a promising alternative manufacturing process for MCrAlY (with Ni and/or Co as the base metal (M)) coatings (Ref 19–29). These coatings are commonly applied by thermal spray processes as the bond coat for thermal barrier coating (TBC) used on the hot-section components of gas turbines (Ref 30–34). In addition to their bonding function between the ceramic top-coat and the underlying metallic components, MCrAlY coatings also serve as an oxidation resistance barrier, protecting the components from the hot oxidizing gases that can diffuse through the ceramic top-coat (Ref 35–37). The durability of TBCs, as well as the performance of MCrAlY coatings, was found to be significantly influenced by MCrAlY coating characteristics, such as composition (Ref 38–41), microstructure (Ref 21, 42–44), and surface finish (Ref 45–48). Dense CS MCrAlY coatings with low roughness are generally desirable and can potentially outperform MCrAlY coatings produced by traditional thermal spray processes, such as air plasma spray (APS), high velocity oxygen fuel (HVOF), and low-pressure plasma spray (LPPS) (Ref 21, 22, 27).

CS MCrAlY coatings are primarily produced using helium as the process gas (Ref 20–26) due to favorable thermophysical properties that lead to high gas velocities, high particle impact velocities, and deposition efficiencies (DE) (Ref 49–52). However, helium is a costly and non-renewable sensitive resource that is not always readily available. For instance, a global shortage of helium recently restricted the use of helium in eastern Canada to

limited medical applications for a period of over 4 months (Ref 53, 54). Being a renewable and less expensive resource than helium, nitrogen has been explored as an alternative process gas for CS deposition of MCrAlY coatings (Ref 27–29). However, it was generally thought that MCrAlY coatings deposited using nitrogen are inferior to those deposited using helium under the same spray conditions. This is primarily attributed to the low particle impact velocities and limited plastic deformation when nitrogen is used, which results in non-optimized coating characteristics (high porosity, rough surface, etc.) and consequently unfavorable oxidation behavior of the coatings (Ref 55). Another concern over CS MCrAlY coatings using nitrogen is low DE giving rise to increasing powder waste and cost. Furthermore, disposal of the waste powder adds extra cost to the CS process and can have a large environmental impact if it is not done properly. These issues, however, can be largely circumvented by recycling the non-deposited feedstock powder. Feedstock powders for traditional thermal spray processes suffer appreciable in-process oxidation and are generally not suitable for reuse (Ref 56). In contrast, low process temperature and use of inert gas in CS minimize these effects and provide an opportunity for powder recycling and potential cost savings. These savings can be significant for CS applications (Ref 56, 57) and possibly overcome the drawback of low DE when CS using nitrogen. It is, therefore, both economically and ecologically driven to perform powder recycling for CS applications. Yet no study has been performed regarding the feasibility of MCrAlY powder recycling and the process economics of CS MCrAlY coatings production involving such an operation.

The present study is part of an ongoing project that explores the CS deposition of MCrAlY coatings on single-crystal nickel-based superalloy substrates, as well as the oxidation performance of such coating-substrate systems. Single-crystal superalloys are widely used for high-pressure turbine blades in modern aero-engines (Ref 58). These blades experience severe operating environment and are typically coated with a thin diffusion platinum aluminide (35–50 μm) as the bond coat plus an electron beam physical vapor deposition (EBPVD) ceramic top-coat to form the TBC. As the cost of platinum is extremely high, substituting platinum aluminide with a CS MCrAlY coating of similar thickness could achieve economic benefits without compromising the performance requirements. While CS MCrAlY coatings reported in the literature are mainly based on CoNiCrAlYs (Ref 20–22, 26–28) and are mostly produced on polycrystalline Ni-based superalloys [e.g., Inconel alloys (Ref 19, 22–28)], little is known on the deposition and oxidation behavior of the CS MCrAlY coating on single-crystal superalloys.

In this study, a premium grade MCrAlY powder (NiCoCrAlTaY) (Ref 59) was deposited on a second-generation single-crystal superalloy (CMSX-4) by the CS technique using nitrogen and helium, respectively. Moderate spray parameters are used in an aim to reduce thermal input to the substrate as well as to minimize potentially detrimental residual stresses that are originated from thermal mismatch (Ref 60, 61), while being enough to produce desirable coatings. The concept of recycling and re-utilizing the non-deposited powder for CS deposition was also examined. Process costs of CS MCrAlY coating production, with and without powder recycling, are discussed for both nitrogen and helium. Criteria as to when CS MCrAlYs using nitrogen are cost effective are suggested, and the effects of powder recycling on the criteria are highlighted.

Experimental Procedures

Feedstock Materials

The feedstock powder used is a commercially available gas-atomized NiCoCrAlTaY powder (Amdry 997, 5–38 μm , Oerlikon Metco, USA). Powder morphology and cross-section microstructure of the as-received powder are shown in Fig. 1, where the spherical shape of the powder and three-phase constituents can be seen in the scanning electron microscopy (SEM) images. The β -NiAl phase, which is in relatively darker gray contrast, is arbitrarily dispersed in the light gray γ -matrix throughout the powder. The white areas at the γ and β phase boundaries are tantalum-rich phases owing to the local segregation of tantalum in this MCrAlY powder.

A second-generation single-crystal Ni-based superalloy (CMSX-4, Cannon Muskegon, USA) was used as the

substrate for this study. The single-crystal superalloy bars ($\phi 16$ mm) were received in solution heat-treated condition and cut into 3-mm-thick disks by electrical discharge machining (EDM). The CMSX-4 disks were then manually ground before CS deposition to remove the oxidized surface layer resulting from the EDM cutting. Figure 2 shows the overview and cross section of a ground CMSX-4 substrate. The substrate has a high volume fraction of dark gray γ' phase (Ni_3Al) among the intertwining light gray matrix of γ nickel-based solid solution (Fig. 2b), typical for single-crystal Ni-based superalloys (Ref 62). The nominal composition of the feedstock powder and CMSX-4 substrate is provided in Table 1.

Cold Spray Deposition

A commercial CS system (SST-EP, Centerline Technology (Winsor), Canada) was used to deposit the MCrAlY powder on the CMSX-4 substrates. The converging–diverging (de Laval) nozzle has a 2-mm throat diameter, a 120-mm diverging section length, and a 6.5-mm exit diameter. The feedstock powder was fed through a powder-preheating unit before being introduced into the nozzle diverging section. Nitrogen was used as the process gas and powder-feeding gas for the coating preparation, while helium was utilized for some tests for comparison purpose and cost analysis. The spray parameters were used for both gases, except a traverse speed of 100 mm/s and a single pass was used for helium to achieve a similar coating thickness. Detailed spray parameters are listed in Table 2. DE was calculated as the ratio of coating mass (substrate weight gain after deposition) to the mass of powder fed on the substrate. Powder feedrate was measured at the powder feeder exit prior to coating deposition and used to estimate the amount of powder fed. To ensure adequate precision in the DE measurements for the case of nitrogen, the

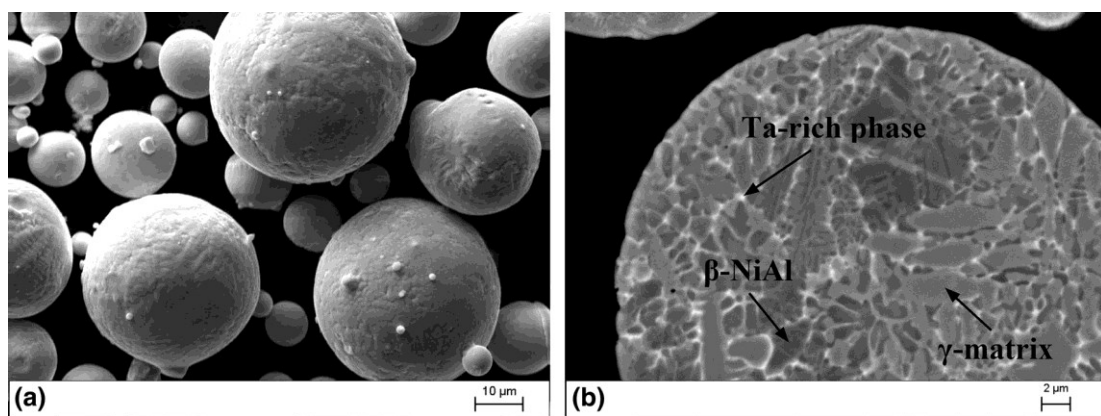


Fig. 1 SEM images of the as-received NiCoCrAlTaY powder. (a) An overview of the powder showing the morphology. (b) A cross section showing the three-phase constituents: γ -matrix (light gray), β -NiAl (dark gray), and tantalum-rich phase (white)

Fig. 2 Geometry and cross section of a ground CMSX-4 substrate. (a) Overview. (b) Cross section of the single-crystal substrate showing the flat surface finish and high volume fraction of γ' -Ni₃(Al, Ti) phase (dark gray) among the γ nickel-based solid solution matrix (light gray)

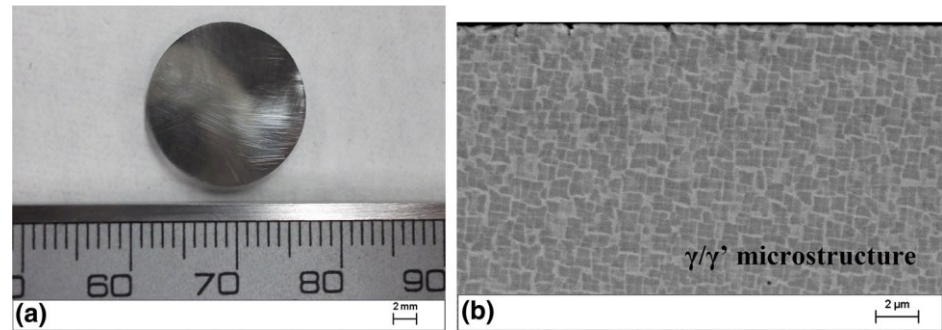


Table 1 Nominal composition of Amdry 997 powder and CMSX-4 superalloy (wt.%)

	Ni	Co	Cr	Al	Ta	Y	W	Re	Ti	Others
Amdry 997	43.9	23.0	20.0	8.5	4.0	0.6	...	...	...	...
CMSX-4	61.7	9.0	6.5	5.6	6.5	...	6.0	3.0	1.0	Mo 0.6 Hf 0.1

Table 2 CS parameters for depositing MCrAlY coatings onto single-crystal superalloy

Stagnation pressure, MPa	Stagnation temperature, °C	Powder preheating, °C	Powder feedrate, g/min	Stand-off distance, mm	Step increment, mm	Traverse speed, mm/s	Number of passes
3.45	400	400	13.3 ± 0.3	15	1	5 (N ₂) 100 (He)	2 (N ₂) 1 (He)

deposited coating masses were similar to those used for the cases of helium.

Material Characterization

Feedstock powder particle size and particle velocity distributions were characterized using a laser diffraction analyzer (S3500, Microtrac, Nikkiso, Japan) and a laser Doppler velocimetry meter (ColdSprayMeter, Tecnar, Canada), respectively. Coating thickness and porosity level were measured using an optical microscope (NMM-800TRF, Kingdak, China) with an image analysis software (Vision-Lite, Clemex, Canada). Coating roughness was measured at nine locations on the coating surface using a stylus roughness tester (SRG-4000, Phase II Plus, USA). A Vickers hardness tester (Duramin-I, Struers, Denmark) was used to create micro-indentations on the samples using a setting of 0.05 kg load and 15 s dwelling time. To avoid oversized indentations that introduce edge effects, a load of 0.01 kg was used for the feedstock powder to accommodate its small size (5–38 μ m). The dimensions of the indentations were measured under high magnification using a scanning electron microscopy (SEM) (EVO-MA10, Zeiss, Germany) and were used to calculate the materials

micro-hardness. The SEM equipped with energy-dispersive x-ray spectrometry (EDS) (INCA-x-act, Oxford Instruments, UK) and the x-ray diffraction (XRD) using Cu K α radiation (X-Pert PW1830, PANalytical, Netherlands) were used to characterize the microstructure, chemical composition, and phase constituents of the feedstock powders and as-sprayed coatings.

Results and Discussion

Coating Characteristics

NiCoCrAlTaY coatings were successfully deposited on the single-crystal superalloy (CMSX-4) substrates by CS using either nitrogen or helium. However, the characteristics of the coatings differ considerably depending on the gas used. Figure 3 shows a typical surface morphology of the CS MCrAlY coatings using nitrogen and helium, respectively. The MCrAlY coatings deposited using nitrogen show bumps and dimples of small magnitude with the absence of large protrusions of undeformed particles. In contrast, rough surfaces with undeformed particles are observed on the coatings prepared using helium. This difference in

Fig. 3 SEM images showing the surface morphology of CS MCrAlY coatings using nitrogen (a) and helium (b)

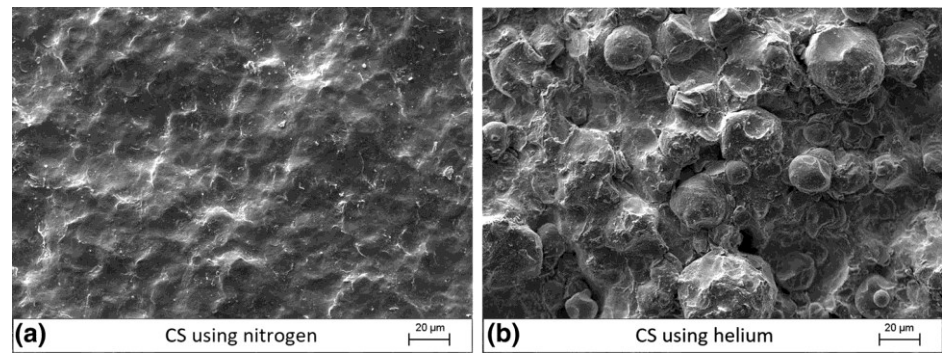


Table 3 Characteristics of CS MCrAlY coatings using nitrogen and helium

Process gas	Roughness, μm				DE, %	Thickness, μm	Porosity, %	Hardness, HV _{0.05}
	R_a	R_z	R_q	R_t				
Nitrogen	2.8 ± 0.8	8.0 ± 2.3	2.7 ± 0.4	8.2 ± 2.6	0.3	33.4 ± 3.9	0.1 ± 0.1	600 ± 17
Helium	7.6 ± 2.7	21.5 ± 7.8	7.3 ± 2.3	22.5 ± 8.8	12.0	35.9 ± 8.5	0.9 ± 1.0	507 ± 39

coating surface morphology is further reflected in their measured roughness, as shown in Table 3 along with other coatings characteristics. The nitrogen-sprayed MCrAlY coatings show significantly lower values in all roughness parameters, compared to those of the coatings deposited using helium.

These results indicate that the surface of the nitrogen-sprayed coatings experienced extensive plastic deformation during CS deposition. This is attributed to enhanced particle impingement as a result of the considerably low DE in the case of CS using nitrogen (0.3%), approximately 40 times lower than that of CS using helium (12.0%). The use of nitrogen and moderate spray parameters resulted in low particle impact velocities. Consequently, only a small portion of the particles was able to adhere, while most particles simply rebounded after impact. These non-deposited particles, similar to the shot balls in shot-peening surface treatment, repeatedly impinged on the adhered particles and plastically deformed the deposited coating, leading to a smoothed surface morphology as seen in Fig. 3(a). A low roughness is believed to benefit the oxidation performance of MCrAlY coatings, as rough surfaces not only promote the formation of unfavorable mixed oxides (NiO, Cr₂O₃, and Ni(Cr, Al)₂O₄ spinels) (Ref 24, 46, 63), but also amplify the out-of-plane stresses in the thermally grown oxide (TGO) scale (Ref 45). Post-deposition surface treatment, such as shot peening, has been demonstrated as an effective process to reduce the coating roughness and improve the performance of MCrAlY coatings (Ref 23, 46, 64). However, if appropriate roughness can be obtained in the as-sprayed condition, the need

for post-deposition surface treatment would then be unnecessary, thus simplifying the overall manufacturing processes.

Cross-section images showing the microstructures of the CS MCrAlY coatings deposited using the two gases are provided in Fig. 4. CS coatings deposited using helium are generally expected to have a favorable microstructure, given helium's advantages over nitrogen in particle acceleration. However, this is not what has been observed. Using the same moderate spray parameters, the helium-sprayed MCrAlY coatings (Fig. 4b, d, and f) present some undesirable characteristics, such as rough surface, noticeable defects (pores, cracks). In contrast, the nitrogen-sprayed MCrAlY coatings show a dense microstructure without the presence of such defects (Fig. 4a, c, and e).

The backscattered electron (BSE) images of the two coatings also reveal interesting microstructural features. The feedstock particles sprayed using nitrogen are highly deformed, resulting in a relatively uniform microstructure throughout the coatings (Fig. 4e). On the contrary, less deformed particles are observed when deposited using helium (Fig. 4f). In these particles, the feedstock powder's microstructure (see Fig. 1) or phase constituents (e.g., γ and β phases) were retained. This is in contrast to coating regions where only the γ phase is present. The bimodal coating microstructure has been commonly observed in CS MCrAlY coatings prepared using helium (Ref 20, 65). It is believed that β -phase dissolution occurred during the coating process, and the extent of this phase transformation depends on the plastic deformation levels of the deposited particles (Ref 20, 65). As such, highly deformed particle

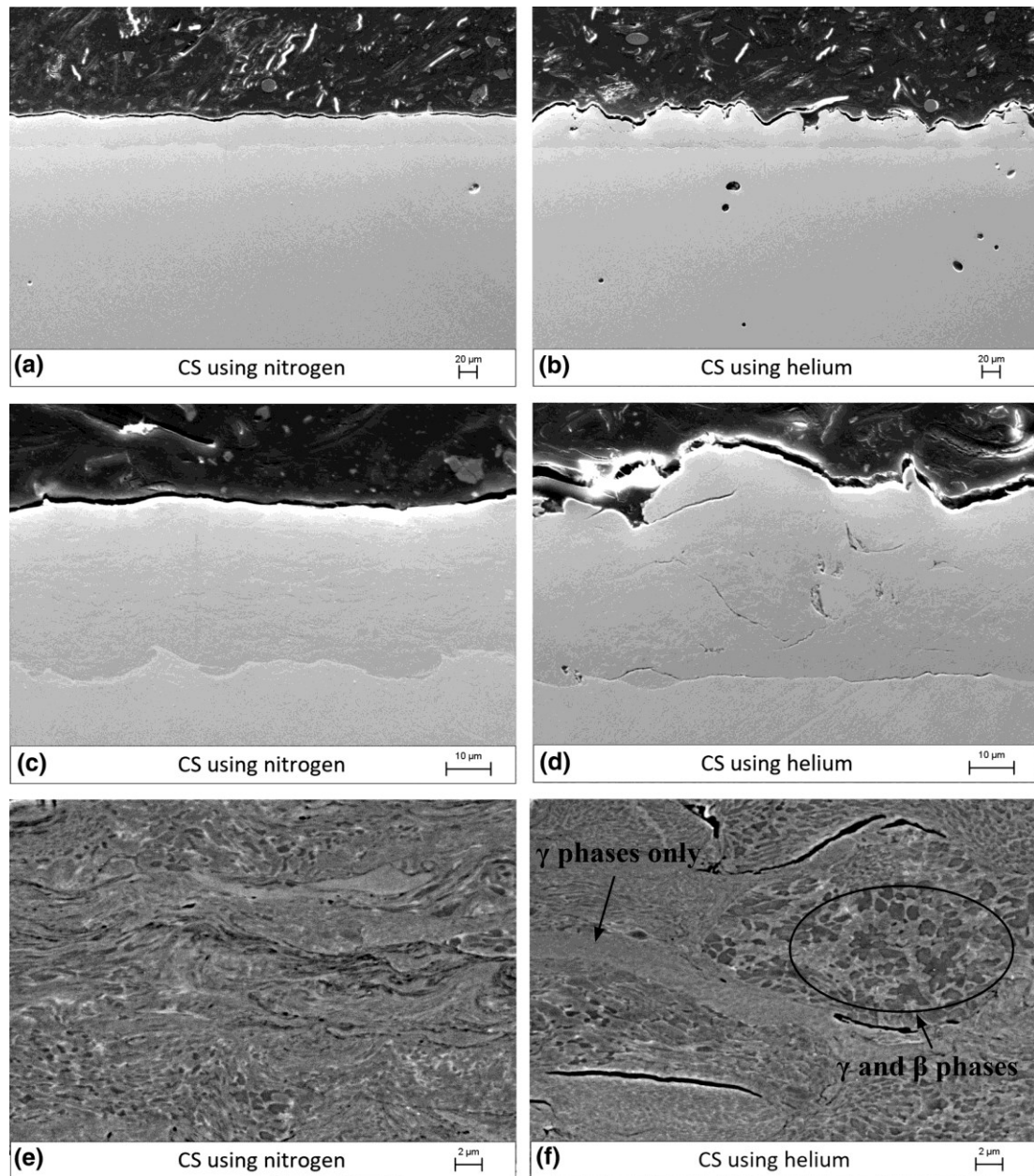


Fig. 4 Cross section of CS MCrAlY coatings using nitrogen (left) and helium (right). (a–d) Secondary electron (SE) images, (e, f) backscattered electron (BSE) images

regions are expected to experience significant β dissolution resulting in only γ phase, whereas negligible microstructural changes occur in particle regions undergoing limited plastic deformation. This helps explain the microstructure differences observed in the two coatings (Fig. 4) and reveals a higher overall deformation in the nitrogen-sprayed coatings that is promoted by the enhanced particle impingements. Increased plastic deformation facilitates a

great degree of grain refinement, resulting in a fine coating grain structure (Ref 20). This may be beneficial to the oxidation performance of MCrAlY coatings due to enhanced element diffusion via grain boundaries (Ref 66–68). The CS MCrAlY coatings produced using nitrogen in the present study are promising improved oxidation behavior. Detailed and focused oxidation evaluation of the MCrAlY coatings will be reported in another paper.

Powder Recycling

This section explores the concept of powder recycling to reduce the powder waste and cost for the CS deposition process of MCrAlY coatings. All spray trials in this section were performed using nitrogen as the process gas, as the cost savings by powder recycling are prominent in the case of CS using nitrogen due to low DE (or, in other words, high powder waste). In contrast, this powder cost savings are insignificant when helium is used (as demonstrated in “Process Economics” section).

To collect and characterize the powder particles that did not deposit, trials were performed using an in-house powder reclamation chamber. The morphology and

microstructure of the recycled powder are shown in Fig. 5. The high velocity particle impacts caused severe plastic deformation of the particles, resulting in hemisphere-like shapes of the recycled powder. Cross sections of the recycled powder show similar phase constituents (γ -matrix, β -NiAl, and Ta-rich phase) as the as-received powder; however, the phases are compacted and elongated in the impact zones. Unlike in the coatings (Fig. 4) where evident β dissolution was observed, the β phases were retained in most of the recycled powder volume despite severe particle deformation (Fig. 5c and d). In some rare recycled particles, however, evidence of indiscernible β phases that implies the β dissolution can be seen near the particle deformed zones (e.g., Fig. 5e and f). These observations

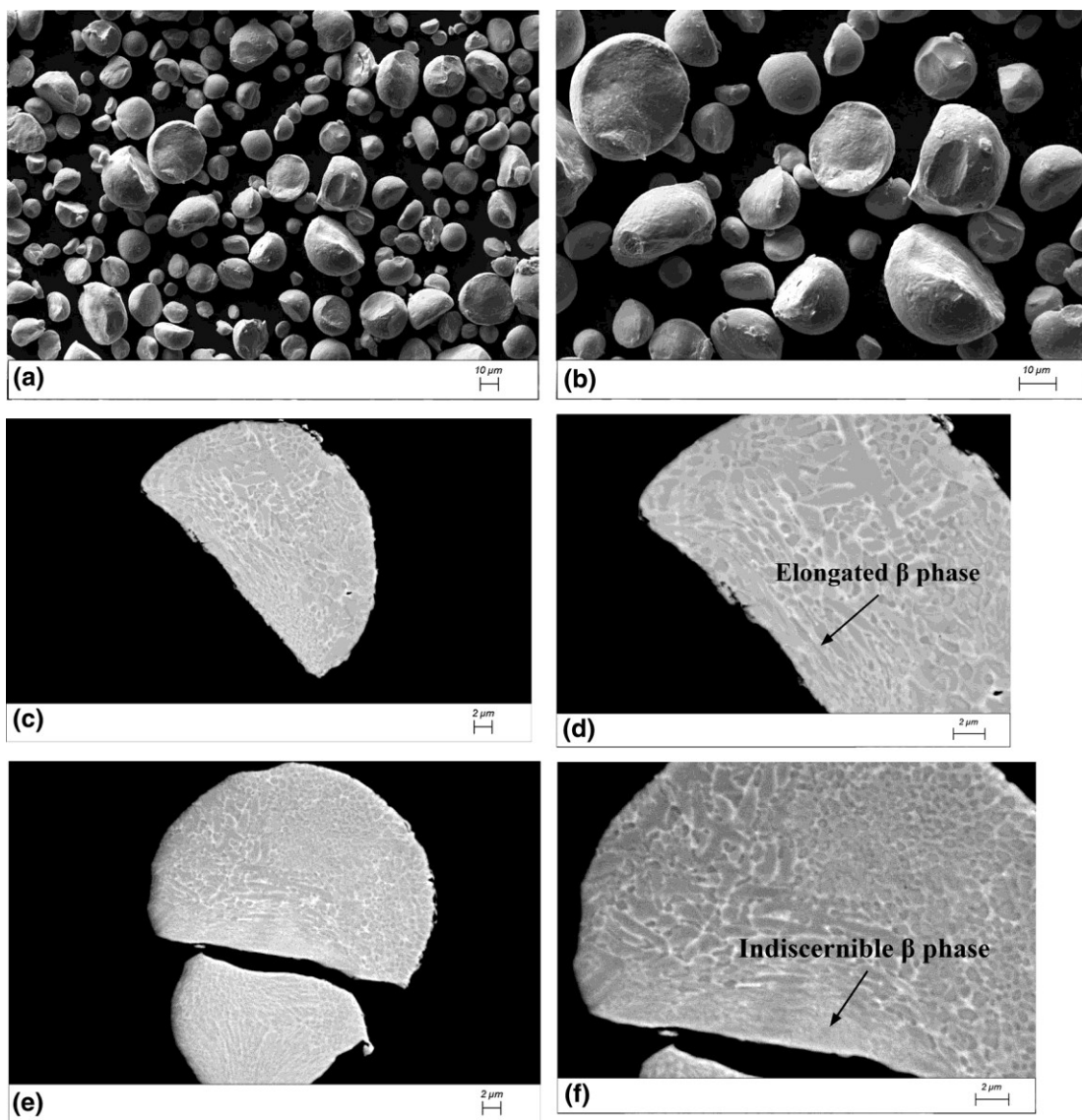


Fig. 5 SEM images of recycled MCrAlY powder particles. (a, b) Powder morphology; (c, d) cross section showing deformed and elongated β phase near the impact locations; (e, f) evidence of indiscernible β phase that implies the β dissolution

suggest that a critical plastic deformation (strain) level is required to initiate the β dissolution. Most non-deposited particles experienced insufficient plastic deformation due to only one impact. In contrast, extensive particle impingements during coating deposition provide the essential plastic deformation that promotes β dissolution in the coatings. This is also confirmed by x-ray diffraction (XRD) results of the powders and CS coatings (presented in Fig. 6), which show a gradual γ -peak broadening and β -peak reduction. The progressive microstructural evolution found in the recycled powder and the coatings may be taken as direct evidence for the strain-induced nature of the β -phase transformation, which was suggested in previous studies (Ref 20, 65).

Despite the obvious powder morphology difference between the as-received and recycled powders, similar particle size distribution profiles are observed for the two powders, as shown in Fig. 7. This similarity is also reflected in Table 4, where MV, MN, and MA stand for the mean particle sizes based on volume, number, and area distribution, respectively; and D10, D50, and D90 represent the particle sizes corresponding to the 10th, 50th, and 90th percentile of the cumulative volume, respectively. It is worth noting that the non-spherical morphology of the recycled powder may affect the particle size distribution results. Nevertheless, the results can be used to assume that the overall size distribution is similar, while acknowledging that the recycled particles are likely to exhibit a semi-hemispherical shape.

The powder hardness and in-flight particle velocities (measured at 10 mm from the nozzle exit with the absence of a substrate) were also evaluated with the mean values reported in Table 4. The hardness of the recycled powder

seems to be slightly higher than that of the as-received powder; however, this value may not accurately reflect the hardness change to the recycled powder given the way how it was measured. The indentations on the recycled powder were made in such a way that they are neither too close to the particle periphery (to minimize the edge effect), nor too far from the deformed region (to better represent the change in the recycled powder). As such, this hardness increase of the recycled powder implies that the strain hardening is not limited to the powder periphery, and the deformed region can be considerably harder than the as-received powder as a result of work hardening. The mean particle velocity is also noticeably higher for the recycled powder. This is likely attributed to an increased drag coefficient caused by the geometry change of the recycled particles, which leads to an enhanced drag force allowing for greater momentum transfer to the particles. The increased particle velocity and particle hardness represent opposite effects (promoting and hindering, respectively) on the coating deposition, which potentially offset each other during the CS deposition of the recycled powder.

Figure 8 presents the cross section of the CS MCrAlY coatings produced from the as-received and recycled powders using nitrogen and same number of passes. The recycled powder results in a thinner coating, suggesting a lower DE. However, it is worth noting that the feedrate of the recycled powder was lower than that of the as-received powder, as the changes in powder morphology affected powder flowability. Dedicated recycling equipment would be needed to collect a sufficient amount of recycled powder to match the powder feedrates and carry out further investigations. Nevertheless, the results presented in the study show that the recycled MCrAlY powder is suitable for CS deposition and the resulting coatings characteristics (e.g., porosity < 0.5%, $HV_{0.05} = 609 \pm 23$) are similar to that of the MCrAlY coatings prepared from the as-received powder. For the current study, a similar DE is

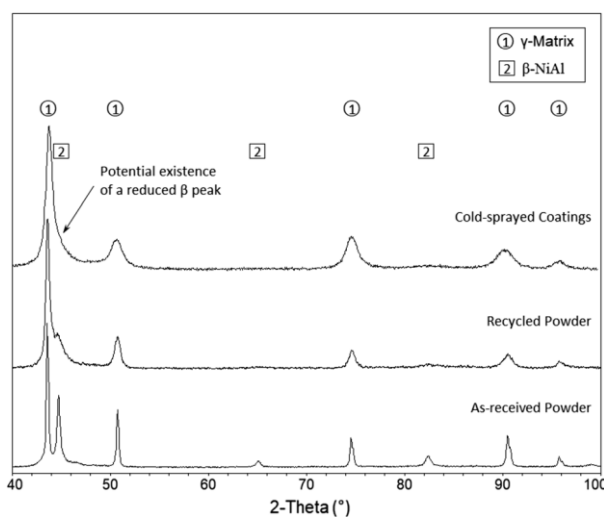


Fig. 6 XRD patterns of as-received powder, recycled powder, and as-sprayed coatings

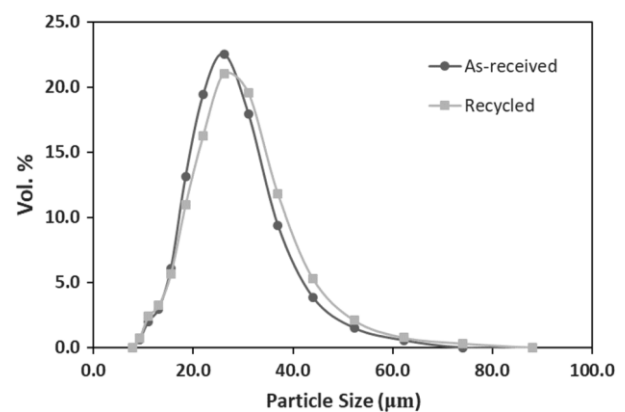
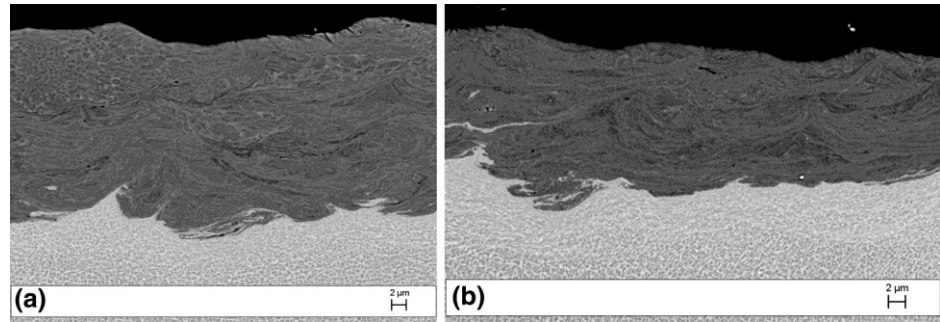


Fig. 7 Particle size distribution of the as-received and recycled MCrAlY powders

Table 4 Particle characteristics of the as-received and recycled MCrAlY powders

Powder	Mean and percentile particle size, μm						Hardness, HV _{0.01}	Particle velocity, m/s
	MV	MN	MA	D10	D50	D90		
As-received	23.91	16.91	21.47	15.02	23.00	33.77	352 $\pm$ 22	503 $\pm$ 116
Recycled	25.03	16.63	22.06	14.83	24.11	35.97	392 $\pm$ 18	571 $\pm$ 131

Fig. 8 Cross section of CS MCrAlY coatings using nitrogen produced from (a) as-received powder and (b) recycled powder

considered for the recycled powder in the analysis of process economics in the next section.

It is also interesting to observe from Fig. 8 that the γ/γ' microstructure of the single-crystal substrate was noticeably distorted in the vicinity of the coating-substrate interface. This suggests some plastic deformation in this substrate region as a result of high velocity particle impacts during CS deposition. However, the affected region is limited to a range of approximately 2–5 μm . The single-crystal nature and thermomechanical properties of the underlying superalloy substrate should not be affected by CS deposition of the MCrAlY coatings.

Process Economics

Cost models for the CS process have been developed and reported by Stier (Ref 69) and MacDonald (Ref 70). These studies also examined the effects of nitrogen and helium gas mixing on the process cost of CS MCrAlY coatings and suggested that the use of pure nitrogen is not recommended due to the high powder cost as a result of low DE. However, potential cost savings by powder recycling were not considered in these studies. The present section introduces a general CS cost model that includes the economics of powder recycling.

The most significant cost factors for the CS process are feedstock powder, process gas, and labor costs (Ref 57, 69, 70). Electricity cost (e.g., for gas heating) is generally negligible, especially when expensive feedstock powder is used (Ref 57, 69, 70). As such, the total cost for the CS process can be simplified as:

$$C_{\text{total}} = C_{\text{powder}} + C_{\text{gas}} + C_{\text{Labor}} \quad (\text{Eq 1})$$

where C_{powder} is the powder cost (\$), C_{gas} is the gas cost

(\$), and C_{Labor} is the labor cost (\$). For the CS process with powder recycling, the net powder cost is the cost of powder fed subtracting the powder savings due to recycling. This can be written in a rate form as

$$C_{\text{powder}} = \$_{\text{powder}} * (\dot{F}_{\text{powder}} - \dot{R}_{\text{powder}}) * t \quad (\text{Eq 2})$$

where $\$_{\text{powder}}$ is the unit price of powder (\$/kg), $\dot{F}_{\text{powder}}$ is the powder feed rate (kg/s), $\dot{R}_{\text{powder}}$ is the powder recycling rate (kg/s), and t is the time of the spray (s). $\dot{R}_{\text{powder}}$ depends on both deposition efficiency (DE) and powder recycling efficiency (RE),

$$\dot{R}_{\text{powder}} = \dot{F}_{\text{powder}} * (1 - \text{DE}) * \text{RE} \quad (\text{Eq 3})$$

In the case of $\text{RE} = 0$, i.e., $\dot{R}_{\text{powder}} = 0$, Eq 2 would then represent the powder cost of the CS process without powder recycling. The gas cost of the CS process can be determined from the amount of gas consumed per unit of time and the time of spray,

$$C_{\text{gas}} = \$_{\text{gas}} * \dot{m}_{\text{gas}} * t \quad (\text{Eq 4})$$

where $\$_{\text{gas}}$ is the unit price of gas (\$/kg) and $\dot{m}_{\text{gas}}$ is the gas mass flow rate through the nozzle (kg/s). Gas mass flow rate is a function of nozzle throat area (A^*), specific spray parameters (stagnation pressure P_0 and temperature T_0) used, and spray gas properties (gas heat capacity ratio γ , and R_s), and can be approximated by the 1D isentropic relation (Ref 52, 71):

$$\dot{m}_{\text{gas}} = \frac{P_0 A^*}{\sqrt{T_0}} \sqrt{\frac{\gamma}{R_s}} \left(\frac{\gamma + 1}{2} \right)^{-\frac{\gamma+1}{2(\gamma-1)}} \quad (\text{Eq 5})$$

Note that stagnation pressure in absolute value should be used for estimating the gas mass flow rate.

The labor cost can be simply calculated using,

$$C_{\text{labor}} = \$_{\text{labor}} * t \quad (\text{Eq 6})$$

where $\$_{\text{labor}}$ is the labor rate (\$/s). The spray time, which dictates the amount of powder fed, gas consumption, and labor cost, can be different from one spray condition to another. To have a simple comparison between different spray conditions, cost per unit mass of coating deposited is preferred. This can be achieved by considering the time needed to deposit 1 kg coating,

$$t = \frac{1}{\text{DE} * \dot{F}_{\text{powder}}} \quad (\text{Eq 7})$$

Combining Eqs 1–4, 6 and 7, the total cost can be rearranged into the following forms,

$$C_{\text{total}} = [\$_{\text{powder}} * (\dot{F}_{\text{powder}} - \dot{R}_{\text{powder}}) + \$_{\text{gas}} * \dot{m}_{\text{gas}} + \$_{\text{labor}}] * t \quad (\text{Eq 8})$$

$$C_{\text{total}} = \frac{1}{\text{DE}} \left\{ \$_{\text{powder}} * [1 - (1 - \text{DE}) * \text{RE}] + \frac{\$_{\text{gas}} * \dot{m}_{\text{gas}}}{\dot{F}_{\text{powder}}} + \frac{\$_{\text{labor}}}{\dot{F}_{\text{powder}}} \right\} \quad (\text{Eq 9})$$

Note that Eq 6, 8, and 9 only consider the labor cost related to the CS operation. With the use of automated industrialized equipment, the labor cost required for the powder recycling process should be negligible and was hence neglected in the cost analysis.

Let ω be the powder-to-gas mass loading ratio in kg (powder) per kg (gas):

$$\omega = \frac{\dot{F}_{\text{powder}}}{\dot{m}_{\text{gas}}} \quad (\text{Eq 10})$$

The powder feed rate ($\dot{F}_{\text{powder}}$) can then be expressed as a function of $\dot{m}_{\text{gas}}$ and ω , and thus, Eq 9 becomes

$$C_{\text{total}} = \frac{1}{\text{DE}} \left\{ \$_{\text{powder}} * [1 - (1 - \text{DE}) * \text{RE}] + \frac{\$_{\text{gas}}}{\omega} + \frac{\$_{\text{labor}}}{\dot{m}_{\text{gas}} * \omega} \right\} \quad (\text{Eq 11})$$

Unit prices for powder ($\$_{\text{powder}}$), gas ($\$_{\text{gas}}$), and labor ($\$_{\text{labor}}$) are either directly available or can be estimated. Equation 11, therefore, shows that the total cost of CS coatings is a function of DE, RE, ω , and $\dot{m}_{\text{gas}}$. Intuitively, DE and RE should be maximized as this would minimize the amount of powder waste. In addition to the powder cost reduction, a higher DE also decreases the time of spray to deposit coating (Eq 7), which provides further savings on both the gas and labor costs. Similarly, increasing ω and/or $\dot{m}_{\text{gas}}$ also leads to a reduction in spray time due to an increased powder feed rate (Eq 7). As such, higher ω and $\dot{m}_{\text{gas}}$ are always desirable from a cost reduction perspective; however, powder overloading may result in lower particle velocities (and lower DE) and can cause feeding

and clogging issues, while high gas flow rate presents a challenge for gas heating due to the limited power of gas heaters and requires larger nozzle throat area. These considerations inevitably put a limitation on the actual ω and $\dot{m}_{\text{gas}}$ that can be reached. For practical CS applications, maximum allowable gas stagnation properties (P_0 , T_0) of a given CS system should generally be used to maximize DE and $\dot{m}_{\text{gas}}$, if the coating quality is favorable and the substrate maximum allowable temperature is not reached when using these spray parameters. Gas mass flow rate ($\dot{m}_{\text{gas}}$) can then be easily estimated by Eq 5 once the spray parameters and nozzle specifications are known. RE is also obtainable for an established powder recycling process, and values of 80–90% can be realistic. The effect of powder-to-gas mass loading ratio (ω) or powder feed rate ($\dot{F}_{\text{powder}}$) on coating quality and DE is rather complex and may vary for different powder–substrate material combinations. Experiments are generally needed to determine the ω value that yields the optimal coating characteristics, highest DE, and lowest process cost for a specific CS application.

Case Study: Cost Comparison of CS MCrAlY Coatings Using Nitrogen and Helium

The following case study, which compares the cost of CS MCrAlY coatings using helium and nitrogen, uses prices (listed in Table 5) available as of January 2020 at the University of Ottawa, Canada, and a powder recycling efficiency (RE) of 90%.

Knowing the spray parameters, the respective gas mass flow rates for helium and nitrogen can be estimated (Eq 5) and Eq 11 can then be modified for the two gases as,

$$C_{\text{total}}(\text{He}) = f(\text{DE}_{\text{He}}, \omega_{\text{He}}) \\ = \frac{1}{\text{DE}_{\text{He}}} \left\{ \$_{\text{powder}} * [1 - (1 - \text{DE}_{\text{He}}) * \text{RE}] + \frac{\$_{\text{He}}}{\omega_{\text{He}}} + \frac{\$_{\text{labor}}}{\dot{m}_{\text{He}} * \omega_{\text{He}}} \right\} \quad (\text{Eq 12})$$

$$C_{\text{total}}(\text{N}_2) = f(\text{DE}_{\text{N}_2}, \omega_{\text{N}_2}) \\ = \frac{1}{\text{DE}_{\text{N}_2}} \left\{ \$_{\text{powder}} * [1 - (1 - \text{DE}_{\text{N}_2}) * \text{RE}] + \frac{\$_{\text{N}_2}}{\omega_{\text{N}_2}} + \frac{\$_{\text{labor}}}{\dot{m}_{\text{N}_2} * \omega_{\text{N}_2}} \right\} \quad (\text{Eq 13})$$

where $C_{\text{total}}(\text{He})$ and $C_{\text{total}}(\text{N}_2)$ are the total costs, DE_{He} and DE_{N_2} are the deposition efficiencies, ω_{He} and ω_{N_2} are the powder-to-gas mass loading ratios, $\dot{m}_{\text{He}}$ and $\dot{m}_{\text{N}_2}$ are the gas mass flow rates, for CS using helium and nitrogen,

Table 5 Unit prices for powder, gases (helium and nitrogen), and labor

Powder, \$/kg	Helium, \$/kg	Nitrogen, \$/kg	Labor, \$/h
255.7	178.6	0.5	70

respectively; $\$_{\text{He}}$ and $\$_{\text{N}_2}$ are the unit prices for helium and nitrogen gases, respectively.

It is possible to perform a series of experiments at different ω_{He} and ω_{N_2} , and determine the corresponding DE_{He} and DE_{N_2} for each of the experiments. Comparisons between the total cost of CS using helium and nitrogen can then be made by using the results into Eqs 12 and 13. However, these experiments are resource consuming and are normally required for each powder and substrate material combination to determine the choice of process gas and the optimal spray conditions. An alternative way (as presented below) of comparing different spray conditions can be used, which may reduce the number of experiments to be conducted.

For CS using one of the gases (e.g., helium) to be economical, the corresponding total cost must be lower, i.e., $C_{\text{total}}(\text{He}) < C_{\text{total}}(\text{N}_2)$, or

$$\frac{1}{\text{DE}_{\text{He}}} \left\{ \$_{\text{powder}} * [1 - (1 - \text{DE}_{\text{He}}) * \text{RE}] + \frac{\$_{\text{He}}}{\omega_{\text{He}}} + \frac{\$_{\text{labor}}}{\dot{m}_{\text{He}} * \omega_{\text{He}}} \right\} < \frac{1}{\text{DE}_{\text{N}_2}} \left\{ \$_{\text{powder}} * [1 - (1 - \text{DE}_{\text{N}_2}) * \text{RE}] + \frac{\$_{\text{N}_2}}{\omega_{\text{N}_2}} + \frac{\$_{\text{labor}}}{\dot{m}_{\text{N}_2} * \omega_{\text{N}_2}} \right\} \quad (\text{Eq 14})$$

Reorganizing Eq 14 leads to

$$\frac{\text{DE}_{\text{He}}}{\text{DE}_{\text{N}_2}} > \frac{\$_{\text{powder}} * (1 - \text{RE}) + \frac{\$_{\text{He}}}{\omega_{\text{He}}} + \frac{\$_{\text{labor}}}{\dot{m}_{\text{He}} * \omega_{\text{He}}}}{\$_{\text{powder}} * (1 - \text{RE}) + \frac{\$_{\text{N}_2}}{\omega_{\text{N}_2}} + \frac{\$_{\text{labor}}}{\dot{m}_{\text{N}_2} * \omega_{\text{N}_2}}} \quad (\text{Eq 15})$$

Therefore, a criterion ratio of $\text{DE}_{\text{He}}/\text{DE}_{\text{N}_2}$ exists, above which the total CS cost would be lower for helium. This criterion is a function of ω_{He} and ω_{N_2} , given that $\$_{\text{powder}}$, $\$_{\text{He}}$, $\$_{\text{N}_2}$, $\$_{\text{labor}}$ and RE are known and $\dot{m}_{\text{He}}$ and $\dot{m}_{\text{N}_2}$ can be calculated based on the selected spray parameters.

Figure 9 presents the dependence of the critical $\text{DE}_{\text{He}}/\text{DE}_{\text{N}_2}$ ratios on the $\omega_{\text{He}}/\omega_{\text{N}_2}$ ratios with a typical

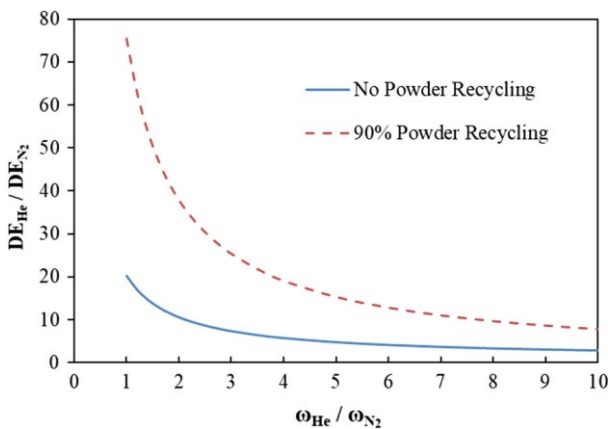


Fig. 9 $\text{DE}_{\text{He}}/\text{DE}_{\text{N}_2}$ ratios above which CS using helium would be cost effective versus nitrogen for various $\omega_{\text{He}}/\omega_{\text{N}_2}$ ratios with $\omega_{\text{N}_2} = 3\%$, $P_0 = 3.45$ MPa, $T_0 = 400$ °C

ω_{N_2} of 3% (Ref 50, 69). Stagnation pressure was converted to absolute value for the gas mass flow rate calculations. The $\text{DE}_{\text{He}}/\text{DE}_{\text{N}_2}$ decreases with increasing $\omega_{\text{He}}/\omega_{\text{N}_2}$ or, in other words, higher powder loading in helium. High powder loading significantly reduces the spray time for depositing unit coating mass and hence decreases the gas and labor costs, thus permitting a lower $\text{DE}_{\text{He}}/\text{DE}_{\text{N}_2}$ ratio for helium to be preferable. Figure 9 also shows that powder recycling has a prominent influence on the $\text{DE}_{\text{He}}/\text{DE}_{\text{N}_2}$ criterion, particularly at lower $\omega_{\text{He}}/\omega_{\text{N}_2}$ ratios. For example, at a $\omega_{\text{He}}/\omega_{\text{N}_2}$ ratio of 2 (i.e., $\omega_{\text{He}} = 6\%$, $\omega_{\text{N}_2} = 3\%$), DE_{He} must be 10.6 times higher than DE_{N_2} to make the use of helium economical without powder recycling. When the powder is recycled with a RE of 90%, $\text{DE}_{\text{He}}/\text{DE}_{\text{N}_2}$ would need to be 37.9.

It may seem that CS using helium can be cost effective as long as DE_{He} is sufficiently high (above the critical/ $\text{DE}_{\text{He}}/\text{DE}_{\text{N}_2}$ ratio required at specific $\omega_{\text{He}}/\omega_{\text{N}_2}$). However, this may not always be the case as DE_{He} cannot be greater than 100%. When an appropriate DE_{N_2} is achieved, CS using nitrogen can be economical. Figure 10 highlights the regions of cost-effective gases on a DE_{N_2} versus DE_{He} plot. Powder loading ratio for helium (ω_{He}) and nitrogen (ω_{N_2}) was set to be 6 and 3%, respectively, and a RE of 90% was used for the case involving powder recycling. The regions whether nitrogen or helium should be used are well defined in Fig. 10. At a given DE_{He} , the use of nitrogen is economical as long as a minimum DE_{N_2} is reached. This DE_{N_2} threshold, as well as the distribution of the regions, should only be marginally changed for CS using different parameters. This is attributed to the facts that different sets of spray parameters affect the gas mass flow rates in the cost model (Eq 5) and increasing both pressure and temperature cancel each other out given their opposite effects on the gas mass flow rate. Furthermore, a different gas mass flow rate modifies only the labor cost terms through Eq 11 to 15. The labor cost proportion is usually low compared to that of gas and powder costs. As such, the influence of different spray parameters on the maps shown in Fig. 10 is generally negligible.

More importantly, Fig. 10 shows the DE_{N_2} values at the 100% DE_{He} . For the specific CS conditions considered in Fig. 10(a), if a DE_{N_2} over 9.5% can be achieved, it would always be preferable to use nitrogen rather than helium, as this yields a lower total cost no matter what the DE_{He} is. In such cases, trials of CS using helium would be unnecessary to assess the process economics, and attention could be focused on the improvement of DE_{N_2} . A previous study reported that a DE_{N_2} of 30–50% is attainable with desirable coating characteristics when CS MCrAlY coatings using nitrogen (Ref 28). The high DE_{N_2} values are attributed to the use of more elevated spray parameters and refined

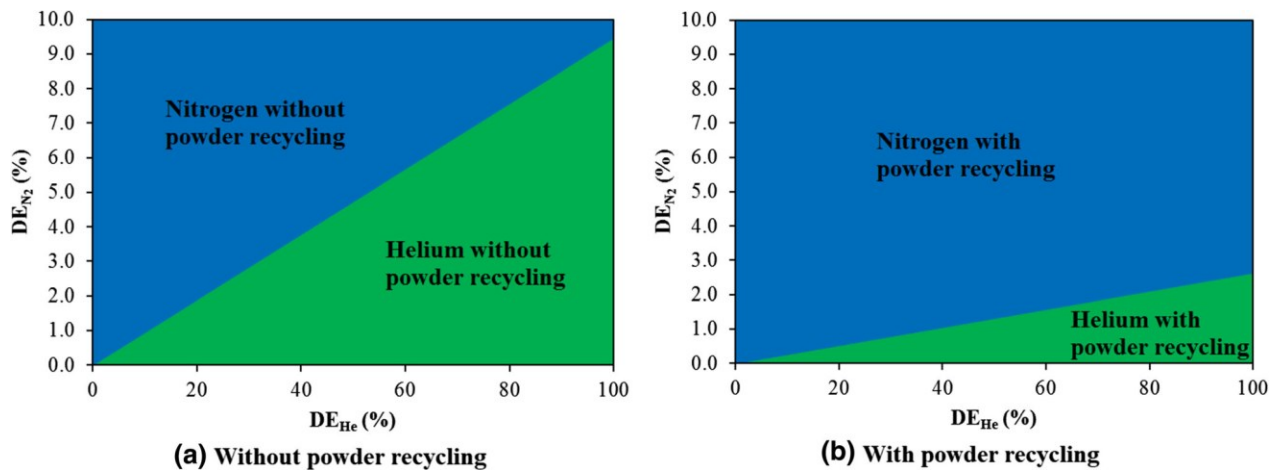


Fig. 10 Regions of cost-effective gases based on DE_{He} and DE_{N_2} , evaluated using $\omega_{He} = 6\%$, $\omega_{N_2} = 3\%$, $P_0 = 3.45$ MPa, and $T_0 = 400$ °C. (a) Without powder recycling; (b) with powder recycling (RE = 90%)

particle size distributions than the ones used in the current study. These parameters should also benefit CS MCrAlY coatings on single-crystal superalloys promoting DE_{N_2} and could potentially find it more economical using nitrogen. However, the effects of elevated spray parameters on the coating quality and substrate microstructure would need to be evaluated.

The adoption of powder recycling also makes it more economically achievable for nitrogen by significantly reducing the required DE_{N_2} . With powder recycling (Fig. 10b), a DE_{N_2} of only 2.6% (compared to 9.5% without powder recycling) is needed for nitrogen to be competitive even at a DE_{He} of 100%. The significant benefits from powder recycling are further highlighted in Fig. 11, which presents the relative coating cost for CS MCrAlY coatings using helium and nitrogen. In the analysis, powder loading ratios of 6 and 3% were used for helium and nitrogen, respectively, with a powder recycling efficiency of 90%, while DE values were determined experimentally based on spray parameters of 3.45 MPa and 400 °C. It is clear that helium accounts for a predominant percentage of the coating cost when it is used, and the use of nitrogen significantly reduces the gas cost. However, the largely increased powder and labor costs, when nitrogen is used, drastically raise the coating cost, resulting in the most expensive MCrAlY coatings (taken as 100% here) if the powder is not recycled. The effect of powder recycling on the coating cost is different for the two process gases. For CS using helium, this effect is almost negligible due to the limited powder cost proportion. However, the coating cost reduction by powder recycling can be considerable in the case of CS using nitrogen. For example, with a recycling efficiency (RE) of 90%, the total cost would be only 26% of the coatings produced using nitrogen without powder

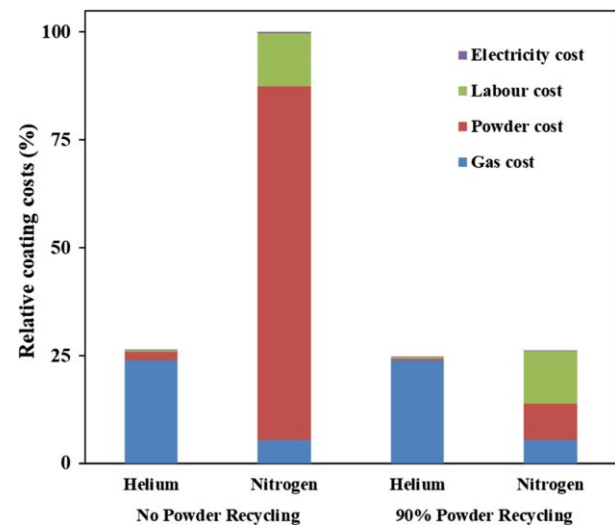


Fig. 11 Relative cost of CS MCrAlY coatings using helium and nitrogen showing the benefits of powder recycling for CS using nitrogen

recycling, which is comparable to the process cost of CS using helium.

While helium gas becomes increasingly expensive over the globe, the labor rate varies significantly from country to country and the price of powder differs depending on the powder specifications. The powder used in the study is a NiCoCrAlTaY powder, which is considered a premium MCrAlY powder by the supplier (Ref 59) and is more expensive than common MCrAlY powders. The use of a cheaper feedstock powder would decrease the powder cost encouraging the use of nitrogen. Furthermore, in regions or countries where the cost of labor is competitive, CS MCrAlY coatings using nitrogen could be more economically attractive.

Conclusions

In this study, NiCoCrAlTaY powder was successfully consolidated into uniform, dense, and highly deformed coatings on single-crystal nickel-based superalloy (CMSX-4) substrates using the CS process with nitrogen gas and moderate spray parameters. These coatings were found to have lower roughness ($R_a = 2.8 \pm 0.8 \mu\text{m}$), lower porosity ($< 0.5\%$), and higher hardness ($\text{HV}_{0.01} = 600 \pm 17$) than coatings sprayed using helium under similar conditions. These properties should possibly result in superior oxidation performance, especially in the as-sprayed condition. However, the DE was drastically lower with nitrogen than with helium. The low DE is thought to be the reason for the increased coating properties, as the process is similar to in situ shot peening. While the low DE may be necessary to obtain the desired coating properties with nitrogen, it could dissuade the adoption of nitrogen as a working gas due to significant powder waste and cost increase.

To improve the economic viability of CS MCrAlY coatings using nitrogen, the concept of powder recycling was introduced and explored. Powder particles that did not adhere during deposition were collected and resprayed in subsequent trials. This resulted in deposits similar to the ones achieved from the original feedstock powders. The economics of the CS processes were analyzed, and it was shown that under the set experimental conditions, powder recycling, and local pricing, the process of CS using nitrogen was similar to using helium in final cost—with the largest proportion being gas cost for the helium coatings and labor cost for the nitrogen coatings. In conclusion, the use of nitrogen and powder recycling for CS MCrAlY coatings was shown to produce coatings of superior properties than that deposited using helium under the same spray parameters while being potentially cost competitive.

References

1. A. Papyrin, V. Kosarev, S. Klinkov, A. Alkimov, and V. Fomin, *Cold Spray Technology*, Elsevier, Amsterdam, 2007
2. E. Irissou, J.G. Legoux, A.N. Ryabinin, B. Jodoin, and C. Moreau, Review on Cold Spray Process and Technology: Part I—Intellectual Property, *J. Therm. Spray Technol.*, 2008, **17**(4), p 495–516
3. H. Assadi, F. Gartner, T. Stoltenhoff, and H. Kreye, Bonding Mechanism in Cold Gas Spraying, *Acta Mater.*, 2003, **51**(15), p 4379–4394
4. B. Jodoin, L. Ajdelsztajn, E. Sansoucy, A. Zuniga, P. Richer, and E.J. Lavernia, Effect of Particle Size, Morphology, and Hardness on Cold Gas Dynamic Sprayed Aluminum Alloy Coatings, *Surf. Coat. Technol.*, 2006, **201**(6), p 3422–3429
5. F. Gärtner, T. Stoltenhoff, T. Schmidt, and H. Kreye, The Cold Spray Process and Its Potential for Industrial Applications, *J. Therm. Spray Technol.*, 2006, **15**(2), p 223–232
6. L. Ajdelsztajn, B. Jodoin, G.E. Kim, and J.M. Schoenung, Cold Spray Deposition of Nanocrystalline Aluminum Alloys, *Metall. Mater. Trans. A*, 2005, **36A**(3), p 657–666
7. T. Hussain, Cold Spraying of Titanium: A Review of Bonding Mechanisms, Microstructure and Properties, *Key Eng. Mater.*, 2013, **533**, p 53–90
8. A. Moridi, S.M. Hassani-Gangaraj, M. Guagliano, and M. Dao, Cold Spray Coating: Review of Material Systems and Future Perspectives, *Surf. Eng.*, 2014, **36**(6), p 369–395
9. S.M. Hassani-Gangaraj, A. Moridi, and M. Guagliano, Critical Review of Corrosion Protection by Cold Spray Coatings, *Surf. Eng.*, 2015, **31**(11), p 803–815
10. H. Assadi, H. Kreye, F. Gartner, and T. Klassen, Cold Spraying—A Materials Perspective, *Acta Mater.*, 2016, **116**, p 382–407
11. J. Pattison, S. Celotto, R. Morgan, M. Bray, and W. O'Neill, Cold Gas Dynamic Manufacturing: A Non-thermal Approach to Freeform Fabrication, *Int. J. Mach. Tool Manuf.*, 2007, **47**(3–4), p 627–634
12. A. Sova, S. Grigoriev, A. Okunkova, and I. Smurov, Potential of Cold Gas Dynamic Spray as Additive Manufacturing Technology, *Int. J. Adv. Manuf. Technol.*, 2013, **69**(9–12), p 2269–2278
13. R.N. Raelison, C. Verdy, and H. Liao, Cold Gas Dynamic Spray Additive Manufacturing Today: Deposit Possibilities, Technological Solutions and Viable Applications, *Mater. Des.*, 2017, **133**, p 266–287
14. S. Pathak and G.C. Saha, Development of Sustainable Cold Spray Coatings and 3D Additive Manufacturing Components for Repair/Manufacturing Applications: A Critical Review, *Coatings*, 2017, **7**(8), p 122
15. R.N. Raelison, Y. Xie, T. Sapanathan, M.P. Planche, R. Kromer, S. Costil, and C. Langlade, Cold Gas Dynamic Spray Technology: A Comprehensive Review of Processing Conditions for Various Technological Developments Till to Date, *Addit. Manuf.*, 2018, **19**, p 134–159
16. J.R. Davis, *Handbook of Thermal Spray Technology*, ASM International, Cleveland, 2004
17. J. Villafuerte, *Modern Cold Spray: Materials, Process, and Applications*, Springer, Berlin, 2015
18. V.K. Champagne, *The Cold Spray Materials Deposition Process: Fundamentals and Applications*, Taylor & Francis, London, 2007
19. Y. Li, C.J. Li, G.J. Yang, and L.K. Xing, Thermal Fatigue Behavior of Thermal Barrier Coatings with the MCrAlY Bond Coats by Cold Spraying and Low-Pressure Plasma Spraying, *Surf. Coat. Technol.*, 2010, **205**(7), p 2225–2233
20. P. Richer, A. Zuniga, M. Yandouzi, and B. Jodoin, CoNiCrAlY Microstructural Changes Induced During Cold Gas Dynamic Spraying, *Surf. Coat. Technol.*, 2008, **203**(3–4), p 364–371
21. P. Richer, M. Yandouzi, L. Beauvais, and B. Jodoin, Oxidation Behaviour of CoNiCrAlY Bond Coats Produced by Plasma, HVOF and Cold Gas Dynamic Spraying, *Surf. Coat. Technol.*, 2010, **204**(24), p 3962–3974
22. A. Manap, A. Nakano, and K. Ogawa, The Protectiveness of Thermally Grown Oxides on Cold Sprayed CoNiCrAlY Bond Coat in Thermal Barrier Coating, *J. Therm. Spray Technol.*, 2012, **21**(3–4), p 586–596
23. Q. Zhang, C.J. Li, C.X. Li, G.J. Yang, and S.C. Lui, Study of Oxidation Behavior of Nanostructured NiCrAlY Bond Coatings Deposited by Cold Spraying, *Surf. Coat. Technol.*, 2008, **202**(14), p 3378–3384
24. Y. Li, C.J. Li, Q.A. Zhang, L.K. Xing, and G.J. Yang, Effect of Chemical Compositions and Surface Morphologies of MCrAlY Coating on Its Isothermal Oxidation Behavior, *J. Therm. Spray Technol.*, 2011, **20**(1–2), p 121–131
25. K.M. Doleker and A.C. Karaoglanli, Comparison of Oxidation Behavior of Shot-Peened Plasma Spray Coatings with Cold Gas Dynamic Spray Coatings, *Oxid. Met.*, 2017, **88**(1), p 121–132

26. A.C. Karaoglanli and A. Turk, Isothermal Oxidation Behavior and Kinetics of Thermal Barrier Coatings Produced by Cold Gas Dynamic Spray Technique, *Surf. Coat. Technol.*, 2017, **318**, p 72-81
27. W.R. Chen, E. Irissou, X. Wu, J.G. Legoux, and B.R. Marple, The Oxidation Behavior of TBC with Cold Spray CoNiCrAlY Bond Coat, *J. Therm. Spray Technol.*, 2011, **20**(1-2), p 132-138
28. V. Crespo, I.G. Cano, S. Dosta, and J.M. Guilemany, The Influence of Feedstock Powders on the CGS Deposition Efficiency of Bond Coats for TBCs, *J. Alloys Compd.*, 2015, **622**, p 394-401
29. A. Bonadei and T. Marrocco, Cold Sprayed MCrAlY + X Coating for Gas Turbine Blades and Vanes, *Surf. Coat. Technol.*, 2014, **242**, p 200-206
30. S. Bose and J. DeMasiMarcin, Thermal Barrier Coating Experience in Gas Turbine Engines at Pratt & Whitney, *J. Therm. Spray Technol.*, 1997, **6**(1), p 99-104
31. D.J. Wortman, B.A. Nagaraj, and E.C. Duderstadt, Thermal Barrier Coatings for Gas Turbine Use, *Mater. Sci. Eng.*, 1989, **A121**, p 433-440
32. M.P. Taylor, An Oxidation Study of an MCrAlY Overlay Coating, *Mater. High Temp.*, 2005, **22**(3-4), p 433-436
33. R. Sivakumar and B.L. Mordike, High Temperature Coatings for Gas Turbine Blades: A Review, *Surf. Coat. Technol.*, 1989, **37**(2), p 139-160
34. T.N. Rhys-Jones, Coatings for Blade and Vane Applications in Gas-Turbines, *Corros. Sci.*, 1989, **29**(6), p 623-646
35. J.R. Nicholls, Designing Oxidation-Resistant Coatings, *Journal of the Minerals Metals & Materials Society*, 2000, **52**(1), p 28-35
36. N.P. Padture, M. Gell, and E.H. Jordan, Thermal Barrier Coatings for Gas-Turbine Engine Applications, *Science*, 2002, **296**(5566), p 280-284
37. T.E. Strangman, Thermal Barrier Coatings for Turbine Airfoils, *Thin Solid Films*, 1985, **127**, p 93-105
38. D. Seo, K. Ogawa, Y. Suzuki, K. Ichimura, T. Shoji, and S. Murata, Comparative Study on Oxidation Behavior of Selected MCrAlY Coatings by Elemental Concentration Profile Analysis, *Appl. Surf. Sci.*, 2008, **255**(5), p 2581-2590
39. M.T. Pace, R.C. Thomson, and J. Wells, Oxidation of MCrAlY Coatings on Ni-Based Superalloys, *Superalloys*, 2008, **2008**, p 651-660
40. A. Fossati, M. Di Ferdinando, A. Lavacchi, U. Bardi, C. Giolli, and A. Scrivani, Improvement of the Isothermal Oxidation Resistance of CoNiCrAlY Coating Sprayed by High Velocity Oxygen Fuel, *Surf. Coat. Technol.*, 2010, **204**(21-22), p 3723-3728
41. W.-X. Weng, Y.-M. Wang, Y.-M. Liao, C.-C. Li, and Q. Li, Comparison of Microstructural Evolution and Oxidation Behaviour of NiCoCrAlY and CoNiCrAlY as Bond Coats Used for Thermal Barrier Coatings, *Surf. Coat. Technol.*, 2018, **352**, p 285-294
42. M. Shibata, S. Kuroda, H. Murakami, M. Ode, M. Watanabe, and Y. Sakamoto, Comparison of Microstructure and Oxidation Behavior of CoNiCrAlY Bond Coatings Prepared by Different Thermal Spray Processes, *Mater. Trans.*, 2006, **47**(7), p 1638-1642
43. W.R. Chen, X. Wu, B.R. Marple, D.R. Nagy, and P.C. Patnaik, TGO Growth Behaviour in TBCs With APS and HVOF Bond Coats, *Surf. Coat. Technol.*, 2008, **202**(12), p 2677-2683
44. P. Song, D. Naumenko, R. Vassen, L. Singheiser, and W.J. Quadakkers, Effect of Oxygen Content in NiCoCrAlY Bondcoat on the Lifetimes of EB-PVD and APS Thermal Barrier Coatings, *Surf. Coat. Technol.*, 2013, **221**, p 207-213
45. A. Gil, V. Shemet, R. Vassen, M. Subanovic, J. Toscano, D. Naumenko, L. Singheiser, and W.J. Quadakkers, Effect of Surface Condition on the Oxidation Behaviour of MCrAlY Coatings, *Surf. Coat. Technol.*, 2006, **201**(7), p 3824-3828
46. L.Y. Ni, Z.L. Wu, and C.G. Zhou, Effects of Surface Modification on Isothermal Oxidation Behavior of HVOF-Sprayed NiCrAlY Coatings, *Prog. Nat. Sci.*, 2011, **21**(2), p 173-179
47. A. Fossati, M. DiFerdinando, U. Bardi, A. Scrivani, and C. Giolli, Influence of Surface Finishing on the Oxidation Behaviour of VPS MCrAlY Coatings, *J. Therm. Spray Technol.*, 2012, **21**(2), p 314-324
48. L.Y. Ni and C.G. Zhou, Effects of Surface Modification on Thermal Cycling Lifetime of Thermal Barrier Coatings With HVOF NiCrAlY Bond Coat, *Prog. Nat. Sci.*, 2012, **22**(3), p 237-243
49. R.C. Dykhuizen and M.F. Smith, Gas Dynamic Principles of Cold Spray, *J. Therm. Spray Technol.*, 1998, **7**(2), p 205-212
50. D.L. Gilmore, R.C. Dykhuizen, R.A. Neiser, T.J. Roemer, and M.F. Smith, Particle Velocity and Deposition Efficiency in the Cold Spray Process, *J. Therm. Spray Technol.*, 1999, **8**(4), p 576-582
51. M. Gruzicic, C.L. Zhao, C. Tong, W.S. Derosset, and D. Helfrich, Analysis of the Impact Velocity of Powder Particles in the Cold-Gas Dynamic-Spray Process, *Mater. Sci. Eng. A Struct.*, 2004, **368**(1-2), p 222-230
52. B. Jodoin, F. Raletz, and M. Vardelle, Cold Spray Modeling and Validation Using an Optical Diagnostic Method, *Surf. Coat. Technol.*, 2006, **200**(14-15), p 4424-4432
53. A. Saltzman, Concerns Rising Over Global Helium Shortage. CBC/Radio-Canada, <https://www.cbc.ca/news/business/helium-smartphones-fibre-optic-cable-mri-internet-scuba-1.5084212>, 2019. Accessed 16 September 2019
54. B. Jodoin, D.L. Guo, and D. MacDonald, Personal Communication With Gas Supplier (Linde Gas Ottawa), 2019
55. A.S. Khanna and W.S. Rathod, Development of CoNiCrAlY Oxidation Resistant Hard Coatings Using High Velocity Oxy Fuel and Cold Spray Techniques, *Int. J. Refract. Met. H*, 2015, **49**, p 374-382
56. A.N. Papyrin, Cold Spray Process for Cost-Sensitive Applications, *High Performance Metallic Materials for Cost Sensitive Applications*, E. Chen, R.R. Boyer, E.M. Taleff, L. Lu, D.L. Zhang, C.M. Ward-Close, D. Elizer, and F.H. Froes, Ed., The Minerals, Metals & Materials Society, Warrendale, 2002, p 137-149
57. J. Perry, P. Richer, B. Jodoin, and E. Matte, Pin Fin Array Heat Sinks by Cold Spray Additive Manufacturing: Economics of Powder Recycling, *J. Therm. Spray Technol.*, 2019, **28**(1), p 144-160
58. R.C. Reed, *The Superalloys: Fundamentals and Applications*, Cambridge University Press, Cambridge, 2006
59. MCrAlY Alloy Powder Materials for Thermal Spray (NiCoCrAlY Powders). Oerlikon Metco, <https://www.oerlikon.com/metco/en/products-services/coating-materials/coating-materials-thermal-spray/mcraly-alloys/>, 2018. Accessed 28 December 2019
60. K. Spencer, V. Luzin, N. Matthews, and M.X. Zhang, Residual Stresses in Cold Spray Al Coatings: The Effect of Alloying and of Process Parameters, *Surf. Coat. Technol.*, 2012, **206**(19-20), p 4249-4255
61. B. Marzbanrad, H. Jahed, and E. Toyserkani, On the Evolution of Substrate's Residual Stress During Cold Spray Process: A Parametric Study, *Mater. Des.*, 2018, **138**, p 90-102
62. P. Caron and T. Khan, Evolution of Ni-Based Superalloys for Single Crystal Gas Turbine Blade Applications, *Aerosp. Sci. Technol.*, 1999, **3**(8), p 513-523
63. M. Tahari and F. Naeimi, Effect of Surface Morphologies on the Isothermal Oxidation Behavior of MCrAlY Coatings Fabricated

- by High-Velocity Oxyfuel Processes, *Int. J. Eng. Trans. C Asp.*, 2017, **30**(3), p 432
64. A. Hesnawi, H.F. Li, Z.H. Zhou, S.K. Gong, and H.B. Xu, Effect of Surface Condition During Pre-oxidation Treatment on Isothermal Oxidation Behavior of MCrAlY Bond Coat Prepared by EB-PVD, *Surf. Coat. Technol.*, 2007, **201**(15), p 6793-6796
 65. C. Borchers, T. Stoltenhoff, M. Hahn, M. Schulze, H. Assadi, C. Suryanarayana, F. Gartner, and T. Klassen, Strain-Induced Phase Transformation of MCrAlY, *Adv. Eng. Mater.*, 2015, **17**(5), p 723-731
 66. Z.Y. Liu, W. Gao, K.L. Dahm, and F.H. Wang, Oxidation Behaviour of Sputter-Deposited Ni-Cr-Al Micro-crystalline Coatings, *Acta Mater.*, 1998, **46**(5), p 1691-1700
 67. C. Kaplin and M. Brochu, The Effect of Grain Size on the Oxidation of NiCoCrAlY, *Appl. Surf. Sci.*, 2014, **301**, p 258-263
 68. Y. Chen, X. Zhao, and P. Xiao, Effect of Microstructure on Early Oxidation of MCrAlY Coatings, *Acta Mater.*, 2018, **159**, p 150-162
 69. O. Stier, Fundamental Cost Analysis of Cold Spray, *J. Therm. Spray Technol.*, 2014, **23**(1-2), p 131-139
 70. D. MacDonald, S. Rahmati, B. Jodoin, and W. Birtch, An Economical Approach to Cold Spray Using In-Line Nitrogen-Helium Blending, *J. Therm. Spray Technol.*, 2019, **28**(1), p 161-173
 71. T. Han, Z. Zhao, B.A. Gillispie, and J.R. Smith, Effects of Spray Conditions on Coating Formation by the Kinetic Spray Process, *J. Therm. Spray Technol.*, 2005, **14**(3), p 373-383

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Chapter 6 Production of In-Situ Nanocrystalline NiCoCrAlTaY Coatings by Cold Spray

This chapter consists of two peer-reviewed journal articles that have been published in the journal Surface & Coatings Technology. They are entitled “Cold Spray for Production of In-Situ Nanocrystalline MCrAlY Coatings – Part I: Process Analysis and Microstructure Characterization” (DOI: <https://doi.org/10.1016/j.surfcoat.2021.126854>) [176] and “Cold Spray for Production of In-Situ Nanocrystalline MCrAlY Coatings – Part II: Isothermal Oxidation Performance” (DOI: <https://doi.org/10.1016/j.surfcoat.2021.126828>) [177]. These two articles aimed at addressing the processing-structure-properties-performance relationship of the cold spray deposition of MCrAlY coatings on single-crystal Ni-base superalloy substrates. They were reproduced with permissions from the copyright owner, Elsevier.

6.1 Process Analysis and Microstructure Characterization

The journal article (Part I of the study [176]) presented in this section proposed a cold spray process that can produce in-situ nanocrystalline NiCoCrAlTaY coatings while using conventional commercial powders of large grain size. SEM and TEM were used to characterize the resulting microstructures of the NiCoCrAlTaY coatings and CMSX-4 single-crystal Ni-base superalloy substrate, as well as their interfacial features. It is demonstrated that the production of in-situ nanocrystalline NiCoCrAlTaY coatings by cold spray is possible when using nitrogen as process gas with low spray parameters. This proposed approach could not only simplify the conventional two-step top-down manufacturing process into one but also avoid powder contamination and oxidation typically associated with the conventional approach.



Cold spray for production of in-situ nanocrystalline MCrAlY coatings – Part I: Process analysis and microstructure characterization

Deliang Guo^{a,*}, Yin Wang^b, Ruben Fernandez^c, Linruo Zhao^d, Bertrand Jodoin^a

^a Cold Spray Research Laboratory, University of Ottawa, Ottawa, Canada

^b AECC Shanghai Commercial Aircraft Engine Manufacturing Co. Ltd., Shanghai, China

^c Faculty of Physical and Mathematical Science, University of Chile, Santiago, Chile

^d Aerospace Research Centre, National Research Council Canada, Ottawa, Canada

ARTICLE INFO

Keywords:

Cold spray
Dynamic recrystallization
Nanocrystalline
MCrAlY
Single crystal
Superalloy

ABSTRACT

Nanocrystalline MCrAlY coatings have been shown excellent oxidation performance as bond coats in thermal barrier coating (TBC) systems. In the first part of the present study, a cold spray (CS) process is proposed, aiming at producing in-situ nanocrystalline NiCoCrAlTaY coatings on CMSX-4 single-crystal Ni-base superalloy substrates while using conventional powders of large grain sizes. Scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), and X-ray diffraction (XRD) were used to characterize the resulting coating-substrate system. Results show that the feedstock powder particles experienced substantial plastic deformation, which promoted dynamic recrystallization and grain refinement resulting in extended nanostructures in the CS NiCoCrAlTaY coatings. Furthermore, interfacial features such as materials mixing and intimate metal-metal contacts without pores or oxide fragments suggest the presence of mechanical and potentially metallurgical bonding between the CS NiCoCrAlTaY coatings and the CMSX-4 substrate. Isothermal oxidation testing results are presented in Part II of the study, which reveals the oxidation performance of the NiCoCrAlTaY coatings produced using the proposed CS process.

1. Introduction

MCrAlY coatings, where M is Ni and/or Co, are commonly used as bond coats in thermal barrier coating (TBC) systems to provide an intermediate bonding layer between the ceramic topcoat and the underlying metallic components and protect the latter from oxidation degradation [1–6]. At high temperatures and in oxidizing environments, MCrAlY coatings develop a thermally grown oxide (TGO) scale. Alpha alumina (α -Al₂O₃), due to its thermal stability, slow growth rate, and low oxygen diffusivity, is the preferential form for the TGO scale [7]. The formation of such an α -Al₂O₃ scale acts as an oxygen diffusion barrier and effectively reduces further oxidation rates [8]. MCrAlY coating compositions are specifically designed to promote selective aluminum oxidation to form α -Al₂O₃ at high temperatures, providing effective oxidation resistance for the underlying components.

The performance of MCrAlY coatings is closely related to their chemical compositions [9–11], microstructural characteristics [12,13], and surface finish [14,15]. Nanocrystallization of MCrAlY coatings, i.e., reducing grain size to 100 nm or less, can significantly improve their

oxidation performance by promoting α -Al₂O₃ formation and adhesion [16,17]. This is attributed to the increased grain boundaries associated with the nanostructure, which not only provide increased nucleation sites during early oxidation but also facilitate aluminum diffusion to the coating surface to sustain α -Al₂O₃ growth [17–19]. Nanocrystalline materials in general can be fabricated by either the “bottom-up” or “top-down” approach [20,21]. The bottom-up approach involves building structures atom by atom or molecule by molecule to assemble nanoscale clusters into bulk material. The top-down approach starts with a bulk solid and obtains a nanostructure by structural decomposition. Both approaches have been successfully utilized to manufacture nanocrystalline MCrAlY coatings. A commonly studied bottom-up technique is physical vapor deposition (PVD) [16–19,22–25]. However, PVD processes usually have low deposition rates (a few microns per hour [23]) and may not be suitable for all commercial MCrAlY coating applications. Besides, the nanocrystalline coatings fabricated by the bottom-up approach tend to mimic the substrate morphology due to the inherent atom-by-atom deposition, making the coating performance susceptible to substrate surface finish conditions [23]. The top-down methods for

<https://doi.org/10.1016/j.surfcoat.2021.126854>

Received 27 October 2020; Received in revised form 23 December 2020; Accepted 30 December 2020

Available online 9 January 2021

0257-8972/© 2021 Elsevier B.V. All rights reserved.

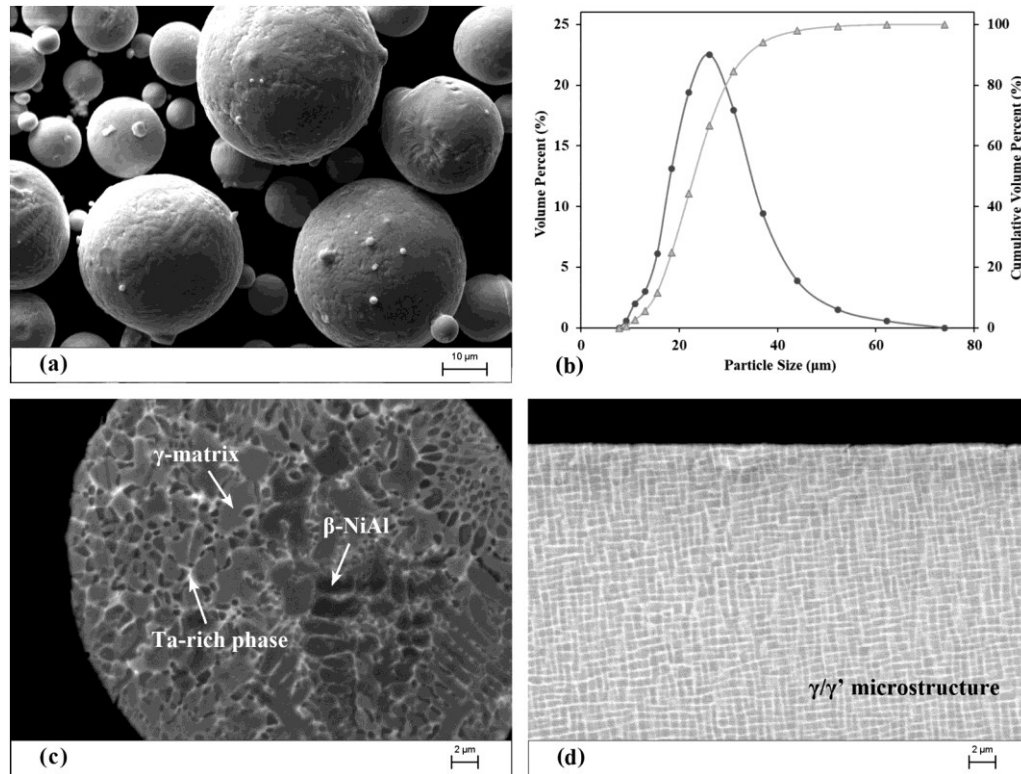


Fig. 1. Characterization of the NiCoCrAlTaY feedstock powder and CMSX-4 single-crystal substrate: (a) SEM image showing the spherical powder morphology, (b) particle size distribution, and (c, d) cross-section backscattered electron (BSE) images showing the three-phase constituents of the feedstock powder and the γ/γ' substrate microstructure, respectively.

producing nanocrystalline MCrAlY coatings typically follow a two-step procedure: (i) mechanical milling (e.g., cryomilling) of conventional feedstock powders to produce nanocrystalline MCrAlY powders and (ii) thermal spraying or consolidation of these nanocrystalline powders. Different processes, e.g., high velocity oxygen fuel (HVOF) [26–31], low-pressure plasma spray (LPPS) [32–34], and Spark-Plasma Sintering (SPS) [35], proved to be capable of preserving the nanostructure of the milled powders in the deposited coatings. However, the separated two-step processing inevitably introduces some drawbacks. Exotic elements (e.g., Fe, N, O) were found in some nanocrystalline MCrAlY powders after mechanical milling [28–30]. High process temperatures during thermal spraying also enhanced in-process oxidation of the nanocrystalline powders due to the presence of increased grain boundaries [36]. The inclusion of contaminants and oxides in the nanocrystalline MCrAlY coatings may promote the formation of oxides other than the preferred $\alpha\text{-Al}_2\text{O}_3$, affecting the coating performance [28–30].

Cold spray (CS), a high strain-rate solid-state material deposition technique, has been demonstrated as a promising alternative to manufacture MCrAlY coatings [37–41]. In the CS process, micron-size feedstock powder particles are accelerated by a supersonic gas stream and consolidated into coatings after large plastic deformation upon impacting a substrate [42–45]. The feedstock particles remain at temperatures well below their melting point throughout the process, as opposed to being molten or semi-molten in other thermal spray processes to produce coatings [46]. The absence of excessive heating and the use of inert gas (typically helium or nitrogen) in CS avoid powder melting/vaporization and minimize potential powder oxidation and grain growth, allowing the deposition of oxidation and temperature sensitive feedstock materials. Following the top-down approach, many nanocrystalline coatings, such as various aluminum alloys [47–51], Al-Mg [52], copper [53], nickel [54], Ni-20Cr [55], NiTi [56], MCrAlY [57,58], and high-entropy alloys [59], have been obtained using the CS

technique. While this CS approach effectively eliminates the high-temperature related conundrum associated with conventional thermal spray processes, it still requires the nanocrystallization process for the feedstock powders prior to coating deposition. The powder milling processes, especially in the case of cryomilling, can be time-consuming and cost-prohibitive and hence could dissuade scale-up industrial applications [60]. Furthermore, milled feedstock powders present some challenges for CS deposition. Particle deformation and grain refinement that occur in the milling process strengthen the feedstock powder and consequently hinder further plastic deformation during subsequent CS coating deposition. This was found to result in nanocrystalline coatings with a higher porosity and surface roughness compared to CS coatings produced from conventional powders [48,51,61]. As a result, spray parameters optimization, post-deposition heat treatment, and/or surface treatment would be needed to improve coating properties and performance.

As a solid-state coating technique involving high velocity impacts and consequently severe plastic deformation, CS is widely reported to induce in-situ grain refinement during coating deposition [62–67], a prominent feature that is unattainable using traditional thermal spray processes where the feedstock powder is molten. This grain refinement process is attributed to dynamic recrystallization [68–72], i.e., the formation of new and refined grains during plastic deformation rather than afterward as part of a separate heat treatment (as in the case of static recrystallization). The size of the recrystallized grains, however, is highly sensitive to the local plastic strain level. King, et al. [62] showed that the microstructure significantly varied across a single Cu particle deposited by CS onto a Cu substrate: grains near the particle surface region were much coarser than that in the vicinity of the particle-substrate interface, where intense plastic deformation occurred. Similarly, Zou, et al. [63,64] observed that particle boundaries in a CS deposited Ni coating contained ultrafine grains of 100–200 nm, whereas

Table 1

Nominal composition of Amdry 997 powder and CMSX-4 superalloy (wt%).

	Ni	Co	Cr	Al	Ta	Y	W	Re	Ti	Others
Amdry 997	43.9	23.0	20.0	8.5	4.0	0.6	–	–	–	–
CMSX-4	61.7	9.0	6.5	5.6	6.5	–	6.0	3.0	1.0	Mo 0.6 Hf 0.1

Table 2

Spray Parameters for different types of cold spray tests.

Test type	Stagnation pressure (MPa)	Stagnation temperature (°C)	Powder preheating (°C)	Traverse speed (mm/s)	Powder feedrate (g/min)	Number of passes
Single-splat spray test	3.45	500	500	200	3.1 ± 0.5	1
Interrupted spray test	3.45	500	500	5	13.3 ± 0.3 (on and off)	1
Coating deposition	3.45	500	500	5	13.3 ± 0.3	2

the central particle regions, due to the lack of plastic deformation, experienced negligible microstructure changes from the feedstock powder. This deformation-dependent grain structure was also observed in the CS deposition of conventional MCrAlY powders. Richer, et al. [66] and Borchers, et al. [67] reported the presence of nanoscale grains at the particle contact regions in the CS MCrAlY coatings, with grain sizes noticeably coarser within the particles. In light of these studies, a more uniform coating microstructure can be anticipated with increased particle deformation, and nanocrystalline coatings may be potentially produced using solely the CS technique.

The objective of the first part of the present study is to explore the potential of CS for producing nanocrystalline MCrAlY coatings from conventional feedstock powders without the need for a prior powder milling process. Specifically, a NiCoCrAlTaY powder and a single-crystal Ni-base superalloy (CMSX-4) substrate are used. Single-crystal superalloys are widely used for high-pressure turbine blades in modern aero-

engines [73]. However, the substrates used for CS MCrAlY coatings deposition are mostly polycrystalline Ni-base superalloys, such as IN625 [38,41], IN718 [74,75], and IN738 [39,40,57,76]. As such, Part I of the study also aims at characterizing the effect of CS deposition on the microstructure of the CMSX-4 single-crystal superalloy substrate as well as the resulting coating-substrate interfacial features. The isothermal oxidation performance of the CS nanocrystalline NiCoCrAlTaY coatings is presented in Part II of the study [91].

2. Experimental procedures

2.1. Feedstock materials

A commercially available NiCoCrAlTaY powder (Amdry 997, 5–38 µm, Oerlikon Metco, USA) and a single-crystal Ni-base superalloy (CMSX-4, Cannon Muskegon, USA) were used in the study as feedstock

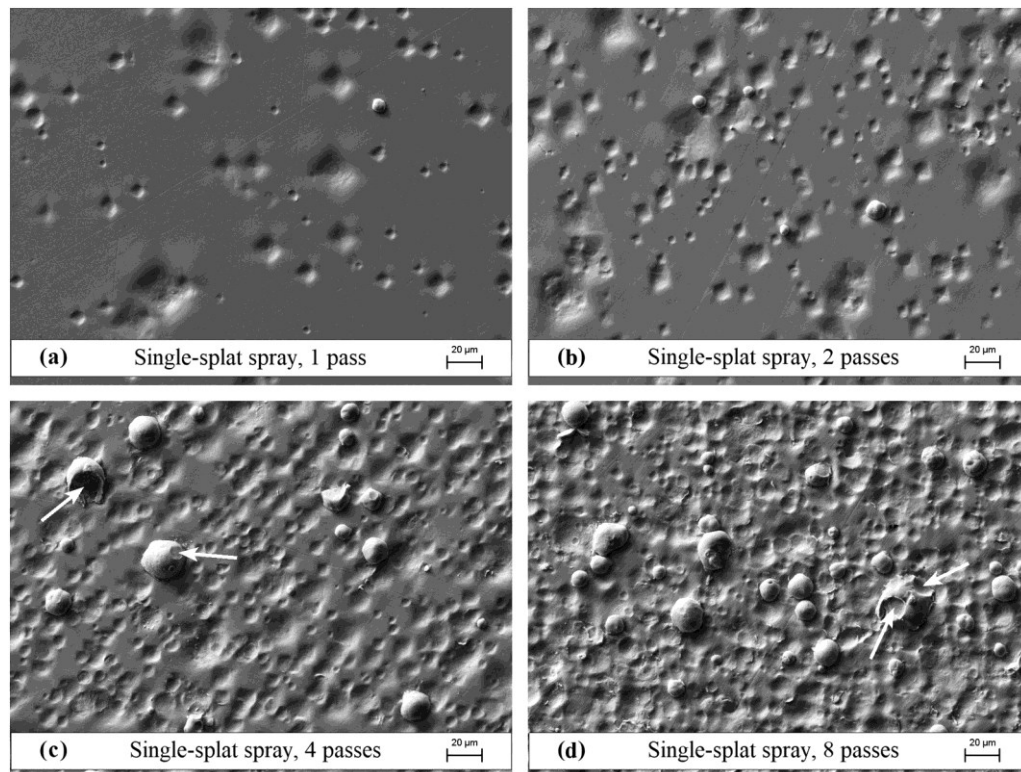


Fig. 2. Top view SEM images showing the surfaces of the CMSX-4 substrates after single-splat spray tests with different spray passes: (a) 1 pass, (b) 2 passes, (c) 4 passes, and (d) 8 passes. Arrows indicate particle deformation induced by impingements of non-deposited particles.

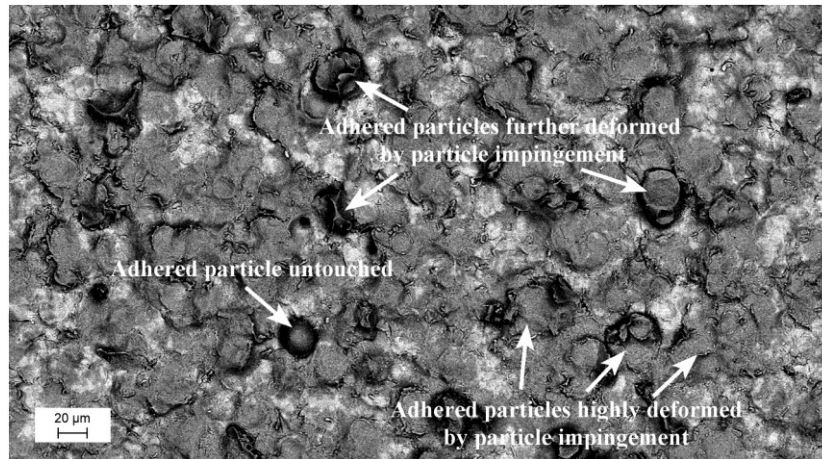


Fig. 3. Top view BSE image showing cumulative particle deformation promoted by enhanced particle impingements in the interrupted spray test: NiCoCrAlTaY particles (grey) and CMSX-4 single-crystal substrate (bright).

powder and substrate, respectively. Fig. 1 shows the powder morphology, particle size distribution, and cross-section microstructures of the powder and the substrate.

The feedstock powder is spherical, typical for gas atomized powders. Particle size distribution analysis confirmed that most particles fall into the 5 to 38 μm diameter range, with a mean particle diameter of 23.9 μm . The powder is comprised of three phases (Fig. 1c): a nickel-based solid solution γ phase (light grey matrix), an aluminum-rich β -NiAl phase (dark grey), and a tantalum-segregated phase (white) at the grain/phase boundaries.

The single-crystal superalloy was received in solution heat-treated condition. Subsequent heat treatments, i.e., primary aging (6 h at 1140 $^{\circ}\text{C}$, air cooling) and secondary aging (20 h at 870 $^{\circ}\text{C}$, air cooling), were performed to promote the γ/γ' microstructure shown in Fig. 1d. The presence of a high volume fraction of the γ' -Ni₃(Al, Ti) phase (dark grey) in the γ matrix (light grey) impedes dislocation movement and enhances the mechanical properties of the single-crystal superalloy [77]. The nominal compositions of the feedstock powder and single-crystal superalloy substrate can be found in Table 1.

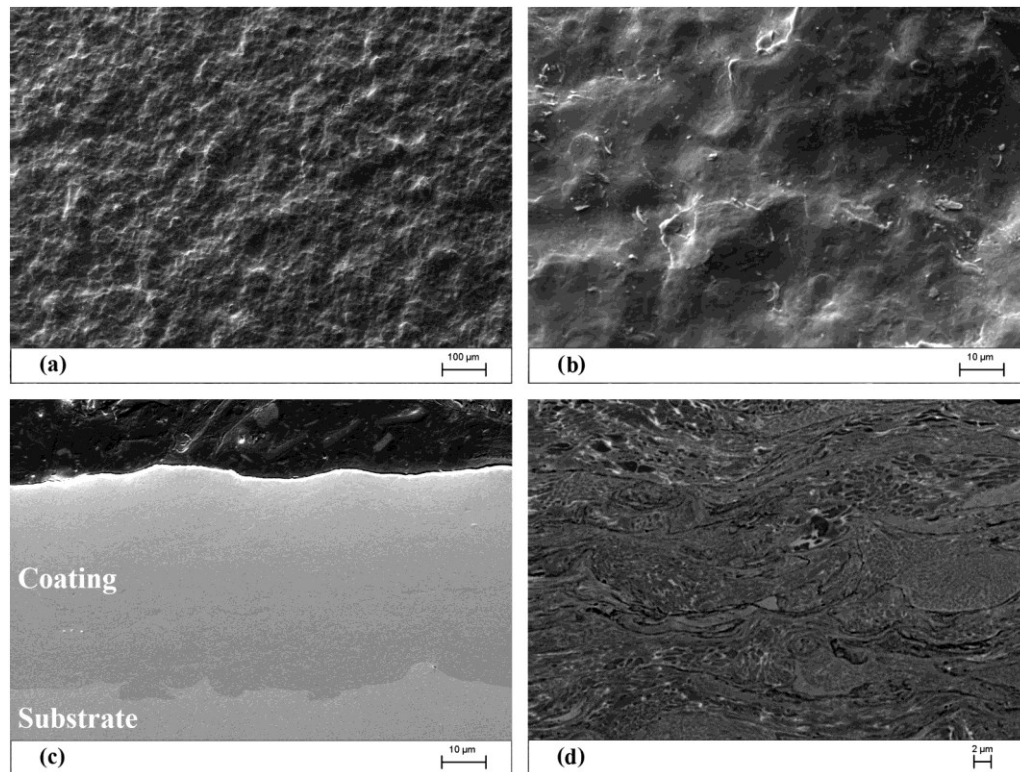


Fig. 4. SEM images of NiCoCrAlTaY coatings deposited on CMSX-4 single-crystal substrates: (a, b) top view of coating at low and high magnifications, respectively, (c) overview of the coating microstructure at low magnification, and (d) cross-section BSE image at a higher magnification revealing severe particle deformation in the coating.

2.2. Splat spray tests and coating deposition

A commercial CS system (SST-EP series, Centerline Technology (Winsor), Canada) with an UltiLife™ nozzle assembly was used for splat spray tests and coating deposition. Nitrogen was used as both the process gas and the powder-feeding gas during the sprays. A stagnation pressure of 3.45 MPa and a stagnation temperature of 500 °C were used along with a powder preheating temperature of 500 °C. The substrate ($\varnothing$ 16 × 3 mm) was manually ground before coating deposition to remove the oxidized surface layer resulting from the aging treatments. Polished substrates were used for the splat spray tests to easily locate the adhered particles and better characterize the substrate-particle interactions. Two different types of splat spray tests were carried out, namely, a single-splat spray test and an interrupted spray test. These tests differ in the nozzle traverse speed and the amount of powder fed to the nozzle. A traverse speed of 200 mm/s and a low powder feed rate were used for the single-splat tests, while a traverse speed of 5 mm/s was used for the interrupted spray tests with a powder-on-and-off technique that allows powder feeding for a short period (a few seconds). Table 2 summarizes the cold spray parameters used for the splat spray tests and actual coating deposition.

2.3. Materials characterization

Coating surface roughness was measured using a stylus profilometer (SRG-4000, Phase II Plus, USA). Standard metallographic procedures (sectioning, mounting, and polishing) were followed to prepare samples for microstructural examination. A Vickers hardness tester (Duramin-1, Struers, Denmark) with a setting of 0.05 kgf load (0.3 kgf was too big for the powder, whereas 0.01 kgf was too small for the CS coatings) and 15 s dwelling time was used to measure the microhardness of the feedstock powder, the CS NiCoCrAlTaY coatings, and the CMSX-4 superalloy substrate. Surface morphology and cross-section microstructure of the NiCoCrAlTaY powder, CS coatings, and CMSX-4 superalloy substrate were characterized using a scanning electron microscope (EVO MA-10, Zeiss, Germany). A focused ion beam (FIB) workstation (GAIA3, Tescan, Czechia) was employed to prepare samples at the coating/substrate interface. A scanning transmission electron microscope (Talos F200X, FEI, USA) along with the high-angle annular dark field (HAADF) imaging and energy-dispersive X-ray spectroscopy (EDS) techniques were used to investigate the coating and substrate microstructures as well as their interfacial bonding features. X-ray diffraction (XRD) using Cu K α radiation (X-Pert PW1830, PANalytical, Netherlands) was used to study the phase constitution of the feedstock powder and as-sprayed coatings.

Adhesion tests were performed following the ASTM C633-13 standard [78] to evaluate the bonding strength of the CS NiCoCrAlTaY coatings to the CMSX-4 single-crystal superalloy substrate. The coating sample was prepared by depositing NiCoCrAlTaY coatings on one side of the CMSX-4 superalloy substrate. An adhesive bonding agent (FM-1000, Solvay, Belgium) was used to attach the coating sample ($\varnothing$ 16 mm) to two loading fixtures of the same diameter on each side. The test specimens were then pulled using a universal tensile testing machine (Model 4482, Instron, USA) at a crosshead speed of 0.02 mm/s. The adhesion tests were performed on three specimens.

3. Results and discussion

3.1. Process analysis

Grain refinement level is directly related to the extent of plastic deformation experienced by the powder particles during the CS deposition. To produce in-situ nanocrystalline MCrAlY coatings using solely the CS technique, extensive particle deformation is therefore required. Two separate impact processes contribute to the ultimate deformation level of an adhered particle: (i) the initial impact of the adhered particle on the substrate or previously deposited coating, and (ii) subsequent

impingements of non-deposited particles on the adhered particle. An intuitive way to promote particle deformation is to increase particle impact velocities by elevating process temperature and pressure. While this increases the particle deformation upon impact, high particle impact velocities also result in an increased deposition efficiency (DE), which means a reduced number of non-deposited particles contributing to particle impingements. This can potentially prevent adequate plastic deformation to induce uniform nanocrystallization. Furthermore, high process temperature may lead to recovery, enhanced recrystallization, and grain growth in the deformed coatings, compromising the intended in-situ nanocrystallization.

An alternative way to enhance particle deformation is to promote the contribution of particle impingements. This can be achieved by CS using low DE spray conditions. Under such conditions, a large population of non-deposited particles repeatedly bombards adhered particles, which can cumulatively lead to substantial particle deformation throughout its thickness. To demonstrate this, single-splat and interrupted spray tests were performed with different nozzle traverse speeds and varied powder amounts injected in the nozzle (as shown in Table 2). Fig. 2 shows some SEM images of the substrate surface after the single-splat spray tests.

Few particles were able to adhere to the substrate after one single-splat spray pass (Fig. 2a). Most of the powder particles impacted and bounced off, leaving craters on the substrate surface. This indicates a low DE of the NiCoCrAlTaY powder on the CMSX-4 single-crystal substrate under the spray conditions used. After two spray passes (Fig. 2b), a few small particles were observed on the substrate in the vicinity of the previously formed craters. This is likely attributed to surface oxide removal by previous particle impacts, facilitating the bonding of subsequent particles impinging the substrate. This trend is more evident

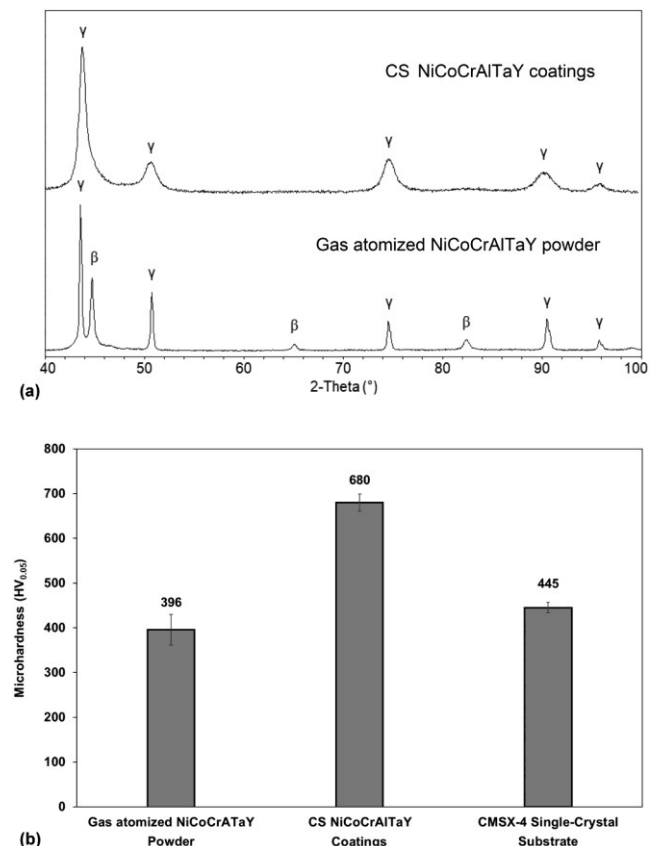


Fig. 5. (a) XRD and (b) microhardness results of the feedstock powder and CS NiCoCrAlTaY coatings deposited on CMSX-4 single-crystal superalloy substrates.

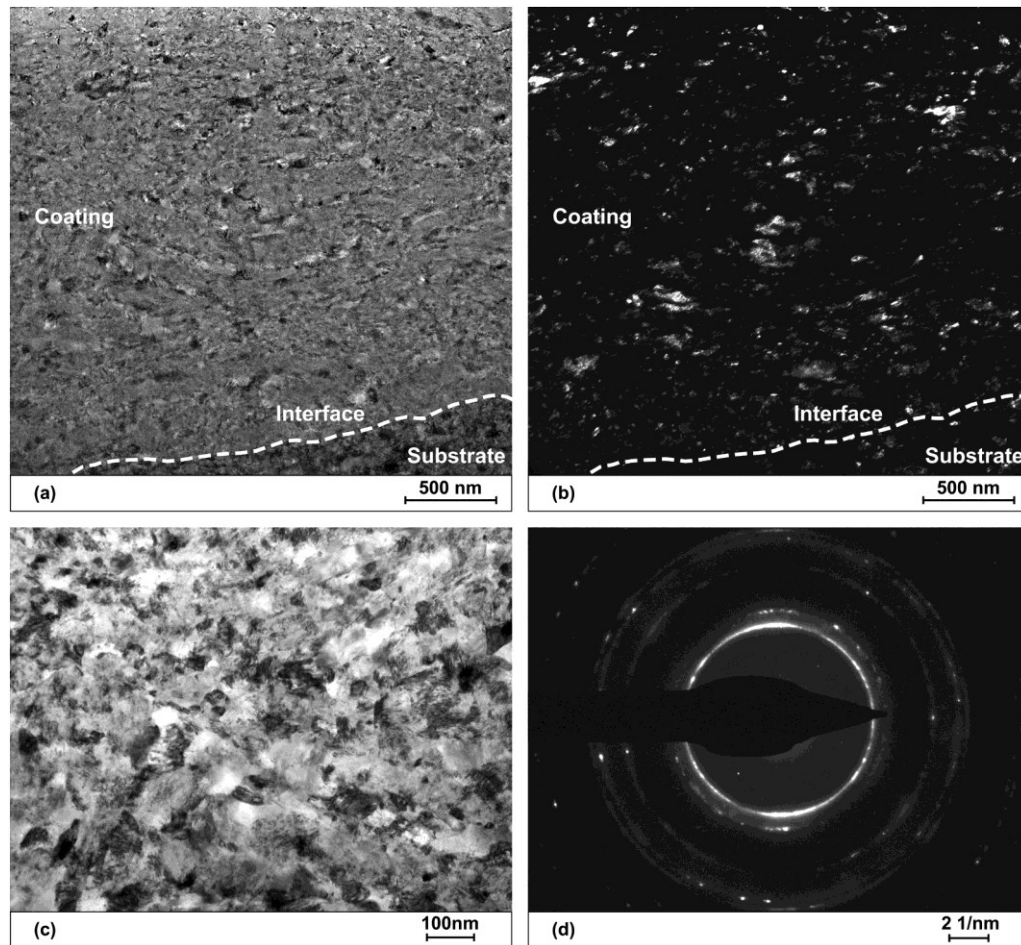


Fig. 6. Grain structure characterization of the CS NiCoCrAlTaY coatings deposited on CMSX-4 single-crystal substrate: (a, b) bright field and dark field TEM image, respectively, (c) bright field STEM image, and (d) selected area electron diffraction (SAED) with a 400 nm aperture.

with further increasing spray passes (Fig. 2c and d), where more craters were created, and more particles were deposited. Low DE also means that the adhered particles were subjected to repeated impingement of non-deposited particles. This promotes further plastic deformation of the adhered particles, as indicated by the arrows in Fig. 2c and d. Although the deformation degree may be limited after an individual particle impingement, the overall deformation accumulated can be profound after a large number of non-deposited particles impinging on one adhered particle. This can be seen from the interrupted spray test (shown in Fig. 3), where more NiCoCrAlTaY particles were sprayed over the CMSX-4 single-crystal substrate, allowing for one adhered particle being impinged multiple times.

Under enhanced particle impingements, many adhered NiCoCrAlTaY particles were highly deformed and even completely flattened starting to build up thin coating layers in some regions. This differs from the particle deformation characteristics under high DE conditions, where only the particle peripheries experience severe plastic deformation [40,79]. As such, the extensive particle deformation promoted by particle impingements under low DE conditions is expected to promote more uniform grain refinement throughout the deposited particles. These observations from the interrupted spray tests provide an important insight into the CS coating process under low DE conditions: such a process essentially combines particle deposition and an in-process shot peening by the same material that leads to in-situ nanocrystallization. By utilizing spray parameters to achieve low DE promoting particle impingements, nanocrystalline NiCoCrAlTaY coatings can be potentially

produced using solely the cold spray technique. A powder milling process is therefore not necessarily required before the coating deposition.

3.2. Coating characterization

To obtain low DE conditions using the CS technique, nitrogen was purposely selected as the process gas and relatively low spray parameters (see Table 2) were used. NiCoCrAlTaY coatings of 20–500 μm thickness were successfully deposited on CMSX-4 single-crystal substrates by changing the number of spray passes. Typical coating morphology and microstructure are shown in Fig. 4.

The CS NiCoCrAlTaY coatings show a low surface roughness ($R_a = 2.8 \pm 0.8 \mu\text{m}$) in comparison to the feedstock powder particle size (5–38 μm). Given the spherical morphology of the feedstock powder (Fig. 1a), the flattened coating surface or the absence of large particle protrusions (Fig. 4a and b) implies that the adhered particles experienced extensive deformation during the CS coating deposition. This is also evident from the coating's cross-section images. A dense coating with no visible pores can be observed from Fig. 4c, while Fig. 4d shows a highly elongated and distorted microstructure compared to that of the feedstock powder (see Fig. 1c). These coating characteristics imply severe particle deformation and are particularly obvious when comparing to similar CS MCrAlY coatings produced under higher DE conditions [40,41,79], where rough surface morphology and limited particle deformation were observed. These comparisons point out the significant contribution of the in-situ particle impingements, as previously observed from the single-splat

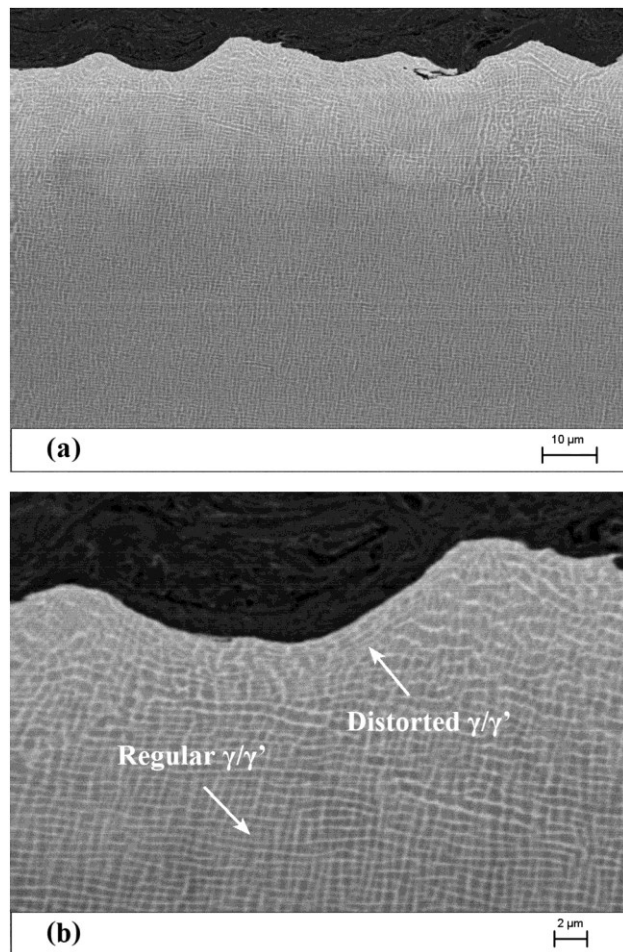


Fig. 7. BSE images showing plastic deformation of the CMSX-4 single-crystal substrate after coating deposition: (a) low magnification and (b) high magnification.

and interrupted spray tests.

The severe particle deformation is also evidenced in the XRD and hardness test results of the feedstock powder and the CS NiCoCrAlTaY coatings, as shown in Fig. 5.

The XRD spectrum of the feedstock powder shows sharp peaks of γ and β phases, in agreement with the cross-section powder microstructure (Fig. 1). The absence of the Ta-rich phase in the powder XRD spectrum is possibly due to its limited quantity. In contrast, the γ -phase diffraction peaks of the CS NiCoCrAlTaY coatings are considerably broadened. This is attributed to the lattice strain and reduced grain size in the CS coatings and has been previously reported along with a drastic decrease of peak intensities in other processes involving severe material deformation [80,81]. The peak broadening and intensity reduction should also occur for the β phase. This would explain the “absence” of the β phase peaks in the coating’s XRD spectrum, as the reduced and broadened β peaks are either overlapped with the widely-broadened γ peaks or embedded in the background [82]. In accordance with the XRD analysis, Fig. 5b shows that the extensive plastic deformation in the CS NiCoCrAlTaY coatings resulted in significantly higher microhardness ($680 \pm 19 \text{ HV}_{0.05}$) than that of the feedstock powder ($396 \pm 34 \text{ HV}_{0.05}$) due to strain hardening and grain size reduction strengthening.

It is possible to evaluate the grain size based on the XRD peak broadening after excluding the lattice strain and instrumental effects [80,83]. However, micro strains and grain refinement are convoluted in the CS coatings, and hence it is difficult to characterize their separate

influence on the peak broadening. As such, TEM analyses were performed to assess the grain structure of the CS NiCoCrAlTaY coatings. Fig. 6 shows the bright field (BF) and dark field (DF) TEM images as well as a selected area electron diffraction (SAED) pattern.

These images reveal that the coating microstructure comprises very fine grains of approximately 10–50 nm, e.g., bright regions in the DF image (Fig. 6b) and dark regions in the BF image (Fig. 6c). The SAED pattern shows polycrystalline diffraction rings as opposed to stand-alone diffraction spots, further confirming that many fine grains with different orientations exist in the selected coating area of a 400 nm aperture. These results indicate that the CS NiCoCrAlTaY coatings in the examined area are nanocrystalline. The thickness of the coating area displayed in the TEM images (Fig. 6a and b) is about 2.5 μm . This is roughly 1/3 to 1/2 of the average splat thickness ($7.1 \pm 2.7 \mu\text{m}$) estimated from the coating cross-sections. Given that the splats were heavily impinged and deformed by the non-deposited particles, the entire splat thickness becomes the particle contact peripheries. As such, different splat regions would likely experience similar levels of grain refinement, resulting in extended nanoscale grains throughout the entire splats. These results suggest that CS and conventional commercial powders can be used for manufacturing NiCoCrAlTaY coatings (and potentially MCrAlY coatings in general) with nanocrystalline microstructures. The desirable characteristics of the present CS coatings, particularly the severe plastic deformation resulting in low porosity and surface roughness, nanoscale grains, and abundant crystallographic defects (grain boundaries, dislocations, etc.), are beneficial to the oxidation performance of the NiCoCrAlTaY coatings, as demonstrated in the second part of this study. Moreover, the fact that a powder milling process is not required with the proposed approach means that potential powder contamination during milling can be eliminated, and the processing time and costs may be reduced for manufacturing nanocrystalline NiCoCrAlTaY coatings.

One might be concerned with increased powder waste and costs involved in the CS process under low DE spray conditions. This issue can be avoided by incorporating a powder reclamation system into the CS process. It has been demonstrated that non-deposited NiCoCrAlTaY powder particles can be recycled and reused for CS deposition [82]. The resulting CS coatings showed similar characteristics (i.e., extensive particle deformation, low porosity, and low surface roughness) as the coatings produced from the original feedstock powder [82]. For an established powder recycling process, a high recycling efficiency can be expected, and the powder waste should be minimal. Considering that most of the powder particles serve as shot balls during the in-situ peening, recycling the non-deposited powder particles is practically feasible and could prove to be economically viable for commercial applications.

3.3. Substrate microstructure and interfacial features

The single-crystal Ni-base superalloy (CMSX-4) substrate, as seen in the single-splat spray tests (Fig. 2), experienced noticeable plastic deformation upon each particle impact. Like what was observed in the coating, repeated particle impingements may lead to increased substrate deformation affecting its microstructure. This, as well as the coating-substrate interfacial features, needs to be characterized. Fig. 7 shows the cross-section images of the CMSX-4 substrate after the CS deposition of NiCoCrAlTaY coatings.

The original flat CMSX-4 substrate surface was roughened by the impacting particles, resulting in an undulating coating-substrate interface (Fig. 7a). A high-magnification image (Fig. 7b) reveals that the regular γ/γ' microstructure observed in the substrate (Fig. 1d) was noticeably distorted near the interface for a depth of 4–10 μm . However, the microstructure below this region is not affected. This suggests that the CS deposition of the NiCoCrAlTaY coatings only influences the substrate surface region despite enhanced particle impingements. As such, the single-crystal nature and thermomechanical properties of the underlying CMSX-4 superalloy should be not affected.

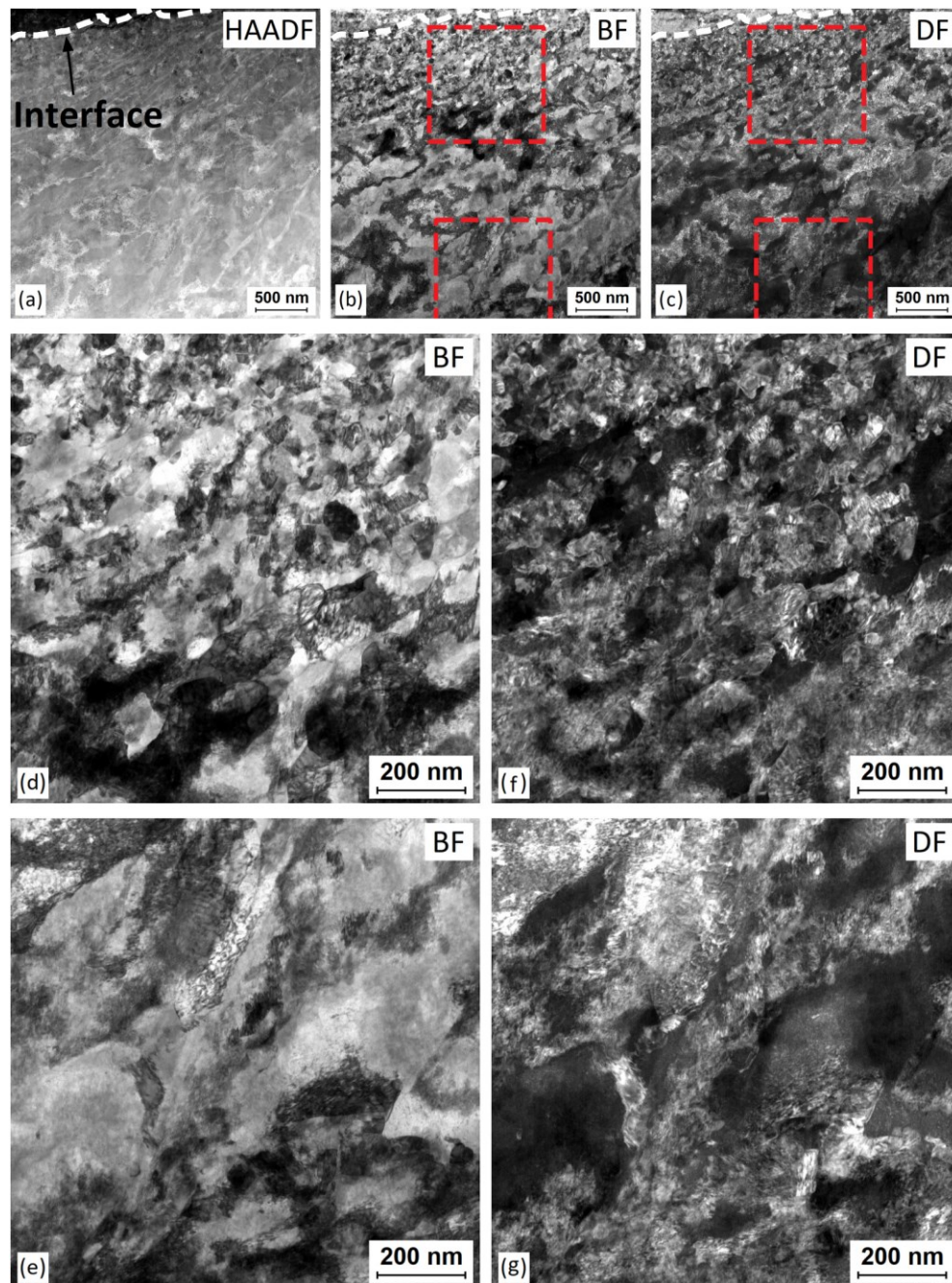


Fig. 8. STEM images showing refined grains in the CMSX-4 single-crystal substrate close to the interface: (a) high-angle annular dark field (HAADF), (b) bright field (BF), (c) dark field (DF), and high-magnification (d, e) BF and (f, g) DF images at two locations specified in (b) and (c), respectively, showing finer grains in the interface regions but larger grains further away from the interface. Individual grains appear dark in BF images and bright in DF images.

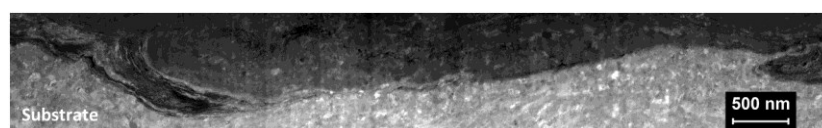


Fig. 9. Merged HAADF images showing an extended range of coating-substrate interface.

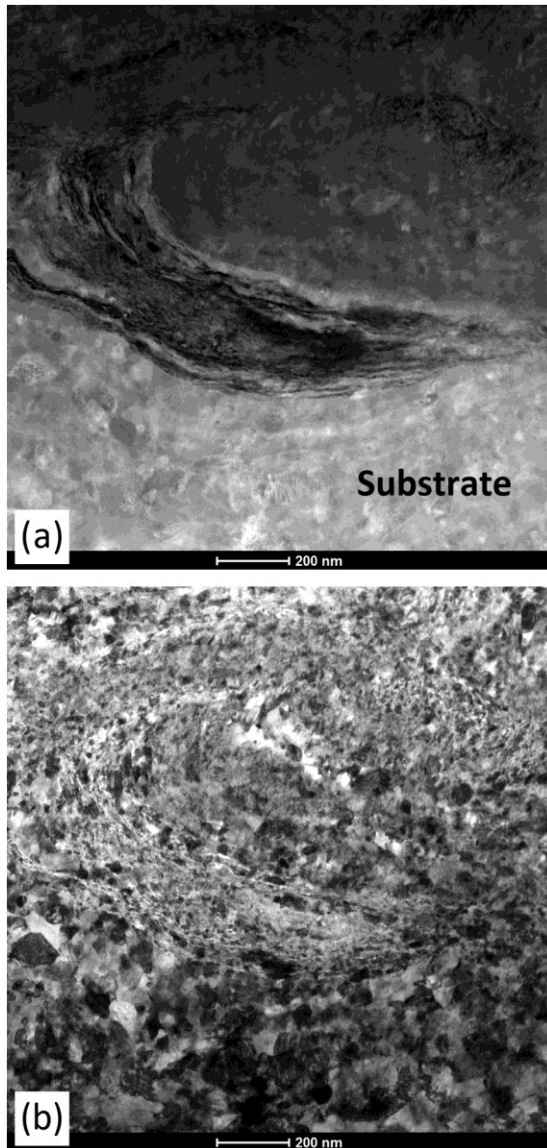


Fig. 10. (a) HAADF image showing the vortex-like structure at a higher magnification, and (b) bright field STEM image of the same location as (a).

STEM characterization was carried out to examine the substrate microstructure within the distorted region. Fig. 8 shows a high-angle annular dark field (HAADF) image along with several bright field (BF) and dark field (DF) images of the coated substrate.

The HAADF imaging technique (Fig. 8a) is based on Rutherford (incoherent) scattering instead of Bragg (coherent) scattering [84]. Consequently, it is highly sensitive to atomic weight, allowing varying contrast to be imaged (or Z-contrast images) for different elements and phases, similar to BSE imaging in SEM. This helps differentiate the coating (top-left corner in Fig. 8a) and substrate, as well as identify the coating-substrate interface. Fig. 8b and c present the bright field (BF) and dark field (DF) STEM images of the CMSX-4 single-crystal substrate at the same spot as Fig. 8a, while Fig. 8d-g show high-magnification BF and DF images of the substrate at locations specified in Fig. 8b and c. These images show a distinct grain size variation in the substrate: grains are smaller (10–50 nm) close to the interface and get significantly coarser (over 200 nm) as they are farther away from the interface. Since the substrate was a single-crystal superalloy, these grains were not there prior to coating deposition. This reveals that refined grains were created during the coating deposition process due to the localized substrate deformation caused by the particle impingements. The large grain size variations also indicate that the grain refinement process was highly sensitive to the strain levels, as the interface region where more plastic deformation occurred has finer grains than that in the inner (2–3 μm deeper) substrate region. The limited nanocrystallization (approximately 1 μm in depth) and large grain size variation in the CMSX-4 substrate imply a lesser extent of plastic deformation than that observed in the CS NiCoCrAlTaY coatings (Fig. 6). This is attributed to the γ/γ' microstructure that imparts high strength to Ni-base superalloys. The L_{12} -ordered γ' -Ni₃(Al, Ti) phase, which is often coherent with the γ matrix, impedes dislocation motion, and thus hinders plastic deformation in the superalloys [73]. More deformation in the NiCoCrAlTaY coatings deposited on a hard CMSX-4 substrate helped produce the extended nanostructure in the coatings.

Fig. 9 presents several merged HAADF images showing an extended coating-substrate interface.

Vortex-like structures are observed at both ends, while a large central portion of the interface shows that the coating and substrate are in close contact without noticeable discontinuity. The vortex structure is a result of materials mixing during particle and substrate deformation and is widely associated with mechanical bonding [47,85,86]. A close-up view of the interface around the vortex structure is shown in Fig. 10.

Both sides of the interface underwent significant grain refinement due to severe plastic deformation. However, the grains in the vortex structure (and in the coating in general) are considerably finer (<20 nm) than that in the substrate (20–50 nm). This further confirms that the CS

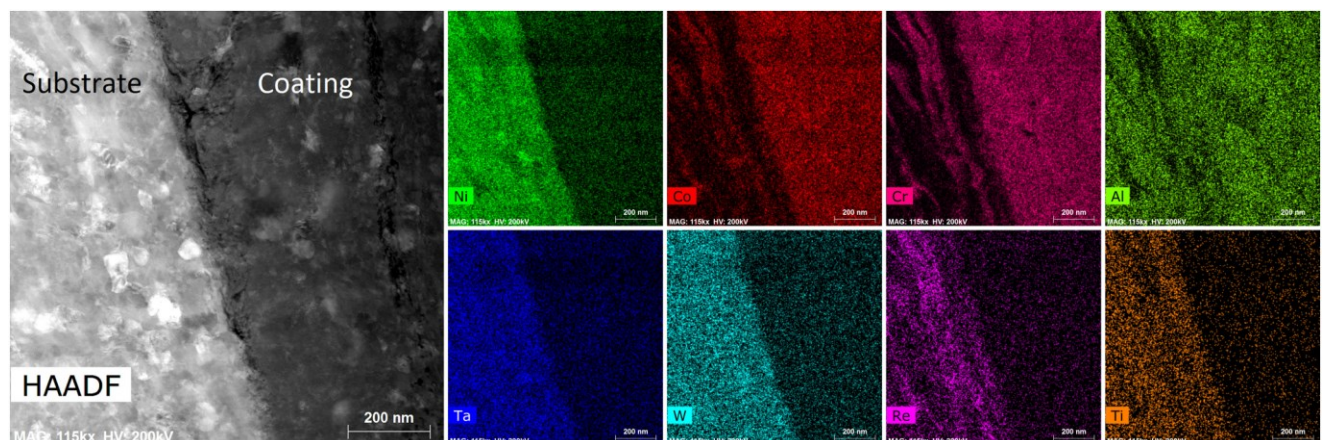


Fig. 11. HAADF image and EDS mapping results showing a distinct substrate-coating interface without evident materials mixing.

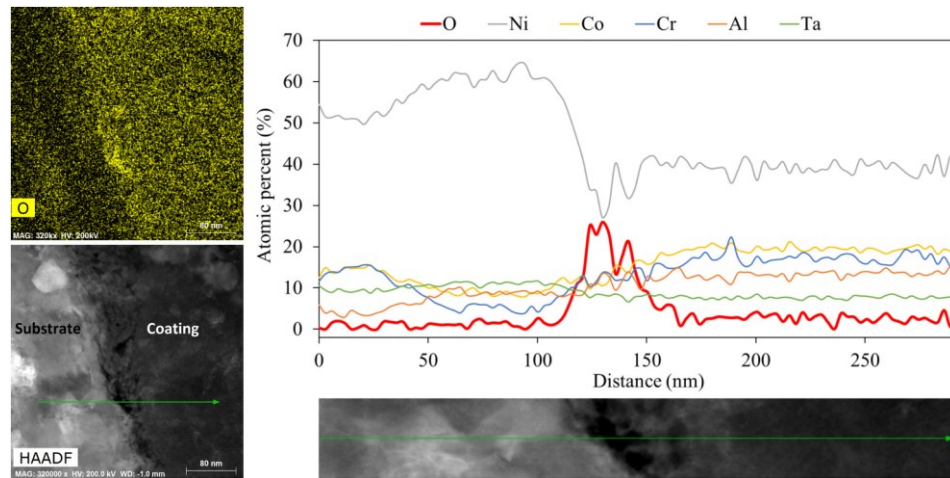


Fig. 12. HAADF image and EDS analysis confirming the existence of oxide fragments at the coating-substrate interface.

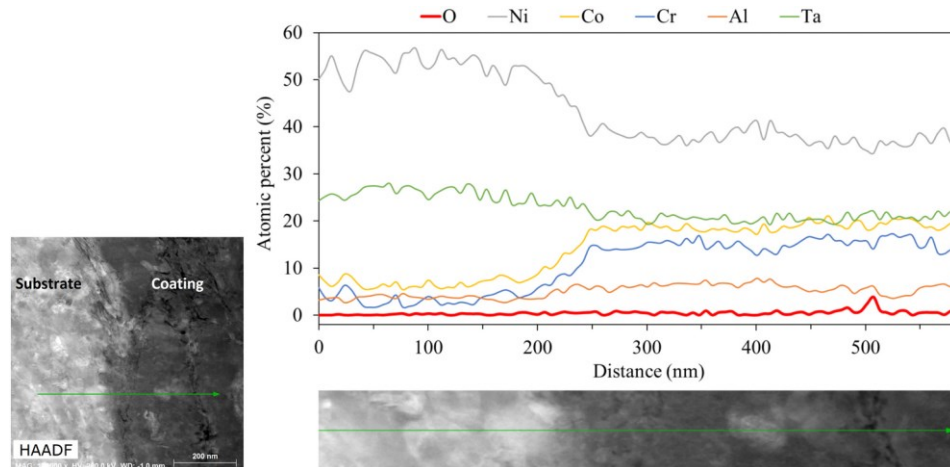


Fig. 13. HAADF image and EDS analysis suggesting metallurgical bonding at the substrate-coating interface.

NiCoCrAlTaY coatings may have experienced a significantly higher plastic deformation in comparison to the CMSX-4 single-crystal substrate.

In contrast to the vortex-like structure where the coating and substrate are intricately mixed, some regions along the interface display distinct boundaries between the coating and substrate, as shown in the HAADF image with its corresponding EDS mapping results (Fig. 11).

The EDS mapping shows the location of the coating-substrate interface and the composition difference between the coating and the substrate: a higher level of Ni, Ta, W, Re, and Ti elements is found in the CMSX-4 substrate, whereas more Co and Cr elements in the NiCoCrAlTaY coatings. These EDS mapping results along with the HAADF image indicate that the coating and substrate are intimately adhered to each other without evident materials mixing. Close examination of Figs. 9 to 11 reveals some dark spots along the interface as well as within the coatings. These spots were identified as oxides by EDS mapping and line scan, as shown in Fig. 12.

The presence of oxides at the coating-substrate interface can explain the phenomenon observed in the single-splat spray tests (Fig. 2), where large particles were only seen to adhere when the substrate was significantly roughened. This process of in-situ substrate preparation during CS is sometimes referred to as “incubation or surface activation” [42,87] and is believed to be attributed to the native oxides covering the feed-stock powder and substrate. Although the CMSX-4 substrate should be

free of surface oxides after manual grinding, a native oxide can develop again on the substrate surface by the time the CS coating deposition is carried out. These oxide layers, even with a thickness of several nanometers, prevent direct metal-metal contact, thus hindering the bonding formation between impacting particles and the substrate [88–90]. To initiate a direct coating-to-substrate contact leading to successful bonding, the oxides must be broken, and the oxide fragments need to be carried away from the interface by the material jetting. From this perspective, the enhanced particle impingements may also be beneficial to the oxide cleaning process, as they repeatedly disrupt and remove the oxides. This would create clean substrate and particle surfaces, promoting the formation of metallurgical bonding. Fig. 13 shows a potential coating-substrate interfacial site where metallurgical bonding was promoted.

The HAADF image shows an interfacial region (where the EDS line locates), where the substrate and coating cleanly adhere without any oxide fragments or pores visible at this magnification. The EDS line-scan indicates a continuous composition transition across the interface. Oxygen level remains negligibly low throughout the interface, confirming the absence of oxides at the examined locations. These results suggest that the substrate and coating are metallurgically bonded. The combination of mechanical mixing and metallurgical bonding along the coating-substrate interface could explain the high bonding strength between the CS NiCoCrAlTaY coatings and the CMSX-4 single-crystal

substrate. The adhesion testing specimens were found to fail within the glue layers with an average strength of 75.7 ± 3.1 MPa. The actual bonding strength is expected to be higher.

4. Conclusions

In the first part of this study, a cold spray (CS) process characterized by low deposition efficiency (DE) was proposed for manufacturing nanocrystalline MCrAlY coatings while using conventional feedstock powders. Single-splat and interrupted spray tests were performed to gain insight into the CS process. It was shown that adhered particles were heavily impinged and deformed by non-deposited particles. Extensive particle deformation led to dense NiCoCrAlTaY coatings with low surface roughness. More importantly, it promoted grain refinement during the CS deposition, resulting in in-situ nanocrystalline NiCoCrAlTaY coatings.

The deformation-induced grain refinement also occurred in the single-crystal Ni-base superalloy (CMSX-4) used as the substrate for CS coating deposition. Nanoscale grains were observed in the substrate close to the coating-substrate interface due to intense substrate deformation promoted by repeated particle impingements. However, the grain size is evidently larger (over 200 nm) within 2–3 μm towards the substrate, implying a lesser extent of plastic deformation and microstructural modification. The original substrate microstructure (i.e., the γ/γ' distribution pattern) was unchanged approximately 10 μm below the interface. Severe particle and substrate deformation caused extensive materials mixing at some locations, resulting in a vortex-like structure. Besides, intimate coating-substrate contact without noticeable mixing, pores, or oxides was observed, suggesting the formation of metallurgical bonding at the interface, which may be assisted by enhanced particle impingements to remove surface oxides.

While the proposed CS approach for manufacturing in-situ nanocrystalline coatings was demonstrated using a NiCoCrAlTaY powder, the general concept should also apply to other MCrAlY compositions as well as other materials. That is, the CS technique under low DE conditions can be utilized as a combined process of coating deposition and in-situ shot peening. This promotes particle deformation and grain refinement, leading to in-situ material nanocrystallization. The use of a conventional powder in the CS process, rather than a pre-milled powder, could avoid the dependence on the powder-milling process and its capacity. This may simplify the conventional two-step manufacturing process into one, potentially reducing the processing time and costs for manufacturing nanocrystalline coatings.

CRedit authorship contribution statement

Deliang Guo: Conceptualization, Investigation, Formal analysis, Visualization, Writing – original draft. **Yin Wang:** Investigation, Formal analysis. **Ruben Fernandez:** Methodology, Formal analysis. **Linruo Zhao:** Resources, Writing – review & editing. **Bertrand Jodoin:** Conceptualization, Resources, Methodology, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to acknowledge the discovery grant program from Natural Sciences and Engineering Research Council (NSERC), Canada for its financial support.

References

- [1] T.E. Strangman, Thermal barrier coatings for turbine airfoils, *Thin Solid Films* 127 (1985) 93–105.
- [2] K.D. Sheffler, D.K. Gupta, Current status and future trends in turbine application of thermal barrier coatings, *J. Eng. Gas Turbines Power* 110 (1988) 605–609.
- [3] R.A. Miller, Thermal barrier coatings for aircraft engines: history and directions, *J. Therm. Spray Technol.* 6 (1997) 35–42.
- [4] N.P. Padture, M. Gell, E.H. Jordan, Thermal barrier coatings for gas-turbine engine applications, *Science* 296 (2002) 280–284, <https://doi.org/10.1126/science.1068609>.
- [5] R. Vaßen, M.O. Jarligo, T. Steinke, D.E. Mack, D. Stover, Overview on advanced thermal barrier coatings, *Surf. Coat. Tech.* 205 (2010) 938–942.
- [6] D.R. Clarke, M. Oechsner, N.P. Padture, Thermal-barrier coatings for more efficient gas-turbine engines, *MRS Bull.* 37 (2012) 891–902.
- [7] J.L. Smialek, N.S. Jacobson, Oxidation of high temperature aerospace materials, in: Y. Bar-Cohen (Ed.), *High Temperature Materials and Mechanisms*, CRC Press, Boca Raton, 2014, pp. 95–154.
- [8] M. Schütze, Fundamentals of high temperature corrosion, in: R.W. Cahn, P. Haasen, E.J. Kramer (Eds.), *Materials Science and Technology: A Comprehensive Treatment: Corrosion and Environmental Degradation*, Wiley, Online, 2000, pp. 67–130.
- [9] W. Brandl, H.J. Grabke, D. Toma, J. Kruger, The oxidation behaviour of sprayed MCrAlY coatings, *Surf. Coat. Tech.* 86 (1996) 41–47, [https://doi.org/10.1016/S0257-8972\(96\)03039-3](https://doi.org/10.1016/S0257-8972(96)03039-3).
- [10] M.T. Pace, R.C. Thomson, J. Wells, Oxidation of MCrAlY coatings on Ni-based superalloys, *Superalloys 2008* (2008) 651–660.
- [11] D. Seo, K. Ogawa, Y. Suzuki, K. Ichimura, T. Shoji, S. Murata, Comparative study on oxidation behavior of selected MCrAlY coatings by elemental concentration profile analysis, *Appl. Surf. Sci.* 255 (2008) 2581–2590, <https://doi.org/10.1016/j.apsusc.2008.07.141>.
- [12] A. Scrivani, U. Bardi, L. Carrafiello, A. Lavacchi, F. Niccolai, G. Rizzi, A comparative study of high velocity oxygen fuel, vacuum plasma spray, and axial plasma spray for the deposition of CoNiCrAlY bond coat alloy, *J. Therm. Spray Technol.* 12 (2003) 504–507.
- [13] W. Brandl, D. Toma, J. Kruger, H.J. Grabke, G. Matthaus, The oxidation behaviour of HVOF thermal-sprayed MCrAlY coatings, *Surf. Coat. Tech.* 94–95 (1997) 21–26.
- [14] A. Gil, V. Shemet, R. Vassen, M. Subanovic, J. Toscano, D. Naumenko, L. Singheiser, W.J. Quadakkers, Effect of surface condition on the oxidation behaviour of MCrAlY coatings, *Surf. Coat. Tech.* 201 (2006) 3824–3828, <https://doi.org/10.1016/j.surfcoat.2006.07.252>.
- [15] A. Fossati, M. DiFerdinando, U. Bardi, A. Scrivani, C. Giolli, Influence of surface finishing on the oxidation behaviour of VPS MCrAlY coatings, *J. Therm. Spray Technol.* 21 (2012) 314–324, <https://doi.org/10.1007/s11666-011-9705-2>.
- [16] Z.Y. Liu, W. Gao, K.L. Dahm, F.H. Wang, Oxidation behaviour of sputter-deposited Ni-Cr-Al micro-crystalline coatings, *Acta Mater.* 46 (1998) 1691–1700, [https://doi.org/10.1016/S1359-6454\(97\)00346-7](https://doi.org/10.1016/S1359-6454(97)00346-7).
- [17] F. Wang, The effect of nanocrystallization on the selective oxidation and adhesion of Al₂O₃ scales, *Oxid. Met.* 48 (1997) 215–224.
- [18] Z.Y. Liu, W. Gao, K. Dahm, F.H. Wang, The effect of coating grain size on the selective oxidation behaviour of Ni-Cr-Al alloy, *Scripta Mater.* 37 (1997) 1551–1558, [https://doi.org/10.1016/S1359-6462\(97\)00291-1](https://doi.org/10.1016/S1359-6462(97)00291-1).
- [19] Z.Y. Liu, W. Gao, Oxidation behaviour of microcrystalline Ni-Cr-Al alloy coatings at 900 degrees C, *Scripta Mater.* 38 (1998) 877–885, [https://doi.org/10.1016/S1359-6462\(97\)00576-9](https://doi.org/10.1016/S1359-6462(97)00576-9).
- [20] P. Iqbal, J. Preece, P. Mendes, Nanotechnology: the “top-down” and “bottom-up” approaches, in: P.A. Gale, J.W. Steed (Eds.), *Supramolecular Chemistry: From Molecules to Nanomaterials*, John Wiley & Sons, Ltd., Online, 2012, <https://doi.org/10.1002/9780470661345.smc195>.
- [21] C.C. Koch, Top-down synthesis of nanostructured materials: mechanical and thermal processing methods, *Rev. Adv. Mater. Sci.* 5 (2003) 91–99.
- [22] H. Lou, F. Wang, S. Zhu, B. Xia, L. Zhang, Oxide formation of K38G superalloy and its sputtered micrograined coating, *Surf. Coat. Technol.* 63 (1994) 105–114, [https://doi.org/10.1016/S0257-8972\(05\)80014-3](https://doi.org/10.1016/S0257-8972(05)80014-3).
- [23] L. Yang, M. Chen, Y. Cheng, J. Wang, L. Liu, S. Zhu, F. Wang, Effects of surface finish of single crystal superalloy substrate on cyclic thermal oxidation of its nanocrystalline coating, *Corros. Sci.* 111 (2016) 313–324, <https://doi.org/10.1016/j.corsci.2016.04.023>.
- [24] Z.M. Li, S.Q. Qian, W. Wang, J.H. Liu, Microstructure and oxidation resistance of magnetron-sputtered nanocrystalline NiCoCrAlY coatings on nickel-based superalloy, *J. Alloy Compd* 505 (2010) 675–679, <https://doi.org/10.1016/j.jallcom.2010.06.112>.
- [25] J. Wang, M. Chen, L. Yang, S. Zhu, F. Wang, Comparative study of oxidation and interdiffusion behavior of AIP NiCrAlY and sputtered nanocrystalline coatings on a nickel-based single-crystal superalloy, *Corros. Sci.* 98 (2015) 530–540, <https://doi.org/10.1016/j.corsci.2015.05.062>.
- [26] L. Ajdelsztajn, F. Tang, G.E. Kim, V. Provenzano, J.M. Schoenung, Synthesis and oxidation behavior of nanocrystalline MCrAlY bond coatings, *J. Therm. Spray Technol.* 14 (2005) 23–30.
- [27] D. Mercier, C. Kaplin, G. Goodall, G. Kim, M. Brochu, Parameters influencing the oxidation behavior of cryomilled CoNiCrAlY, *Surf. Coat. Tech.* 205 (2010) 2546–2553, <https://doi.org/10.1016/j.surfcoat.2010.10.008>.
- [28] L. Ajdelsztajn, J.A. Picas, G.E. Kim, F.L. Bastian, J. Schoenung, V. Provenzano, Oxidation behavior of HVOF sprayed nanocrystalline NiCrAlY powder, *Mat Sci Eng a-Struct* 338 (2002) 33–43.

- [29] F. Tang, L. Ajdelsztajn, J.M. Schoenung, Influence of cryomilling on the morphology and composition of the oxide scales formed on HVOF CoNiCrAlY coatings, *Oxid. Met.* 61 (2004) 219–238.
- [30] K.K. Ma, J.M. Schoenung, Influence of cryomilling on the microstructural features in HVOF-sprayed NiCrAlY bond coats for thermal barrier coatings: creation of a homogeneous distribution of nanoscale dispersoids, *Phil Mag Lett* 90 (2010) 739–751, <https://doi.org/10.1080/09500839.2010.506424>.
- [31] A. Zakeri, E. Bahmani, A.S.R. Aghdam, Impact of MCrAlY feedstock powder modification by high-energy ball milling on the microstructure and high-temperature oxidation performance of HVOF-sprayed coatings, *Surf. Coat. Technol.* 395 (2020) 125935, <https://doi.org/10.1016/j.surfcoat.2020.125935>.
- [32] F. Tang, L. Ajdelsztajn, G.E. Kim, V. Provenzano, J.M. Schoenung, Effects of variations in coating materials and process conditions on the thermal cycle properties of NiCrAlY/YSZ thermal barrier coatings, *Mat Sci Eng a-Struct* 425 (2006) 94–106, <https://doi.org/10.1016/j.msea.2006.03.043>.
- [33] L. Ajdelsztajn, D. Hulbert, A. Mukherjee, J.M. Schoenung, Creep deformation mechanism of cryomilled NiCrAlY bond coat material, *Surf. Coat. Tech.* 201 (2007) 9462–9467.
- [34] C. Giolli, A. Giorgetti, A. Scrivani, B. Bonferroni, G. Bolelli, F. Bozza, L. Lusvarghi, A. Fossati, M. DiFerdinando, G. Kim, Milling and Cryo-milling Affecting MCrAlY High Temperature Oxidation Mechanism, 2011.
- [35] C. Kaplin, M. Brochu, The effect of grain size on the oxidation of NiCoCrAlY, *Appl. Surf. Sci.* 301 (2014) 258–263, <https://doi.org/10.1016/j.apsusc.2014.02.056>.
- [36] F. Tang, L. Ajdelsztajn, G.E. Kim, V. Provenzano, J.M. Schoenung, Effects of surface oxidation during HVOF processing on the primary stage oxidation of a CoNiCrAlY coating, *Surf. Coat. Tech.* 185 (2004) 228–233, <https://doi.org/10.1016/j.surfcoat.2003.11.020>.
- [37] P. Richer, M. Yandouzi, L. Beauvais, B. Jodoin, Oxidation behaviour of CoNiCrAlY bond coats produced by plasma, HVOF and cold gas dynamic spraying, *Surf. Coat. Tech.* 204 (2010) 3962–3974, <https://doi.org/10.1016/j.surfcoat.2010.03.043>.
- [38] W.R. Chen, E. Irissou, X. Wu, J.G. Legoux, B.R. Marple, The oxidation behavior of TBC with cold spray CoNiCrAlY bond coat, *J. Therm. Spray Technol.* 20 (2011) 132–138, <https://doi.org/10.1007/s11666-010-9601-1>.
- [39] A. Manap, A. Nakano, K. Ogawa, The protectiveness of thermally grown oxides on cold sprayed CoNiCrAlY bond coat in thermal barrier coating, *J. Therm. Spray Technol.* 21 (2012) 586–596, <https://doi.org/10.1007/s11666-012-9749-y>.
- [40] Y. Li, C.J. Li, Q.A. Zhang, L.K. Xing, G.J. Yang, Effect of chemical compositions and surface morphologies of MCrAlY coating on its isothermal oxidation behavior, *J. Therm. Spray Technol.* 20 (2011) 121–131, <https://doi.org/10.1007/s11666-010-9590-0>.
- [41] V. Crespo, I.G. Cano, S. Dosta, J.M. Guilemany, The influence of feedstock powders on the CGS deposition efficiency of bond coats for TBCs, *J. Alloy Compd* 622 (2015) 394–401, <https://doi.org/10.1016/j.jallcom.2014.09.216>.
- [42] A. Papyrin, V. Kosarev, S. Klinkov, A. Alkimov, V. Fomin, Cold Spray Technology, Elsevier, Oxford, 2007, <https://doi.org/10.1016/B978-008045155-8/50001-6>.
- [43] H. Assadi, F. Gartner, T. Stoltenhoff, H. Kreye, Bonding mechanism in cold gas spraying, *Acta Mater.* 51 (2003) 4379–4394, [https://doi.org/10.1016/S1359-6465\(03\)00274-X](https://doi.org/10.1016/S1359-6465(03)00274-X).
- [44] F. Gärtner, T. Stoltenhoff, T. Schmidt, H. Kreye, The cold spray process and its potential for industrial applications, *J. Therm. Spray Technol.* 15 (2006) 223–232, <https://doi.org/10.1361/105996306X108110>.
- [45] J. Villafuerte, *Modern Cold Spray: Materials, Process, and Applications*, Springer, 2015.
- [46] J.R. Davis, *Handbook of Thermal Spray Technology*, ASM International, 2004.
- [47] L. Ajdelsztajn, B. Jodoin, G.E. Kim, J.M. Schoenung, Cold spray deposition of nanocrystalline aluminum alloys, *Metall Mater Trans A* 36A (2005) 657–666, <https://doi.org/10.1007/s11661-005-0182-4>.
- [48] B. Jodoin, L. Ajdelsztajn, E. Sansoucy, A. Zuniga, P. Richer, E.J. Lavernia, Effect of particle size, morphology, and hardness on cold gas dynamic sprayed aluminum alloy coatings, *Surf. Coat. Tech.* 201 (2006) 3422–3429, <https://doi.org/10.1016/j.surfcoat.2006.07.232>.
- [49] A.C. Hall, L.N. Brewer, T. Roemer, Preparation of aluminum coatings containing homogenous nanocrystalline microstructures using the cold spray process, *J. Therm. Spray Technol.* 17 (2008) 352–359.
- [50] Y. Zhang, X. Wu, H. Cui, J. Zhang, Cold-spray processing of a high density nanocrystalline aluminum alloy 2009 coating using a mixture of as-atomized and as-cryomilled powders, *J. Therm. Spray Technol.* 20 (2011) 1125–1132.
- [51] R. Ghelichi, S. Bagherifard, D. Mac Donald, M. Brochu, H. Jahed, B. Jodoin, M. Guagliano, Fatigue strength of Al alloy cold sprayed with nanocrystalline powders, *Int. J. Fatigue* 65 (2014) 51–57, <https://doi.org/10.1016/j.jfatigue.2013.09.001>.
- [52] P. Richer, B. Jodoin, L. Ajdelsztajn, Substrate roughness and thickness effects on cold spray nanocrystalline Al-Mg coatings, *J. Therm. Spray Technol.* 15 (2006) 246–254, <https://doi.org/10.1361/105996306X108174>.
- [53] J. Liu, H. Cui, X. Zhou, X. Wu, J. Zhang, Nanocrystalline copper coatings produced by cold spraying, *Met. Mater. Int.* 18 (2012) 121–128, <https://doi.org/10.1007/s12540-012-0014-1>.
- [54] L. Ajdelsztajn, B. Jodoin, J.M. Schoenung, Synthesis and mechanical properties of nanocrystalline Ni coatings produced by cold gas dynamic spraying, *Surf. Coat. Technol.* 201 (2006) 1166–1172, <https://doi.org/10.1016/j.surfcoat.2006.01.037>.
- [55] M. Kumar, H. Singh, S.-M. Hong, L.-S. Choi, J.-Y. Suh, N. Chavan, S. Kumar, S. Joshi, Development of nano-crystalline cold sprayed Ni–20Cr coatings for high temperature oxidation resistance, *Surf. Coat. Technol.* 266 (2015) 122–133.
- [56] S. Tria, O. Elkedim, R. Hamzaoui, X. Guo, F. Bernard, N. Millot, O. Rapaud, Deposition and characterization of cold sprayed nanocrystalline NiTi, *Powder Technol.* 210 (2011) 181–188, <https://doi.org/10.1016/j.powtec.2011.02.026>.
- [57] Q. Zhang, C.J. Li, C.X. Li, G.J. Yang, S.C. Lui, Study of oxidation behavior of nanostructured NiCrAlY bond coatings deposited by cold spraying, *Surf. Coat. Tech.* 202 (2008) 3378–3384, <https://doi.org/10.1016/j.surfcoat.2007.12.028>.
- [58] P. Richer, M. Yandouzi, M. Brochu, A. Zuniga, A. Corbeil, B. Jodoin, Oxidation behaviour of conventional and nanocrystalline CoNiCrAlY bond coats manufactured by cold spray, *Proceedings of the ASME Turbo Expo* 2011 (4) (2012) 737–745.
- [59] D.V. Hushchuk, A.I. Yurkova, V.V. Cherniavsky, I.I. Bilyk, S.O. Nakonechnyy, Nanostructured AlNiCoFeCrTi high-entropy coating performed by cold spray, *Applied Nanoscience* (2020), <https://doi.org/10.1007/s13204-020-011364-4>.
- [60] J. Ye, J.M. Schoenung, Technical cost modeling for the mechanical milling at cryogenic temperature (cryomilling), *Adv. Eng. Mater.* 6 (2004) 656–664, <https://doi.org/10.1002/adem.200400074>.
- [61] L. Ajdelsztajn, A. Zúñiga, B. Jodoin, E.J. Lavernia, Cold-spray processing of a nanocrystalline Al-Cu-Mg-Fe-Ni alloy with Sc, *J. Therm. Spray Technol.* 15 (2006) 184–190, <https://doi.org/10.1361/105996306X107995>.
- [62] P.C. King, S.H. Zahiri, M. Jahedi, Microstructural refinement within a cold-sprayed copper particle, *Metall. Mater. Trans. A* 40 (2009) 2115–2123, <https://doi.org/10.1007/s11661-009-9882-5>.
- [63] Y. Zou, W. Qin, E. Irissou, J.G. Legoux, S. Yue, J.A. Szpunar, Dynamic recrystallization in the particle/particle interfacial region of cold-sprayed nickel coating: electron backscatter diffraction characterization, *Scripta Mater* 61 (2009) 899–902, <https://doi.org/10.1016/j.scriptamat.2009.07.020>.
- [64] Y. Zou, D. Goldbaum, J.A. Szpunar, S. Yue, Microstructure and nanohardness of cold-sprayed coatings: electron backscattered diffraction and nanoindentation studies, *Scripta Mater* 62 (2010) 395–398, <https://doi.org/10.1016/j.scriptamat.2009.11.034>.
- [65] M.R. Rokni, C.A. Widener, V.R. Champagne, Microstructural evolution of 6061 aluminum gas-atomized powder and high-pressure cold-sprayed deposition, *J. Therm. Spray Technol.* 23 (2014) 514–524, <https://doi.org/10.1007/s11666-013-0049-y>.
- [66] P. Richer, A. Zuniga, M. Yandouzi, B. Jodoin, CoNiCrAlY microstructural changes induced during cold gas dynamic spraying, *Surf. Coat. Tech.* 203 (2008) 364–371, <https://doi.org/10.1016/j.surfcoat.2008.09.014>.
- [67] C. Borchers, T. Stoltenhoff, M. Hahn, M. Schulze, H. Assadi, C. Suryanarayana, F. Gartner, T. Klassen, Strain-induced phase transformation of MCrAlY, *Adv. Eng. Mater.* 17 (2015) 723–731, <https://doi.org/10.1002/adem.201400174>.
- [68] R.D. Doherty, D.A. Hughes, F.J. Humphreys, J.J. Jonas, D.J. Jensen, M.E. Kassner, W.E. King, T.R. McNelly, H.J. McQueen, A.D. Rollett, Current issues in recrystallization: a review, *Mat Sci Eng a-Struct* 238 (1997) 219–274.
- [69] H.J. McQueen, Development of dynamic recrystallization theory, *Mater. Sci. Eng. A* 387–389 (2004) 203–208, <https://doi.org/10.1016/j.msea.2004.01.064>.
- [70] K. Kim, M. Watanabe, J. Kawakita, S. Kuroda, Grain refinement in a single titanium powder particle impacted at high velocity, *Scripta Mater* 59 (2008) 768–771, <https://doi.org/10.1016/j.scriptamat.2008.06.020>.
- [71] T. Sakai, A. Belyakov, R. Kaibyshev, H. Miura, J.J. Jonas, Dynamic and post-dynamic recrystallization under hot, cold and severe plastic deformation conditions, *Prog. Mater. Sci.* 60 (2014) 130–207, <https://doi.org/10.1016/j.pmatsci.2013.09.002>.
- [72] K. Huang, R.E. Logé, A review of dynamic recrystallization phenomena in metallic materials, *Mater Design* 111 (2016) 548–574, <https://doi.org/10.1016/j.matdes.2016.09.012>.
- [73] R.C. Reed, *The Superalloys: Fundamentals and Applications*, Cambridge University Press, New York, 2006.
- [74] K.M. Doleker, A.C. Karaoglanli, Comparison of oxidation behavior of shot-peened plasma spray coatings with cold gas dynamic spray coatings, *Oxid. Met.* 88 (2017) 121–132, <https://doi.org/10.1007/s11085-016-9691-3>.
- [75] A.C. Karaoglanli, A. Turk, Isothermal oxidation behavior and kinetics of thermal barrier coatings produced by cold gas dynamic spray technique, *Surf. Coat. Tech.* 318 (2017) 72–81, <https://doi.org/10.1016/j.surfcoat.2016.12.021>.
- [76] Y. Li, C.J. Li, G.J. Yang, L.K. Xing, Thermal fatigue behavior of thermal barrier coatings with the MCrAlY bond coats by cold spraying and low-pressure plasma spraying, *Surf. Coat. Tech.* 205 (2010) 2225–2233, <https://doi.org/10.1016/j.surfcoat.2010.08.144>.
- [77] B.C. Wilson, J.A. Hickman, G.E. Fuchs, The effect of solution heat treatment on a single-crystal Ni-based Superalloy, *Jom-Us* 55 (2003) 35–40, <https://doi.org/10.1007/s11837-003-0158-z>.
- [78] ASTM, C633-13, Standard Test Method for Adhesion or Cohesion Strength of Thermal Spray Coatings, ASTM International, West Conshohocken, PA, 2017. <https://www.astm.org/Standards/C633.htm>.
- [79] A. Bonadei, T. Marrocco, Cold sprayed MCrAlY + X coating for gas turbine blades and vanes, *Surf. Coat. Tech.* 242 (2014) 200–206, <https://doi.org/10.1016/j.surfcoat.2013.08.019>.
- [80] C. Suryanarayana, M.G. Norton, Determination of Crystallite Size and Lattice Strain, in: *X-Ray Diffraction: A Practical Approach*, Springer US, Boston, MA, 1998, pp. 207–221, https://doi.org/10.1007/978-1-4899-0148-4_9.
- [81] J. He, J.M. Schoenung, Nanostructured coatings, *Mater. Sci. Eng. A* 336 (2002) 274–319, [https://doi.org/10.1016/S0921-5092\(01\)01986-4](https://doi.org/10.1016/S0921-5092(01)01986-4).
- [82] D.L. Guo, D. MacDonald, L. Zhao, B. Jodoin, Cold spray MCrAlY coatings on single-crystal superalloy using nitrogen: properties and economics, *J. Therm. Spray Technol.* 29 (2020) 1628–1642, <https://doi.org/10.1007/s11666-020-01058-x>.

- [83] R. Delhez, T.H. de Keijser, E.J. Mittemeijer, Determination of crystallite size and lattice distortions through X-ray diffraction line profile analysis, *Fresenius' Z. Anal. Chem.* 312 (1982) 1–16, <https://doi.org/10.1007/BF00482725>.
- [84] D.E. Jesson, S.J. Pennycook, Incoherent imaging of crystals using thermally scattered electrons, *Proceedings of the Royal Society of London. Series A: Mathematical and Physical Sciences* 449 (1995) 273–293, <https://doi.org/10.1098/rspa.1995.0044>.
- [85] M. Grujicic, J.R. Saylor, D.E. Beasley, W.S. DeRosset, D. Helfritsch, Computational analysis of the interfacial bonding between feed-powder particles and the substrate in the cold-gas dynamic-spray process, *Appl. Surf. Sci.* 219 (2003) 211–227, [https://doi.org/10.1016/S0169-4332\(03\)00643-3](https://doi.org/10.1016/S0169-4332(03)00643-3).
- [86] V.K. Champagne, D. Helfritsch, P. Leyman, S. Grendahl, B. Klotz, Interface material mixing formed by the deposition of copper on aluminum by means of the cold spray process, *J. Therm. Spray Technol.* 14 (2005) 330–334, <https://doi.org/10.1361/105996305x59332>.
- [87] S.V. Klinkov, V.F. Kosarev, M. Rein, Cold spray deposition: significance of particle impact phenomena, *Aerosp. Sci. Technol.* 9 (2005) 582–591, <https://doi.org/10.1016/j.ast.2005.03.005>.
- [88] M. Razavipour, S. Rahmati, A. Zúñiga, D. Criado, B. Jodoin, Bonding mechanisms in cold spray: influence of surface oxidation during powder storage, *J. Therm. Spray Technol.* (2020), <https://doi.org/10.1007/s11666-020-01123-5>.
- [89] S. Rahmati, B. Jodoin, Physically based finite element modeling method to predict metallic bonding in cold spray, *J. Therm. Spray Technol.* 29 (2020) 611–629, <https://doi.org/10.1007/s11666-020-01000-1>.
- [90] C.Y. Chen, Y.C. Xie, R.Z. Huang, S.H. Deng, Z.M. Ren, H.L. Liao, On the role of oxide film's cleaning effect into the metallurgical bonding during cold spray, *Mater. Lett.* 210 (2018) 199–202, doi:j.matlet.2017.09.024.
- [91] Deliang Guo, Linruo Zhao, Bertrand Jodoin, Cold spray for production of in-situ nanocrystalline MCrAlY coatings – Part II: Isothermal oxidation performance, *Surf. Coat. Tech.* (2021), 126828, <https://doi.org/10.1016/j.surfcoat.2021.126828>. In press.

6.2 Isothermal Oxidation Performance

This section contains the journal article (Part II of the study [177]) that presents the isothermal oxidation performance of the nanocrystalline NiCoCrAlTaY coatings produced using the cold spray approach. Morphological, microstructural, and compositional evolutions of the coated samples were characterized following isothermal oxidation tests at 1100°C for durations of 1h to 500h. TGO growth kinetics on the NiCoCrAlTaY coatings was evaluated and compared to similar MCrAlY coatings produced using other coating deposition techniques. The fast establishment of α -Al₂O₃ TGO scale and relatively low scale growth kinetics observed in the study suggested enhanced oxidation performance of the cold spray NiCoCrAlTaY coatings attributable to their microstructural characteristics.



Cold spray for production of in-situ nanocrystalline MCrAlY coatings – Part II: Isothermal oxidation performance

Deliang Guo^{a,*}, Linruo Zhao^b, Bertrand Jodoin^a

^a Cold Spray Research Laboratory, University of Ottawa, Ottawa, Canada

^b Aerospace Research Centre, National Research Council Canada, Ottawa, Canada

ARTICLE INFO

Keywords:

Cold spray

Nanocrystalline

Bond coat

MCrAlY

Isothermal oxidation

Superalloy

ABSTRACT

Cold spray (CS) MCrAlY coatings have been widely explored as potential bond coats for thermal barrier coatings used on the hot-section components of modern gas turbines. In this study, NiCoCrAlTaY coatings were applied on CMSX-4 single-crystal Ni-base superalloy substrates using the CS technique. Nitrogen was used as process gas with low spray parameters to allow the production of in-situ nanocrystalline NiCoCrAlTaY coatings while using conventional powders of large grain size, as demonstrated in Part I of the study using scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM). In this part of the study (Part II), the coated samples were examined under isothermal oxidation conditions at 1100 °C for 1 h to 500 h. The as-deposited NiCoCrAlTaY coatings, characterized by dense microstructure, low surface roughness, nanoscale grains, and a large number of crystallographic defects such as grain boundaries and dislocations, promoted the formation of a protective α -Al₂O₃ scale during short-term oxidation. Fast diffusion via these crystallographic defects facilitated Al diffusion in the coatings. This provides sufficient Al replenishment to the coating subsurface region, sustaining the growth of the α -Al₂O₃ scale during prolonged oxidation. The relatively low scale growth kinetics found in the study demonstrated enhanced oxidation performance of the CS nanocrystalline NiCoCrAlTaY coatings.

1. Introduction

High-pressure turbine blades and nozzle guide vanes in modern aero-engines are manufactured from single-crystal Ni-base superalloys as their operating environment requires the use of materials with high creep and thermo-mechanical fatigue strength at elevated temperatures [1–3]. These components have hollow airfoils with internal cooling and are coated with a thermal barrier coating (TBC) consisting of a ceramic topcoat and a metallic bond coat [4–6]. Combined with air cooling, the ceramic topcoat, typically 7–8 wt.% yttria-stabilized zirconia (7YSZ) produced by electron beam physical vapor deposition (EB-PVD), provides effective heat shielding of the component surface from hot gases, allowing the turbine to operate at higher temperatures with enhanced efficiency and performance [7–9]. The metallic bond coat, typically a diffusion platinum aluminide or low-pressure plasma spray (LPPS) MCrAlY coating, minimizes the mismatch of coefficient of thermal expansion (CTE) between the 7YSZ topcoat and the turbine components and protects the latter from oxidation degradation [6]. This oxidation resistance function is achieved by forming a thermally grown oxide

(TGO) layer between the bond coat and the topcoat. Once established, the TGO scale can effectively hinder the diffusion of oxidation reactants through the scale and hence reduce the oxidation rate of the coated components [10]. While these types of commercial bond coats meet the blade design requirements, they are costly to fabricate as platinum is an expensive precious metal and the LPPS process requires the use of sophisticated vacuum equipment for coating deposition. Therefore, it is desirable to develop alternative manufacturing techniques to substitute diffusion platinum aluminide or LPPS MCrAlY overlay bond coat without compromising oxidation performance.

The durability of TBCs is closely related to the characteristics of the TGO scale developed during thermal exposure [11–15]. A continuous, uniform, dense, chemically stable, and adherent TGO scale is required for a durable TBC [12]. Aluminum oxide, particularly α -Al₂O₃, is known for its high melting point, excellent stability, slow growth rate, and low oxygen diffusivity at high temperatures [16], and thus satisfies most of the requirements for a protective TGO scale. MCrAlY coatings usually contain a sufficient amount of Al, and their compositions are specifically designed such that selective oxidation of Al occurs and the growth of a

<https://doi.org/10.1016/j.surfcoat.2021.126828>

Received 27 October 2020; Received in revised form 14 December 2020; Accepted 30 December 2020

Available online 12 January 2021

0257-8972/© 2021 Elsevier B.V. All rights reserved.

Table 1

Nominal compositions of CMSX-4 superalloy substrate and Amdry 997 feedstock powder (wt.%).

	Ni	Co	Cr	Al	Ta	Y	W	Re	Ti	Others
CMSX-4	61.7	9.0	6.5	5.6	6.5	–	6.0	3.0	1.0	Mo 0.6 Hf 0.1
Amdry 997	43.9	23.0	20.0	8.5	4.0	0.6	–	–	–	–

protective α -Al₂O₃ TGO scale is promoted at temperatures relevant to gas turbines [6]. The oxidation of MCrAlY coatings is a dynamic process, in which the coating composition, microstructure, and TGO characteristics continuously evolve. Under certain circumstances, the TGO scale may contain oxides other than α -Al₂O₃, such as mixed oxides (NiO, CoO, and Cr₂O₃) and spinel-type oxides (Ni, Co)(Al, Cr)₂O₄ [17,18]. These oxides are characterized as porous and fast-growing, and thus considered non-protective and should be avoided or delayed from being formed. Moreover, the TGO scale is often subjected to mechanical stresses, e.g., externally applied stress, growth stress, and residual stress due to thermal expansion misfit between the scale and the underlying coatings [19]. These stresses, when exceeding certain material and geometry-dependent critical values, may provoke scale spallation resulting in premature TGO failure, even before the formation of undesirable oxides in the scale (or known as chemical failure) [20,21]. The protectiveness of MCrAlY coatings is generally considered to come to an end either (i) chemically, when substantial amounts of non-protective oxides are formed, or (ii) mechanically, when excessive TGO scale spallation occurs prior to the chemical failure. It was found that the oxidation behavior and failure mechanisms of MCrAlY coatings strongly depend on the coating and substrate compositions [22–24], coating microstructure and surface morphology [25–30], as well as thermal exposure conditions [31,32].

To improve the performance and durability of MCrAlY coatings, extensive studies have been carried out focusing on composition optimization, microstructure control, and surface modification. One of the topics that have attracted research attention is the fabrication of nanocrystalline MCrAlY coatings (grain size <100 nm). The presence of enhanced grain boundaries associated with the nanostructure promotes atomic diffusion at elevated temperatures and facilitates the formation and growth of a protective α -Al₂O₃ scale [17,33–36]. However, other coating characteristics, e.g., internal oxide content and surface finish, also play a critical role in the performance of nanocrystalline MCrAlY coatings. Mercier, et al. [37] found that grain refinement by cryomilling contributed to the establishment of a single α -Al₂O₃ TGO layer on a cryomilled CoNiCrAlY powder during isothermal oxidation at 1000 °C. In contrast, high velocity oxygen fuel (HVOF) CoNiCrAlY coatings produced from cryomilled powders yielded a duplex TGO scale consisting of α -Al₂O₃ and mixed oxides at the same temperature [25,37]. This change in coating oxidation behavior was attributed to in-process powder oxidation during the HVOF sprays, which led to early nucleation and subsequent growth of mixed oxides [25,37]. Zhang, et al. [38] observed that the surface morphology of nanocrystalline NiCrAlY coatings had a significant impact on the TGO constitution. After 200 h of oxidation at 1000 °C, a TGO scale containing spinel and mixed oxides was formed on the coatings without post-deposition surface treatment ($R_a = 5.6 \pm 1.2 \mu\text{m}$), whereas a continuous and uniform α -Al₂O₃ TGO scale was observed on their shot-peened counterparts ($R_a = 3.1 \pm 0.6 \mu\text{m}$). These findings demonstrated that low oxide content and reduced surface roughness are beneficial to the oxidation performance of MCrAlY coatings.

Cold gas dynamic spray or simply cold spray (CS) has been widely investigated as a promising technique for manufacturing MCrAlY bond coats [30,38–47]. Its low process temperature minimizes in-process feedstock powder oxidation, and the high-velocity particle impacts induce severe plastic deformation leading to adherent and dense coatings. It has been demonstrated in a previous study that NiCoCrAlTaY coatings can be deposited by CS on CMSX-4 single-crystal Ni-base superalloy substrates using either nitrogen or helium as the process gas

[48]. The use of nitrogen with relatively low spray parameters was found to produce extensive plastic deformation in CS NiCoCrAlTaY coatings due to enhanced in-process particle impingements [48]. This allowed the production of in-situ nanocrystalline NiCoCrAlTaY coatings while using conventional powders of large grain size, as demonstrated in the first part of the current study (Part I) [49]. SEM and STEM characterization revealed that the NiCoCrAlTaY coatings produced under such CS conditions were characterized by dense microstructure, low oxide content and surface roughness, and nanoscale grains, offering potentially improved oxidation performance. In this part of the study (Part II), the isothermal oxidation performance of the CS NiCoCrAlTaY coatings was examined at 1100 °C for durations of 1 h to 500 h. Coating morphology, microstructure, and composition were characterized after different oxidation durations. The TGO growth kinetics on the CS NiCoCrAlTaY coatings was evaluated and compared to similar MCrAlY coatings produced using other coating techniques. The beneficial effect of the CS NiCoCrAlTaY coatings characteristics on the oxidation performance is discussed.

2. Experimental procedures

2.1. Substrate and coating preparation

A second-generation single-crystal Ni-base superalloy (CMSX-4, Cannon Muskegon) was used as the substrate ($\varnothing 16 \times 3 \text{ mm}$) for preparing coating samples. The superalloy was received in a vacuum solution-treated condition (2 h at 1321 °C, gas fan quench). Subsequent heat treatments, i.e., primary aging (6 h at 1140 °C, air cooling) and secondary aging (20 h at 870 °C, air cooling), were performed to form a γ/γ' microstructure to achieve the desired mechanical properties [50]. The heat-treated substrates were manually ground before coating deposition to remove the oxidized surface layer resulting from the aging treatments. The nominal composition of the superalloy substrate is given in Table 1.

The feedstock powder used for CS deposition was a commercial gas-atomized NiCoCrAlTaY powder (Amdry 997, 5–38 μm , Oerlikon Metco) with the nominal composition given in Table 1. The powder was deposited on the CMSX-4 single-crystal substrate using a commercial CS system (SST-EP, Centerline (Windsor) Limited) with a build-in powder-preheating unit. Nitrogen was employed as both the process gas and the powder-feeding gas. A stagnation pressure of 3.45 MPa and a stagnation temperature of 500 °C were used along with a powder preheating temperature of 500 °C. More details on the nozzle specification and spray parameters can be found in reference [48].

2.2. Isothermal oxidation evaluation

The coated samples were subjected to isothermal oxidation tests at 1100 °C in air using a laboratory furnace (Lindberg/Blue M™, Thermo Scientific™). The test durations were 1, 2, 5, 10, 25, 50, 100, and 500 h. Samples were loaded into the furnace once the temperature was stabilized at 1100 °C and removed from the furnace immediately after the predetermined test durations, followed by air cooling to room temperature. The changes in surface morphology, microstructure, and composition of oxidized samples were characterized after each duration.

TGO scale thickness was recorded for each sample to evaluate the TGO growth kinetics. A minimum of 12 TGO images was taken using a scanning electron microscope (SEM, EVO MA-10, Zeiss, Germany) for

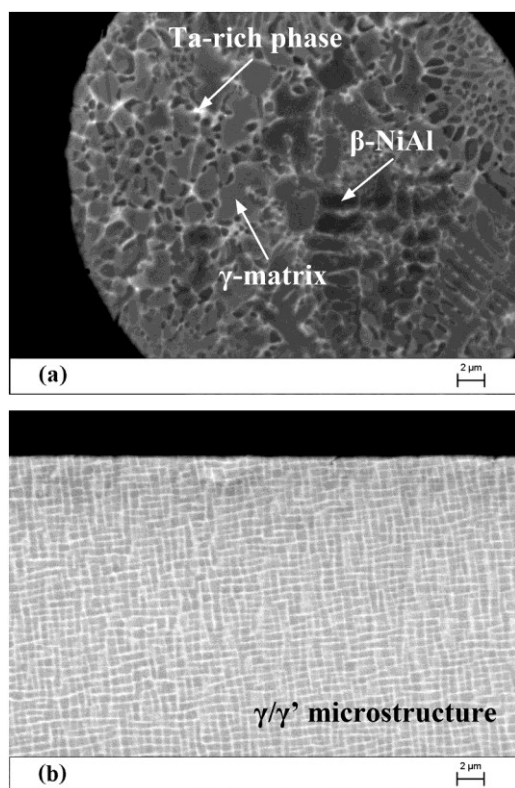


Fig. 1. Cross-section backscattered electron (BSE) images showing: (a) the three-phase constituents of NiCoCrAlTaY powder and (b) the γ/γ' microstructure of CMSX-4 single-crystal substrate.

each sample, and over 100 TGO thickness values were obtained on each of the cross-section images using an image analysis software (Vision-Lite, Clemex). The mean scale thicknesses were used to derive the oxidation rate constants.

2.3. Material characterization

Standard metallographic procedures (sectioning, mounting, and polishing) were followed to prepare samples for metallographic examination and analysis. Coating porosity was measured under an optical microscope using an image analysis software (Vision-Lite, Clemex, Canada). Coating surface roughness was measured using a stylus profilometer (SRG-4000, Phase II Plus, USA). Surface morphology, microstructure, and composition of the as-deposited and oxidized coatings were characterized using the SEM and an energy-dispersive X-ray spectroscopy (EDS, INCA-x-act, Oxford Instrument, UK). X-ray diffraction (XRD) using Cu $K\alpha$ radiation (X-Pert PW1830, PANalytical, Netherlands) was used to study the phase constitution of the feedstock powder as well as the as-deposited and oxidized coatings.

3. Results and discussion

3.1. Microstructural evolution

3.1.1. Starting microstructures

Fig. 1 shows the microstructures of the as-received NiCoCrAlTaY feedstock powder and heat-treated CMSX-4 single-crystal superalloy substrate.

The feedstock powder comprises three phases (Fig. 1a): a face-centered cubic (FCC) nickel-based solid solution γ phase (light grey matrix), a body-centered cubic (BCC) Al-rich β -NiAl phase (dark grey),

and a Ta-segregated phase (white). As an aluminum reservoir, the β -NiAl phase promotes the formation of Al_2O_3 on the coating surface during thermal exposure [51]. The alloying of Ta in the powder improves the oxidation performance of the NiCoCrAlTaY coatings at high temperatures, possibly due to reduced refractory elements (e.g., Ta, W, Re) diffusion from the substrate into the coating [52]. The CMSX-4 single-crystal substrate (Fig. 1b) has a typical γ/γ' microstructure with a high volume fraction of γ' - $Ni_3(Al, Ti)$ cuboidal phase (dark grey) in an intertwining γ matrix (white).

The microstructures of the as-deposited NiCoCrAlTaY coatings and the superalloy substrate adjacent to the coating-substrate interface are presented in Fig. 2.

The as-deposited coating (Fig. 2a) is dense (porosity $<0.5\%$) with low surface roughness ($R_a = 2.8 \pm 0.8 \mu m$). The CMSX-4 substrate beneath the coating (Fig. 2b) was slightly deformed due to the high-velocity particle impacts; however, the original γ/γ' microstructure of the substrate is still discernible despite the distortion of the coating-substrate interface. This suggests that the CS coating deposition process had a limited effect on the microstructure and mechanical properties of the CMSX-4 single-crystal superalloy. TEM (Fig. 2c) and STEM (Fig. 2d) characterization, as well as other results shown in Part I of the study [49], revealed that the CS NiCoCrAlTaY coatings are nanocrystalline (grain size <100 nm). This is attributed to extensive particle deformation during the CS process that led to dynamic recrystallization and grain refinement [40,53]. In addition to grain boundaries, other crystallographic defects (e.g. dislocations) and large microstrain are likely present in CS coatings (as suggested in Fig. 2e and f) due to severe plastic deformation at high strain rates. These crystallographic defects may promote atomic diffusion in the coatings, provide TGO nucleation sites, and facilitate the formation of the α - Al_2O_3 scale during thermal exposure [51].

3.1.2. Short-term oxidation

Fig. 3 shows the surface morphologies of the CS NiCoCrAlTaY coatings in the as-deposited condition and after short-term (1 h, 2 h, and 5 h) isothermal oxidation at $1100^\circ C$.

Small oxide granules clustering on the surface of the coatings were observed after the short-term high-temperature exposure (Figs. 3c-h). Spot EDS analyses were performed on each of the samples to determine and compare the surface chemical compositions. Two typical locations were selected, i.e., one on the peak of the granule clusters and the other in the valley between the granule clusters, as specified in Fig. 3. The EDS results are summarized in Table 2.

Despite the apparent difference in the morphologies between these two locations on each sample, the EDS results revealed similar aluminum- and oxygen-rich compositions after 1 h, 2 h, and 5 h oxidation tests. This suggests the formation of TGO on the coating surface with Al_2O_3 being the dominant constituent. The detection of Ni, Co, Cr, Ta, and Y may result from the SEM electron beam (at 15 kV) penetrating the thin TGO scale into the NiCoCrAlTaY coatings or, if probable, from mixed oxides in the scale. To ascertain the phase constituents in the feedstock powder, as-deposited CS coatings, and TGOs formed during the thermal exposure, XRD measurements were carried out with the results presented in Fig. 4.

The feedstock powder shows two-phase constituents of γ and β , agreeing with the SEM characterization shown in Fig. 1a; the Ta-rich phase observed in the powder, however, is not shown in the XRD spectrum, probably due to its limited quantity. In contrast, only the γ phase was detected by XRD in the as-deposited CS NiCoCrAlTaY coatings. The γ -phase peaks broadening reflects grain refinement and high micro-strains in the coatings, while the absence of β -phase diffraction peaks may be attributed to β -phase dissolution or β -peak broadening and reduction as a result of severe plastic deformation [40,48,53]. After 1 h isothermal oxidation at $1100^\circ C$, diffraction peaks of α - Al_2O_3 , as well as two other small peaks associated with yttrium oxide (Y_2O_3), were identified from the XRD spectrum. This suggests that the TGO formed on

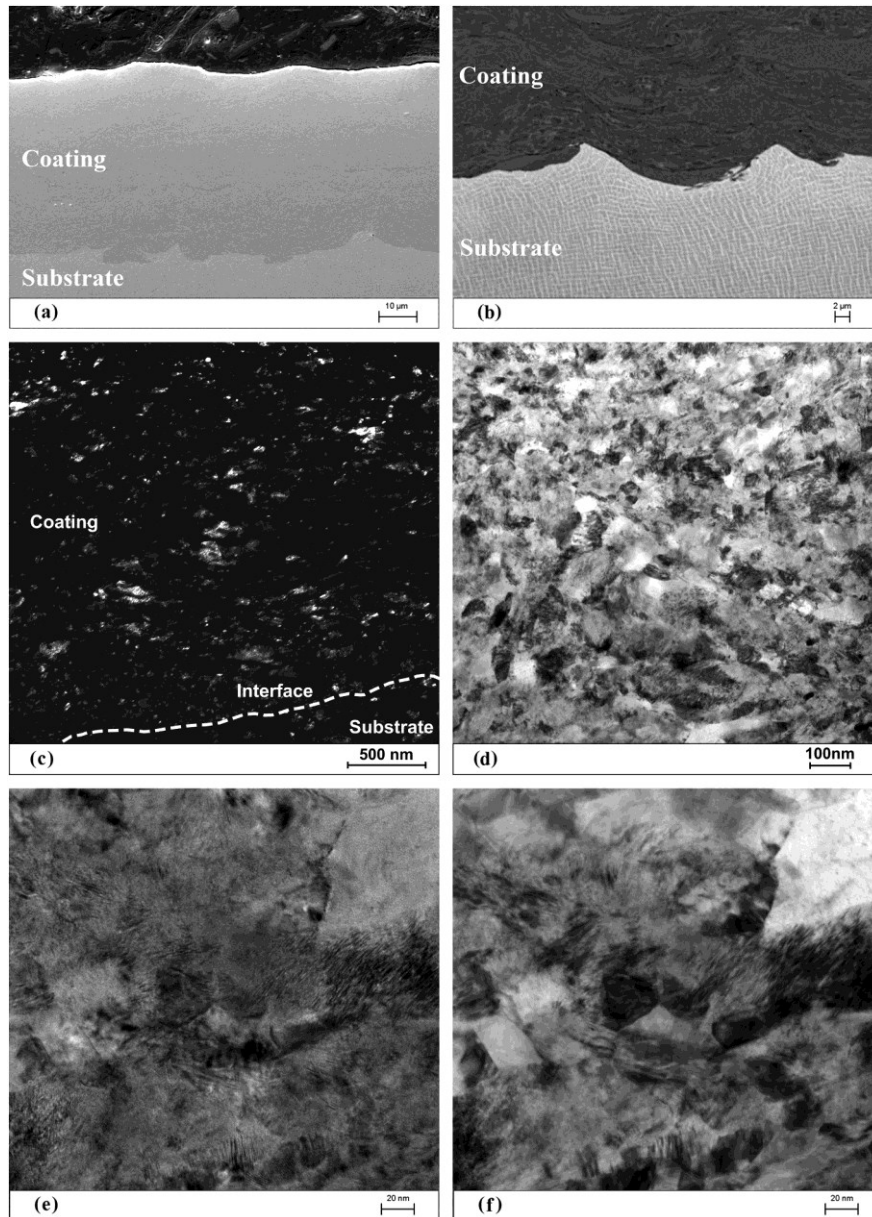


Fig. 2. Microstructure of as-deposited CS NiCoCrAlTaY coatings on CMSX-4 single-crystal super-alloy substrate: (a) SEM image showing the dense coating microstructure with low surface roughness, (b) BSE image showing limited substrate deformation near the coating-substrate interface, (c) dark-field TEM image and (d) bright-field STEM image showing coating microstructure with nanoscale grains, and high-magnification (e) TEM image and (f) bright-field STEM image showing large microstrain and potentially other crystallographic defects.

the coating surface (Fig. 3) was composed of mainly α - Al_2O_3 with a minor amount of Y_2O_3 . As shown in Figs. 3f-h and Table 2, the granule clusters were predominantly α - Al_2O_3 , while more Y_2O_3 were detected in the valleys between the granule clusters. The XRD spectra of CS NiCoCrAlTaY coatings underwent 2 h and 5 h oxidation tests show almost identical diffraction peaks positions as those from 1 h oxidation. However, a progressive increase in α - Al_2O_3 peaks intensities was observed, indicating an increasing TGO scale thickness over longer oxidation times. Since mixed and spinel-type oxides were not observed in the XRD spectra, the EDS signals of Ni, Co, Cr, and Ta (Table 2) detected from the surface must originate from the NiCoCrAlTaY coatings beneath the thin TGO scale.

Further to the surface morphology changes presented in Fig. 3, the NiCoCrAlTaY coatings also experienced significant through-depth microstructural evolution during the short-term isothermal oxidation. Fig. 5 shows cross-section microstructures and EDS line scan analyses of the CS NiCoCrAlTaY coatings in the as-deposited condition and after thermal exposure at 1100 °C for 1 h.

The as-deposited CS NiCoCrAlTaY coatings, as well as the gas-atomized feedstock powder (Fig. 1), show a heterogeneous distribution of β -NiAl phase among γ matrix. This β/γ microstructure was found to be metastable and would eventually transform into an equilibrium β/γ configuration at elevated temperatures [53]. As shown in Fig. 5b, the CS NiCoCrAlTaY coatings after 1 h oxidation evolved into a uniform two-phase microstructure: a distinct dark-grey β phase and a light-grey γ matrix. Furthermore, a continuous TGO scale was confirmed on the coating surface after the thermal exposure. This, along with the EDS (Table 2) and XRD (Fig. 4) results, proves that a uniform and continuous α - Al_2O_3 TGO scale has been established after 1 h oxidation at 1100 °C. Previous studies on MCrAlY coatings have shown that although α - Al_2O_3 is the thermodynamically stable phase at high temperatures, other types of aluminas (e.g., γ - Al_2O_3 , θ - Al_2O_3) may form as transitional reaction products during the early stages of oxidation [54]. These transient aluminas will eventually transform to the stable α - Al_2O_3 with time [55]; however, the rate at which the transformation proceeds depends largely on the temperature [56]. It is possible that transient aluminas may be

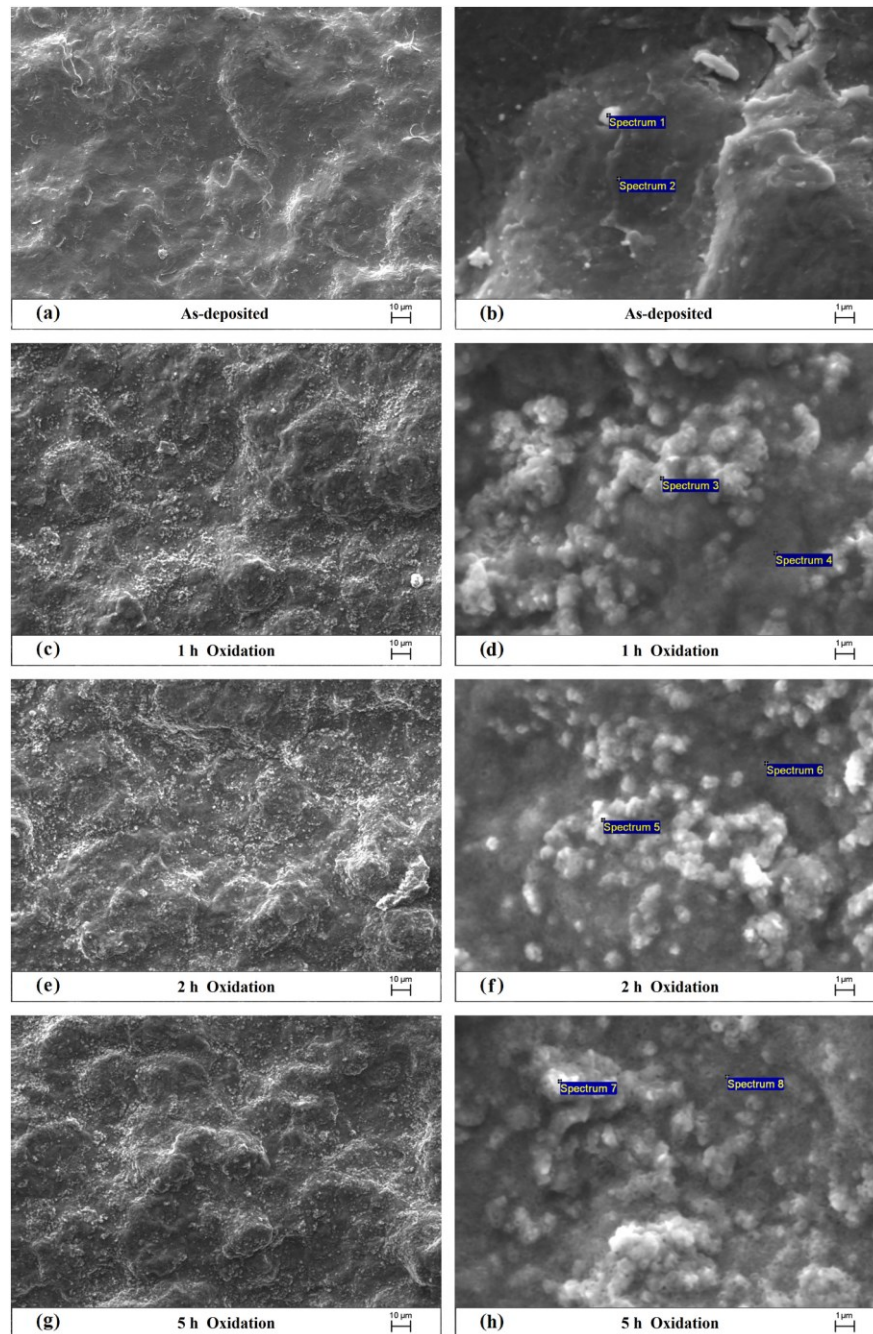


Fig. 3. Surface morphologies of CS NiCoCrAlTaY coatings in as-deposited condition (a, b) and after isothermal oxidation at 1100 °C for 1 h (c, d), 2 h (e, f), and 5 h (g, h).

Table 2

Spot EDS analyses results on the coating surfaces (wt.%). The spectra correspond to the locations specified in Fig. 3.

Sample ID	Spectrum	O	Al	Ni	Co	Cr	Ta	Y
As-deposited	#1	—	9.3	41.3	21.7	18.9	5.3	3.5
	#2	—	9.5	41.1	22.7	20.2	5.0	1.5
1 h Oxidation	#3	51.6	39.0	3.1	2.1	3.7	0.4	0.1
	#4	44.8	41.1	4.3	2.6	4.7	0.7	1.8
2 h Oxidation	#5	53.1	37.3	3.9	2.6	2.9	0.1	0.1
	#6	46.5	42.0	3.6	2.5	3.3	0.7	1.5
5 h Oxidation	#7	54.2	41.2	1.6	0.4	2.5	0.2	0.0
	#8	44.7	44.9	3.7	2.5	2.6	0.1	1.8

formed on the CS NiCoCrAlTaY coatings at the very beginning of thermal exposure at 1100 °C but were fully converted to α -Al₂O₃ after 1 h oxidation. This fast conversion may have been facilitated by the nanostructure of the CS NiCoCrAlTaY coatings, as enhanced grain boundaries could provide nucleation sites for α -Al₂O₃ and thus promote the transition from transient Al₂O₃ to stable α -Al₂O₃ [37]. The rapid establishment of a stable α -Al₂O₃ TGO scale is desirable as it can significantly reduce the oxidation kinetics subsequently [57].

The formation and growth of the α -Al₂O₃ scale continually consumed Al from the underlying coating, resulting in a β depletion zone below the scale (Fig. 5b) where the β -NiAl phase transformed into γ' -Ni₃Al and then γ solid solution. These microstructural features caused distinct Al

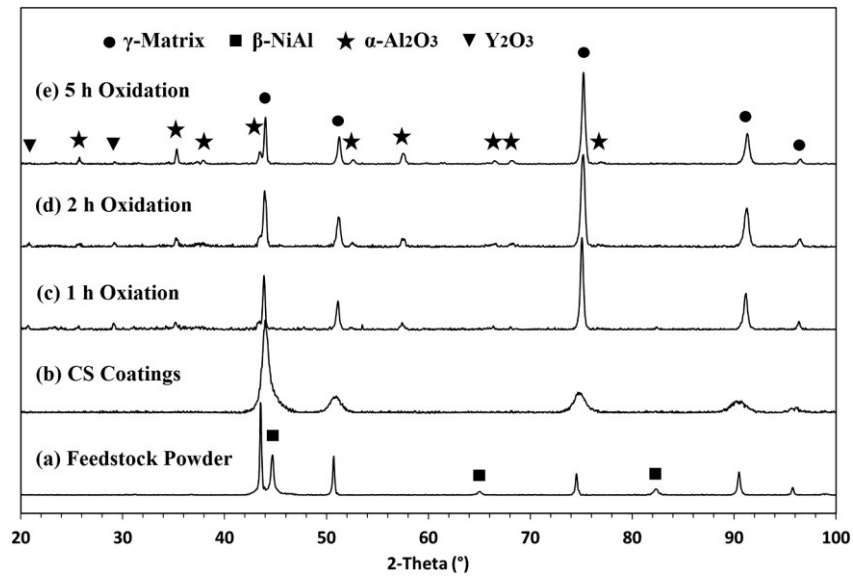


Fig. 4. XRD results of the NiCoCrAlTaY feedstock powder, as-deposited CS coatings, and coatings oxidized at 1100 °C for 1 h, 2 h, and 5 h.

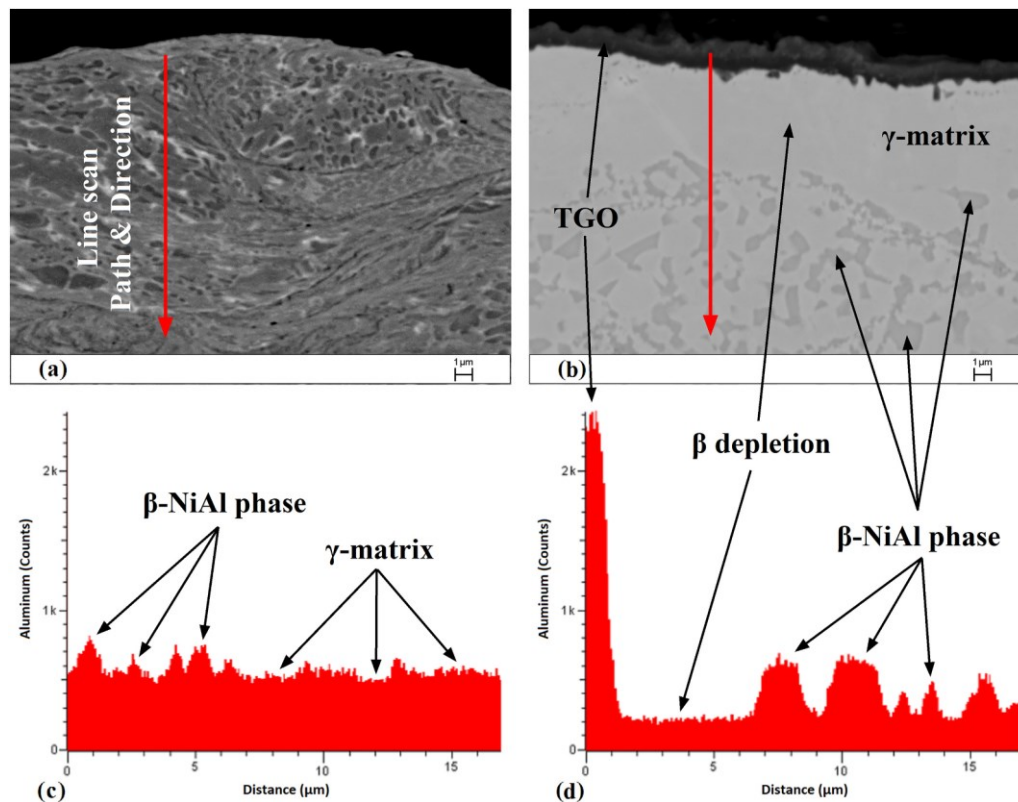


Fig. 5. Cross-section BSE images showing microstructures and EDS line scan results of the CS NiCoCrAlTaY coatings: (a, c) as-deposited condition and (b, d) after thermal exposure at 1100 °C for 1 h.

distribution profiles across the as-deposited and thermally exposed CS NiCoCrAlTaY coatings. In the as-deposited condition, Al distributed relatively uniformly with localized concentration increases associated with the β -NiAl phase (Fig. 5a and c). After 1 h oxidation at 1100 °C, three regions of different Al distribution characteristics were evident (Fig. 5b and d): (i) a surface region with a high Al concentration due to the α -Al₂O₃ scale formation; (ii) a subsurface region with a significantly

lower Al concentration as a result of the β -phase depletion; and (iii) an interior region with distinct aluminum peaks and valleys corresponding to the intermittent β and γ phases. These three regions kept developing with increasing oxidation durations, resulting in a thicker TGO scale, a larger β depletion depth, and a reduced amount of remaining β phase, as shown in Fig. 6 and Table 3. Nevertheless, internal oxides were not observed in any of the CS NiCoCrAlTaY coatings after the short-term

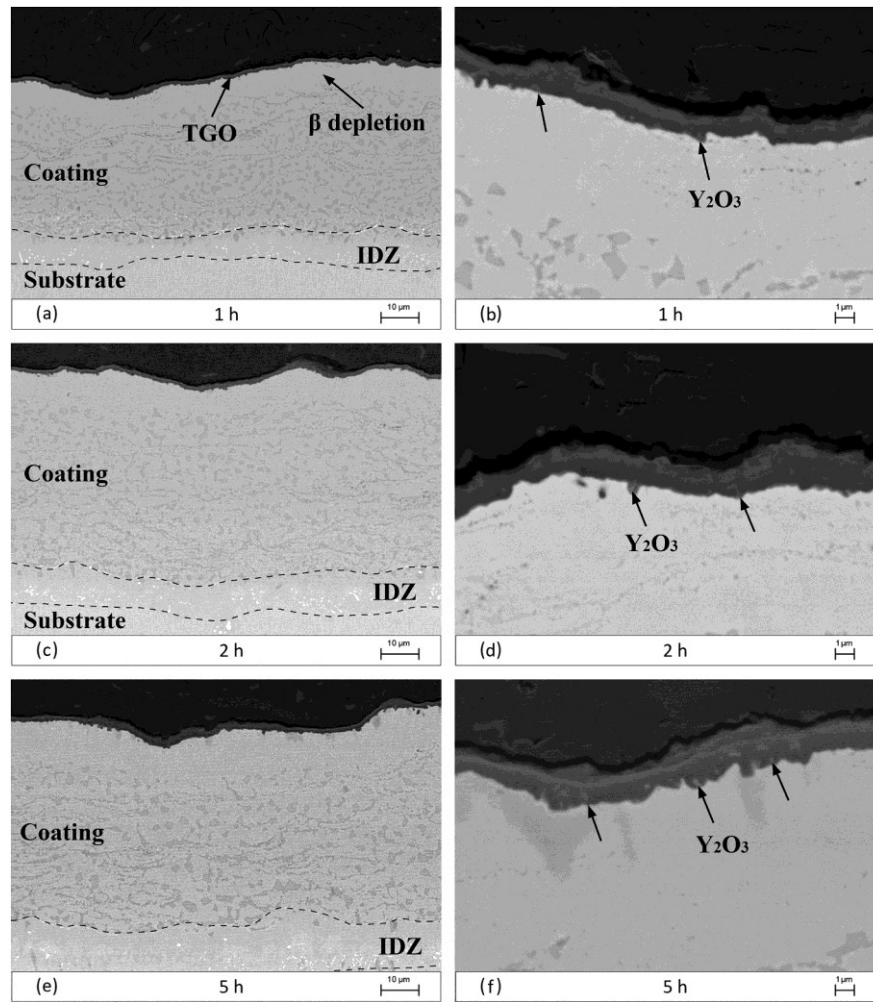


Fig. 6. Cross-section BSE images showing the formation of TGO scale, β -NiAl depletion, and inter-diffusion zone (IDZ) in CS NiCoCrAlTaY coatings after isothermal oxidation at 1100 °C for 1 h (a, b), 2 h (c, d), and 5 h (e, f). A close-up view of the scale-coating interface (b, d, f) highlights the presence of Y_2O_3 .

Table 3

TGO scale thickness, β depletion depth, and remaining β -phase content of the CS NiCoCrAlTaY coatings after 1 h, 2 h, and 5 h isothermal oxidation at 1100 °C.

Oxidation duration	TGO thickness (μm)	β Depletion depth (μm)	Remaining β phase (Area %)
1 h	1.1 ± 0.1	6.3 ± 0.4	18.1 ± 1.7
2 h	1.3 ± 0.1	7.9 ± 0.6	17.1 ± 2.1
5 h	1.6 ± 0.2	10.8 ± 0.7	15.1 ± 1.0

exposure.

Near the original coating-substrate interface, an inter-diffusion zone (IDZ) was observed (Fig. 6a and c). This is attributed to the compositional difference between the coating and the substrate (see Table 1). The CMSX-4 substrate contains refractory elements such as Ta, W, and Re, whereas the NiCoCrAlTaY coating is rich in Co, Cr, and Al. Consequently, counter-diffusion of these elements inevitably occurred during the thermal exposure at 1100 °C resulting in the IDZ. The white granular phases in the IDZ are typically referred to as the topologically close-packed (TCP) phases, which have various chemical formulae but can be generalized as A_xB_y , where A and B are transition metals [58,59]. These phases have been well characterized in single-crystal nickel-base superalloys [60,61].

Close examination of the TGO scales (Fig. 6b, d, and f) revealed the

presence of Y_2O_3 (as determined by the XRD results in Fig. 4) at the scale-coating interface. Although yttrium (Y) is generally added with a low concentration (typically 0.5–1.0 wt.%) to MCrAlY, preferential oxidation of Y has been widely reported due to its high oxygen affinity [62,63]. It has been proposed that the addition of reactive elements, such as Y, hafnium (Hf), and cerium (Ce), can promote the formation of peg-like oxides at the scale-coating interface, thus improving scale adhesion via mechanical keying effect (or pegging effect) [64,65]. The Y_2O_3 shapes observed at the interface in Fig. 6 conform to this pegging theory and hence are expected to benefit the scale adhesion.

3.1.3. Prolonged oxidation

To evaluate the long-term oxidation behavior of the CS NiCoCrAlTaY coatings after the early oxidation stages, prolonged isothermal oxidation tests were carried out at 1100 °C for 25 h, 50 h, 100 h, and 500 h. Fig. 7 shows an overview of the NiCoCrAlTaY coatings that underwent different oxidation durations.

The coating microstructures and TGO characteristics continually evolved as the oxidation duration extended. Specifically, the TGO scale further grew, the β depletion zone deepens accompanying the reduced presence of the β phase, and the IDZ developed but became less distinct. The fact that the β phase is no longer observed after 100 h isothermal oxidation (Fig. 7c) implies that it could have been completely depleted between 50 h and 100 h exposure at 1100 °C. Thereafter, the β -depleted

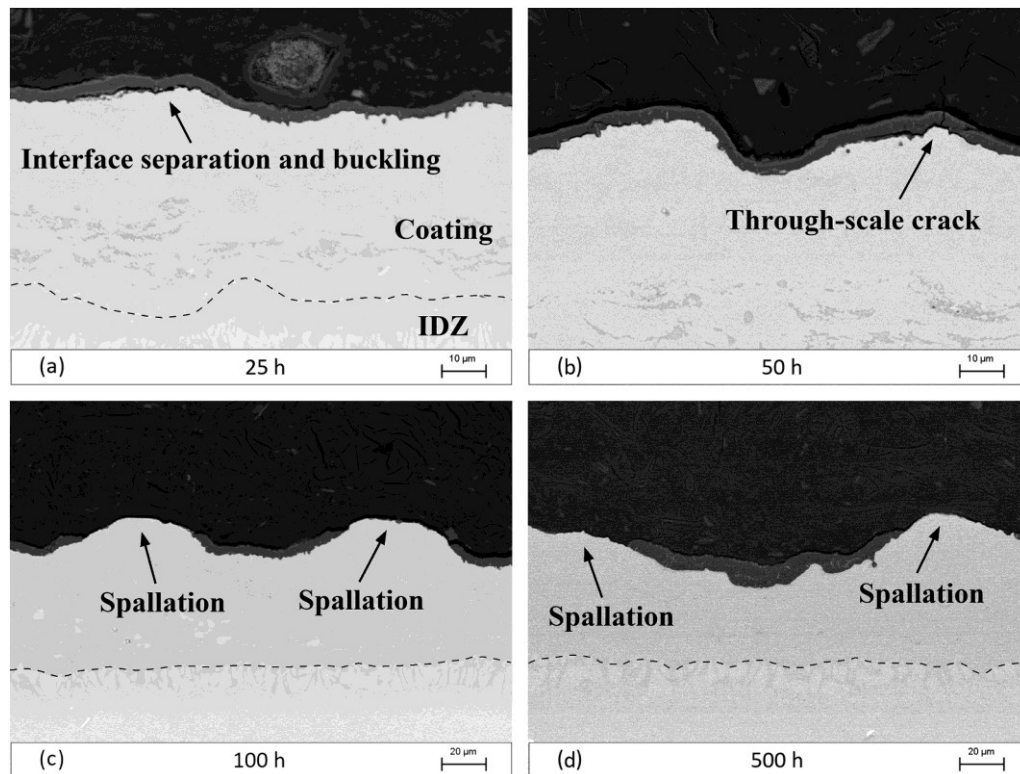


Fig. 7. Overview of CS NiCoCrAlTaY coatings and TGO scales after isothermal oxidation at 1100 °C for 25 h (a), 50 h (b), 100 h (c), and 500 h (d). Arrows indicate local scale failures, such as separation, buckling, crack, and spallation. The dashed lines approximate the interface between the coating and inter-diffusion zone (IDZ).

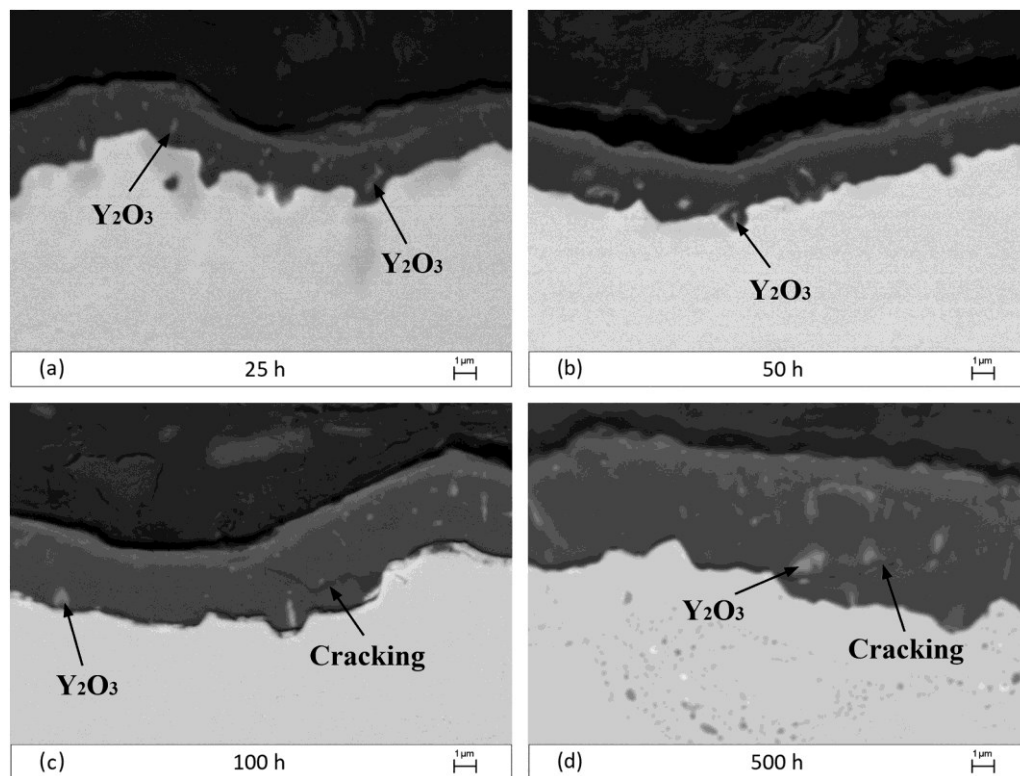


Fig. 8. Close-up BSE images of TGO scales after prolonged isothermal oxidation at 1100 °C for 25 h (a), 50 h (b), 100 h (c), and 500 h (d). Arrows indicate the Y₂O₃ pegs at the interface as well as the presence of Y₂O₃ particles and cracks in the TGO scales.

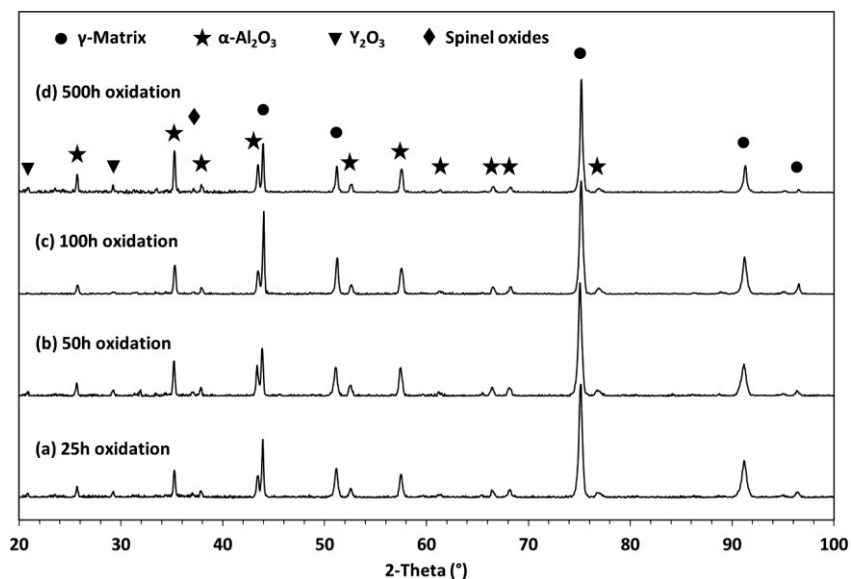


Fig. 9. XRD Spectra of the NiCoCrAlTaY coatings after 25 h, 50 h, 100 h, and 500 h isothermal oxidation at 1100 °C.

coating microstructure did not significantly change even after 500 h oxidation (Fig. 7d). No internal oxides were found in the CS NiCoCrAlTaY coatings throughout the prolonged oxidation tests.

Fig. 7 also shows localized TGO scale failures, such as interface separation, buckling, through-scale cracks, and scale spallation. Scale failures resulting from isothermal oxidation are generally not as severe as those observed after thermal cycling. In the present study, however, the test samples were directly cooled in air from 1100 °C to ambient temperature. The fast cooling rates induced significant thermal stresses in the TGO scale due to the large CTE mismatch between the scale and the coatings. The scale thickness also plays a critical role in the stress level and distribution [66,67]. Due to smaller scale thicknesses and hence lower scale stresses, scale failures did not occur after the short-term exposure (Fig. 6). Once the TGO scale grows beyond a certain critical value, increased thermal and TGO growth stresses would inevitably cause scale failures [68], as observed in Fig. 7. A slower cooling rate (e.g., furnace cooling) may allow for better stress accommodation and thus ease the local scale failures upon temperature drop. However, it would extend the oxidation duration, resulting in an inaccurate estimation of TGO growth kinetics, particularly for short-term exposure.

It is interesting to observe that the TGO scales primarily failed in the convex regions of the undulated scale-coating interface. This may be attributed to the geometry-dependent stress distribution along the interface. When a TGO scale is in compression, tensile stresses normal to the interface can develop at the undulation peaks [67,69,70]. This renders the convex scale regions more susceptible to local failures compared to the concave regions, where compressive stresses normal to the interface prevail. The observed scale failures also imply a failure mechanism involving the following sequence: (i) interface separation at locations of imperfections under out-of-plane normal tensile stresses; (ii) buckling upon sufficient interface separation; (iii) initiation and propagation of through-scale cracks at pre-existing defects within the scale; and (iv) scale spallation. This type of failure sequence agrees with the buckle-driven failure mechanism and is the result of a mechanically strong TGO scale with relatively weak adhesion [11,20,69]. To prevent the early scale separation that leads to subsequent scale buckling and spallation, it is necessary to achieve strong interfacial bonding by minimizing the interface defects to avoid localized stress concentration. It is also desirable to have a less undulated interface to reduce the out-of-plane tensile stress [71], and to minimize the TGO growth kinetics such that a relatively low stress magnitude is maintained in the scale [67].

These TGO characteristics may alleviate, postpone, or avoid premature scale failures.

The local scale failures should not affect the characteristics of the remaining TGO segments, as they occurred during the out-of-furnace air cooling period after the isothermal oxidation tests. Therefore, the TGO phase constituents, microstructure, and growth kinetics can still be examined from the scale remnants. Fig. 8 shows a close-up view of the TGO scales after prolonged isothermal oxidation.

Compared to short-term oxidation (Fig. 6), the TGO scale grew significantly over long-term thermal exposure, yet its microstructure remained similar, featuring α -Al₂O₃ and minor Y₂O₃ particles. However, the Y₂O₃ particles, as well as the pegs developed from them, became more apparent at the scale-coating interface. Besides, Y₂O₃ particles were also observed inside the TGO scales, suggesting that yttrium has diffused into the scale. The large yttrium cations, when segregating to scale grain boundaries with a sufficient concentration, are believed to suppress the outward transport of aluminum cations and consequently change the scale growth mechanism to predominantly inward diffusion of oxygen anions [72,73]. This mechanism change can significantly reduce the scale growth kinetics [72]. However, the presence of Y₂O₃ particles in the scale may also pose a potential risk to TGO integrity due to stress concentration at sites where Y₂O₃ particles reside and changes in local scale plasticity. This may result in crack initiation and propagation, facilitating through-scale cracking (Fig. 8c and d) and eventually leading to TGO spallation.

Fig. 9 shows the XRD results of the CS NiCoCrAlTaY coatings after 25 h to 500 h oxidation.

The diffraction patterns of the coatings are similar to those after the short-term oxidation (Fig. 4) and almost identical to each other after the long-term oxidation. This implies that the TGO scale did not experience major phase changes during thermal exposure of 25 h to 500 h at 1100 °C. A tiny diffraction peak that may originate from spinel oxides, (Ni, Co)(Al, Cr)₂O₄, is also indicated in the XRD spectra (labeled with a diamond symbol). However, the low peak intensity, lack of other diffraction peaks, and the fact that they were not observed from the cross-section images even after 500 h oxidation at 1100 °C (Figs. 7 and 8), suggest that the spinel oxides (if they were formed) must be localized and not typical in the TGO scales.

These observations are different from the oxidation behavior of similar MCrAlY coatings reported in the literature. Mixed and spinel oxides were reported by Ajdelsztajn et al. [74] and Tang, et al. [75] for

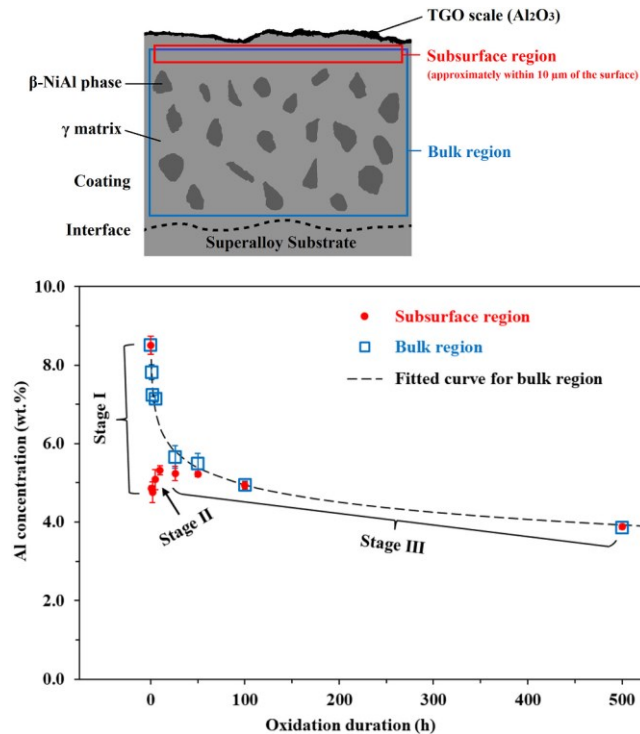


Fig. 10. Evolution of Al concentrations in the coating subsurface and bulk regions. Data points for the two regions overlap at 0 h (as-deposited CS coatings), 100 h, and 500 h. Three distinct stages are indicated on the subsurface Al concentration profile.

HVOF NiCrAlY and CoNiCrAlY coatings that were produced from cryomilled powders and oxidized for 95 h and 330 h at 1000 °C, respectively. Chen, et al. [45] investigated the oxidation behavior of three TBCs with CoNiCrAlY bond coats produced by CS, HVOF, and air plasma spray (APS). The durability of the TBCs with CS and HVOF CoNiCrAlY coatings was substantially improved over their APS counterparts during thermal cycling tests at 1050 °C in air [45]. However, chromium oxide, spinel, and nickel oxide (CSN) were found in all three TBCs after 100 h thermal exposure (or 1 cycle in their study) [45]. Similar findings were also obtained by Doleker and Karaoglanli [43] that the TBC with a CS CoNiCrAlY bond coat significantly outperformed the TBCs with either an untreated or a shot-peened APS bond coat. While the untreated and shot-peened APS CoNiCrAlY bond coats showed mixed oxides as early as 8 h under isothermal oxidation condition at 1100 °C, the CS CoNiCrAlY bond coat postponed the formation of mixed oxides to 50 h or 100 h exposure [43]. In contrast, these undesirable mixed oxides were not observed in the current isothermal oxidation study at 1100 °C for up to 500 h. This suggests that the present CS NiCoCrAlTaY coatings could offer improved oxidation performance.

It is worth noting that the CS CoNiCrAlY coatings in Doleker and Karaoglanli [43] and Chen, et al. [45] were produced using helium (600 °C, 3 MPa) and nitrogen with relatively high spray parameters (700 °C, 4 MPa), respectively. These spray conditions likely resulted in high deposition efficiency due to elevated particle impact velocities, but inconsistent particle deformation throughout the CS coatings given the lack of particle impingements. In the present study, nitrogen and reduced sprayed parameters (500 °C, 3.45 MPa) were used to achieve extensive particle deformation utilizing low deposition efficiency and enhanced particle impingements (see Part I of the study [49]). The as-deposited CS NiCoCrAlTaY coatings were characterized by dense microstructure, nanoscale grains, and a large number of crystallographic defects such as grain boundaries and dislocations. These microstructural characteristics contributed to the desirable oxidation behavior of the

present CS NiCoCrAlTaY coatings, as demonstrated in the next section.

3.2. Aluminum concentration evolution

The formation of non-Al₂O₃ oxides on MCrAlY coatings after prolonged thermal exposure is generally associated with severe local Al depletion in the coating subsurface region. The results presented in the previous sections show that such a situation did not occur in the CS NiCoCrAlTaY coatings studied. This can also be seen from Fig. 10, which shows the Al concentrations in the coating subsurface and bulk regions as a function of oxidation time.

The subsurface Al concentration remained above 3.9 wt.% for all oxidation durations. This value is higher than the critical Al level of 2.5–3 wt.% required for preferential Al oxidation [71,76,77]. The readily available Al in the coating subsurface region, as well as the absence of internal oxidation, promoted the establishment and growth of a continuous α -Al₂O₃ TGO scale and prevented the formation of undesirable mixed or spinel oxides during the isothermal oxidation at 1100 °C for up to 500 h.

Furthermore, Fig. 10 shows how the Al concentration evolved in the coating subsurface region with respect to that in the bulk region. The Al content in the bulk region monotonically decreased with increasing oxidation duration. This can be attributed to the continuous α -Al₂O₃ scale growth on the coating surface as well as the inter-diffusion between the CS coatings and the superalloy substrate, both of which consumed Al from the coating. In contrast, the subsurface Al concentration profile was characterized by three distinct stages: a sharp drop within the first 2 h oxidation (stage I), a steady increase from 2 h to 10 h oxidation (stage II), and a gradual decrease over the extended oxidation duration (stage III).

In the first stage, the subsurface Al level decreased from 8.5 ± 0.2 wt.% in the as-deposited CS coatings to 4.8 ± 0.3 wt.% in the coatings after 2 h oxidation at 1100 °C. This sharp decrease in Al concentration within a relatively short time frame (2 h) reflects a significant Al consumption attributed to the early establishment of the α -Al₂O₃ TGO scale, as shown in Figs. 5 and 6. This also implies that the rate at which Al was consumed was considerably higher than the rate at which Al was supplied to the coating subsurface region. Once a dense, continuous α -Al₂O₃ TGO scale forms, subsequent scale growth generally follows the parabolic law characterized by a decreasing growth/Al consumption rate with increasing time [78]. This decrease in Al consumption rate is obvious when comparing the relative changes of Al concentration in the coating subsurface region after the 1 h and 2 h oxidation tests. The Al level was reduced from 8.5 ± 0.2 wt.% to 4.9 ± 0.1 wt.%, a decrease of approximately 42%, after the first hour, whereas it was barely changed after another hour of oxidation, from 4.9 ± 0.1 wt.% to 4.8 ± 0.3 wt.%. It is worth noting that the decrease of α -Al₂O₃ TGO growth rate, as well as associated Al consumption rate in the coating subsurface region, is a continuous rather than a discrete process: if the oxidation tests and coating analyses were performed at a shorter interval, a more gradual Al concentration decrease would be observed. As the oxidation proceeds, it is possible that at some point the Al consumption rate may reduce to a level that is equal to or even lower than the Al supply rate from the coating bulk region. This would allow for Al replenishment to the coating subsurface region, enabling the rise of Al concentration as observed between 2 h and 10 h oxidation (stage II) in Fig. 10. In this stage, the large Al concentration difference between the coating subsurface and bulk regions (Fig. 10) provided a strong driving force for Al diffusion from the bulk to the subsurface. This may be assisted by the coating microstructure promoting Al diffusion kinetics. The rapid Al replenishment, plus the reduced α -Al₂O₃ scale growth rate, resulted in the Al concentration rise in the coating subsurface region. However, the narrowed Al concentration difference between these two regions beyond 10 h oxidation lowered the driving force for Al diffusion, and grain growth in the coatings with longer thermal exposure also reduced Al diffusion kinetics. These factors, combined with continuing Al

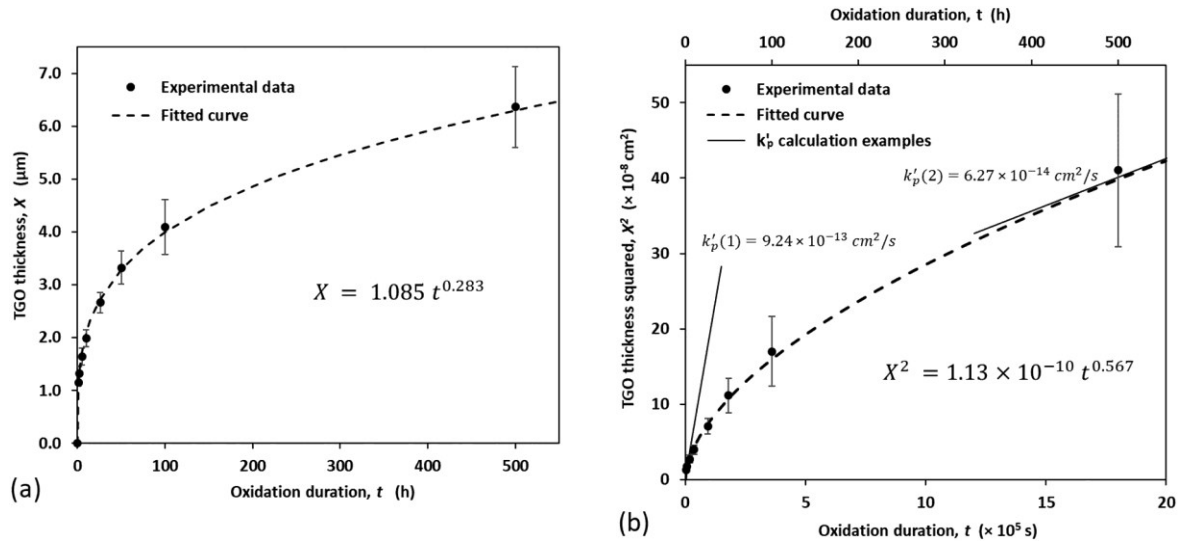


Fig. 11. TGO growth kinetics on the CS NiCoCrAlTaY coatings under isothermal oxidation at 1100 °C: (a) TGO thickness as a function of oxidation duration, and (b) plotting of squared TGO thickness vs. oxidation duration. Two instantaneous rate constants, $k_p'(i)$, were calculated at 3.6×10^3 s (1 h) and 1.8×10^6 s (500 h) to show its general magnitude and variation.

consumption through α -Al₂O₃ scale growth, led to decreasing Al level in the coating subsurface region as shown in Fig. 10, stage III. Nevertheless, the coating subsurface region was able to maintain the same Al concentration as that of the bulk region after prolonged oxidation for 100 h to 500 h. This suggests that sufficient Al diffusion occurred during the isothermal oxidation at 1100 °C, which prevented severe local Al depletion that would result in the formation of mixed or spinel oxides.

The results shown in Fig. 10 illustrate an important point about promoting the α -Al₂O₃ TGO scale on MCrAlY coatings: not only the Al content in the bulk region has a strong influence, but the ability to deliver Al to the coating surface can be equally crucial. The fast Al replenishment to the coating subsurface region observed in the present study can be attributed to the microstructural characteristics of the CS NiCoCrAlTaY coatings. Considering the contribution from grain boundaries, the diffusion of Al in the coatings can be assessed by examining an effective diffusion coefficient (D_{eff}) [34,73,79],

$$D_{eff} = D_L + \frac{2\delta}{d} D_{gb}$$

where D_L and D_{gb} are the lattice and grain-boundary diffusion coefficients for Al, respectively, δ is the grain boundary width, and d is the grain size. Since D_{gb} is typically several orders of magnitude higher than D_L [80,81], and δ is commonly assumed as 1 nm [34,73], the presence of nanoscale grains (or a greatly reduced d value) in the CS NiCoCrAlTaY coatings therefore increases the $2\delta/d$ ratio leading to a larger D_{eff} . In addition, dislocation diffusion may also play a significant part in increasing the D_{eff} . Typically, this contribution from dislocations is neglected due to low dislocation density [73,75]. However, the CS coating process, particularly under the studied spray conditions, involves repeated particle impacts, deposition, and impingements. This induces extensive plastic deformation resulting in numerous dislocation creation and accumulation [82]. As such, the dislocation density can be substantially higher in the CS NiCoCrAlTaY coatings, and the dislocation diffusion contribution could be significant [83]. These enhancements to Al diffusion in the CS NiCoCrAlTaY coatings may explain the desirable Al concentration evolution in the coating subsurface region (see Fig. 10), which helps maintain an adequate subsurface Al concentration to sustain the continuous α -Al₂O₃ scale growth.

3.3. TGO growth kinetics

In addition to promoting Al diffusion in the coating, the microstructural characteristics of the CS NiCoCrAlTaY coatings also have an impact on the TGO growth kinetics during the isothermal oxidation. Fig. 11 shows the evolution of TGO thickness with increasing oxidation duration at 1100 °C.

The growth of the TGO scale at 1100 °C was found to follow the power-law:

$$X = 1.085 t^{0.283}$$

where X is the TGO thickness (in μm) and t is the oxidation duration (in hour). With the exponent (0.283) being different from 0.5, the power-law TGO growth kinetics represents a deviation from the parabolic oxidation behavior, i.e., $X \propto t^{0.5}$ or $X^2 = 2 k_p' t$, where k_p' is the parabolic oxidation rate constant.

The oxidation rate constant (k) is an important parameter that allows for comparing oxidation performance among different coating systems and test conditions. A smaller k represents a slower rate of oxidation and metal consumption, and thus a better oxidation performance [10]. For metals and alloys that follow parabolic oxidation, a linear relationship exists when the squared TGO thickness or sample weight gain is plotted as a function of oxidation duration. The parabolic oxidation rate constant, i.e., k_p' for squared TGO thickness (cm^2/s) or k_p'' for squared sample weight gain ($\text{g}^2 \text{cm}^{-4} \text{s}^{-1}$), can then be determined from the slope of the straight line [10]. For TGO growth kinetics that is not perfectly parabolic, the squared TGO thickness or sample weight gain is, conventionally, also plotted against oxidation time to enable meaningful comparisons. In such a case, the curve is not linear and an instantaneous oxidation rate constant can be defined by the tangent to the curve at a specific oxidation duration as follows [84]:

$$k_p'(i) = \frac{1}{2} \left[\frac{d(X^2)}{dt} \right]_{t_i}$$

where $k_p'(i)$ is the instantaneous rate constant at oxidation duration t_i .

Fig. 11b is a replot of Fig. 11a using squared TGO thickness vs. oxidation time. The fitted curve then follows the power law:

$$X^2 = 1.13 \times 10^{-10} t^{0.567}$$

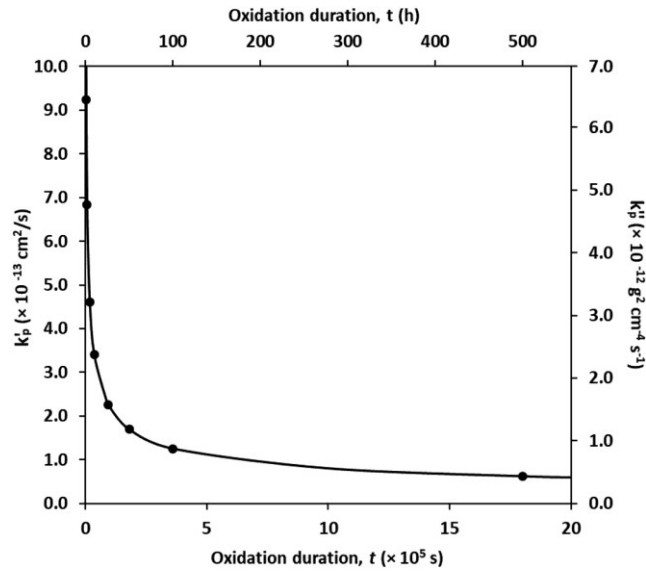


Fig. 12. The change of instantaneous rate constants with oxidation duration for the CS NiCoCrAlTaY coatings during isothermal oxidation at 1100 °C.

where X is the TGO thickness (in μm) and t is the oxidation duration (in s). Given the non-linear nature of the fitted curve, the instantaneous rate constant, $k_p'(t)$, as defined above, varies at different oxidation durations. Fig. 12 presents the relationship between $k_p'(t)$ and oxidation duration. To better compare with the data published in the literature, $k_p'(t)$ was converted to $k_p''(t)$ using the following Eq. [10] with assumptions that the TGO scale was free of pores and cavities and consisted of only Al_2O_3 :

$$k_p' = 2f^2 k_p''$$

where f is a factor that can be approximated by the product of the Al_2O_3 density (3.97 g/cm^3) and the mass ratio of oxygen in Al_2O_3 (0.47). A f value of 1.866 was used for the calculation, and the results are also presented in Fig. 12.

The instantaneous rate constants decreased rapidly during the early stages of oxidation exposure, followed by a more gradual decrease during prolonged oxidation. This phenomenon may be linked to the microstructural evolution of the TGO scale developed on the coating. It is generally observed that oxide scales growing on metals have rather

fine grain sizes [78]. When a nanocrystalline coating is present, the TGO scale initially formed is also comprised of nanosized grains [33,51]. Similar to the coatings, the presence of nanosized grains in the scale can significantly promote the diffusion of oxidation reactants via scale grain boundaries, thus contributing to a high TGO growth kinetics during the early stages of oxidation. As grain growth occurs with time at high temperatures, the density of grain boundaries in the scale decreases, leading to a reduced contribution of grain-boundary diffusion and thus a decreasing k_p . Another possible mechanism is that the initial high k_p could result from the formation of transient Al_2O_3 with fast growth rates at the very beginning of thermal exposure. The transient Al oxides then quickly transformed into the stable $\alpha\text{-Al}_2\text{O}_3$, which has a much lower and decreasing growth rate during subsequent short-term oxidation (1 h to 5 h). This phase transformation would be facilitated by the nanostructure of the CS NiCoCrAlTaY coatings, as suggested for nanocrystalline CoNiCrAlY coatings produced using cryomilled powder and HVOF [37].

The instantaneous rate constants, $k_p'(t)$ and $k_p''(t)$, calculated at 1 h and 500 h oxidation durations are given in Table 4 along with parabolic rate constants from the literature.

It is found that the rate constant calculated at 1 h for the present CS NiCoCrAlTaY coatings ($9.24 \times 10^{-13} \text{ cm}^2/\text{s}$ or $6.44 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$) is in the range of the rate constant values reported in previous studies [86,89–92]. However, the rate constant determined at 500 h oxidation duration ($6.27 \times 10^{-14} \text{ cm}^2/\text{s}$ or $4.36 \times 10^{-13} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$) is at least one order of magnitude lower than those of thermal sprayed MCrAlY coatings [22,88–91], and comparable to those for EB-PVD MCrAlY coatings [86,87], diffusion nickel aluminide, and Pt-modified aluminide coatings [85]. It should be pointed out that these comparisons are for general reference only. Many factors, such as testing temperature, coating composition, coating microstructure resulting from different manufacturing processes, and post-deposition treatments may all play a role in the TGO growth kinetics. Nevertheless, the relatively low TGO growth kinetics observed in the current study suggests that the $\alpha\text{-Al}_2\text{O}_3$ scale formed on the CS NiCoCrAlTaY coatings was sustained during the long-term isothermal exposure at 1100 °C. The dense coating microstructure, low surface roughness, and nanoscale grains could all contributed to the suppression of mixed and spinel oxides forming in the TGO scale.

4. Conclusions

The processing-structure-properties-performance relationship of

Table 4

Summary of parabolic rate constants for TGO growth on MCrAlY coatings prepared by different manufacturing processes.

Author	Temp. (°C)	Material	Processing		$k_p' (\text{cm}^2/\text{s})$	$k_p'' (\text{g}^2 \text{ cm}^{-4} \text{ s}^{-1})$
Present study	1100	NiCoCrAlTaY	Cold spray	Calculated at 1 h	9.24×10^{-13}	6.44×10^{-12}
				Calculated at 500 h	6.27×10^{-14}	4.36×10^{-13}
Reed [85]	1100	Aluminide	Aluminizing			4.67×10^{-13}
		Pt-modified aluminide	Electroplating + aluminizing			$1.4\text{--}2.9 \times 10^{-13}$
Peng [86]	1100	NiCoCrAlY	EB-PVD			2.9×10^{-12}
			PA-EB-PVD			8.0×10^{-13}
Hesnawi [87]	1100	NiCoCrAlY	EB-PVD + polished			1.23×10^{-13}
			EB-PVD + shot-peened			0.26×10^{-13}
Saeidi [88]	1100	CoNiCrAlY	VPS			5×10^{-10}
			HVOF			3×10^{-10}
Brandl [22]	1050	CoNiCrAlY	VPS			4.11×10^{-10}
		NiCoCrAlY	VPS			3.74×10^{-10}
Ni [89]	1050	NiCrAlY	HVOF			4.98×10^{-12}
			HVOF + ground			2.29×10^{-12}
			HVOF + shot-peened			3.09×10^{-12}
Mercier [90]	1050	CoNiCrAlY	Cryomilled + HVOF			4.97×10^{-12}
			Cryomilled + HVOF + ground			1.28×10^{-12}
Kaplin [91]	1050	NiCoCrAlY	SPS + ground			5.18×10^{-12}
			Cryomilled + SPS + ground			4.85×10^{-12}
Richer [92]	1000	CoNiCrAlY	Cold spray		1.9×10^{-13}	
			HVOF		1.3×10^{-13}	

cold spray NiCoCrAlTaY coatings deposited on CMSX-4 single crystal Ni-base superalloy was investigated in this study. Nitrogen was used as the CS process gas, and low spray parameters were employed for the coating deposition. The feedstock powder was found to be extensively deformed, leading to NiCoCrAlTaY coatings characterized by dense microstructure, low surface roughness, nanoscale grains, and enhanced crystallographic defects such as grain boundaries and dislocations. Short-term (1, 2, and 5 h) and prolonged (10, 25, 50, 100, and 500 h) isothermal oxidation tests were performed in air at 1100 °C. The microstructural evolution, compositional change, and TGO growth kinetics as a function of oxidation time were analyzed.

After the short-term oxidation, a continuous α -Al₂O₃ TGO scale with a small amount of Y₂O₃ particles and pegs was established on the coating surface. Al consumption by the TGO resulted in a β phase depletion zone in the coating underneath the scale, which widened with increasing oxidation time and TGO thickness. During prolonged oxidation from 25 h to 500 h, the TGO scale continued to thicken and experienced localized separation, buckling, cracking, and spallation, attributed to the high cooling rates outside the furnace. While the Al-rich β phase in the coating was completely depleted between 50 h and 100 h oxidation, the Al concentration in the coating subsurface region evolved through three stages and remained above 3.9 wt.% up to 500 h and hence sustained the α -Al₂O₃ scale during the prolonged oxidation. The TGO growth kinetics deviated from the parabolic rate law. The instantaneous rate constants decreased rapidly during the short-term oxidation, followed by a gradual decrease during the prolonged oxidation. The beneficial Al concentration evolution in the coating subsurface region and the relatively low TGO growth kinetics found in the study can be attributed to the microstructural characteristics of the CS NiCoCrAlTaY coatings and is desirable for effective oxidation protection of gas turbine components.

CRedit authorship contribution statement

Deliang Guo: Conceptualization, Investigation, Formal analysis, Visualization, Writing - original draft. **Linruo Zhao:** Resources, Methodology, Writing - review & editing. **Bertrand Jodoin:** Conceptualization, Resources, Methodology, Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to acknowledge the discovery grant program from Natural Sciences and Engineering Research Council (NSERC), Canada for its financial support.

References

- [1] R.C. Reed, *The Superalloys: Fundamentals and Applications*, Cambridge University Press, New York, 2006.
- [2] R.W. Broomfield, D.A. Ford, J.K. Bhangu, M.C. Thomas, D.J. Frasier, P. S. Burkholder, K. Harris, G.L. Erickson, J.B. Wahl, Development and turbine engine performance of three advanced rhenium containing superalloys for single crystal and directionally solidified blades and vanes, *J. Eng. Gas Turbines Power* 120 (1998) 595–608.
- [3] P. Caron, T. Khan, Evolution of Ni-based Superalloys for single crystal gas turbine blade applications, *Aerosp. Sci. Technol.* 3 (1999) 513–523, [https://doi.org/10.1016/S1270-9638\(99\)00108-X](https://doi.org/10.1016/S1270-9638(99)00108-X).
- [4] T.E. Strangman, Thermal barrier coatings for turbine airfoils, *Thin Solid Films* 127 (1985) 93–105.
- [5] K.D. Sheffler, D.K. Gupta, Current status and future trends in turbine application of thermal barrier coatings, *J. Eng. Gas Turbines Power* 110 (1988) 605–609.
- [6] N.P. Padture, M. Gell, E.H. Jordan, Thermal barrier coatings for gas-turbine engine applications, *Science* 296 (2002) 280–284, <https://doi.org/10.1126/science.1068609>.
- [7] R.A. Miller, Thermal barrier coatings for aircraft engines: history and directions, *J. Therm. Spray Technol.* 6 (1997) 35–42.
- [8] R. Vaßen, M.O. Jarligo, T. Steinke, D.E. Mack, D. Stover, Overview on advanced thermal barrier coatings, *Surf. Coat. Technol.* 205 (2010) 938–942.
- [9] D.R. Clarke, M. Oechsner, N.P. Padture, Thermal-barrier coatings for more efficient gas-turbine engines, *MRS Bull.* 37 (2012) 891–902.
- [10] M. Schütze, Fundamentals of high temperature corrosion, in: R.W. Cahn, P. Haasen, E.J. Kramer (Eds.), *Materials Science and Technology: A Comprehensive Treatment: Corrosion and Environmental Degradation*, Wiley, Onlien, 2000, pp. 67–130.
- [11] P.K. Wright, A.G. Evans, Mechanisms governing the performance of thermal barrier coatings, *Curr Opin Solid St M* 4 (1999) 255–265.
- [12] A.G. Evans, D.R. Mumm, J.W. Hutchinson, G.H. Meier, F.S. Pettit, Mechanisms controlling the durability of thermal barrier coatings, *Prog. Mater. Sci.* 46 (2001) 505–553.
- [13] D.R. Clarke, C.G. Levi, Materials design for the next generation thermal barrier coatings, *Annu. Rev. Mater. Res.* 33 (2003) 383–417, <https://doi.org/10.1146/annurev.matsci.33.011403.113718>.
- [14] D. Naumenko, V. Shemet, L. Singheiser, W.J. Quadackers, Failure mechanisms of thermal barrier coatings on MCrAlY-type bondcoats associated with the formation of the thermally grown oxide, *J. Mater. Sci.* 44 (2009) 1687–1703.
- [15] L.Y. Ni, C.G. Zhou, Effects of surface modification on thermal cycling lifetime of thermal barrier coatings with HVOF NiCrAlY bond coat, *Prog. Nat. Sci.* 22 (2012) 237–243.
- [16] J.L. Smialek, N.S. Jacobson, Oxidation of high temperature aerospace materials, in: Y. Bar-Cohen (Ed.), *High Temperature Materials and Mechanisms*, CRC Press, Boca Raton, 2014, pp. 95–154.
- [17] L. Ajdelsztajn, F. Tang, G.E. Kim, V. Provenzano, J.M. Schoenung, Synthesis and oxidation behavior of nanocrystalline MCrAlY bond coatings, *J. Therm. Spray Technol.* 14 (2005) 23–30.
- [18] W.R. Chen, X. Wu, B.R. Marple, D.R. Nagy, P.C. Patnaik, TGO growth behaviour in TBCs with APS and HVOF bond coats, *Surf. Coat. Technol.* 202 (2008) 2677–2683, <https://doi.org/10.1016/j.surfcoat.2007.09.042>.
- [19] M. Schütze, Failure of oxide scales on advanced materials due to the presence of stresses, in: *High Temperature Corrosion of Advanced Materials and Protective Coatings*, 1992, pp. 39–49.
- [20] H.E. Evans, R.C. Lobb, Conditions for the initiation of oxide scale cracking and spallation, *Corros. Sci.* 24 (1984) 209–222, [https://doi.org/10.1016/0010-938x\(84\)90051-9](https://doi.org/10.1016/0010-938x(84)90051-9).
- [21] M.M. Nagl, W.T. Evans, The mechanical failure of oxide scales under tensile or compressive load, *J. Mater. Sci.* 28 (1993) 6247–6260, <https://doi.org/10.1007/BF01352181>.
- [22] W. Brandl, H.J. Grabke, D. Toma, J. Kruger, The oxidation behaviour of sprayed MCrAlY coatings, *Surf. Coat. Technol.* 86 (1996) 41–47, [https://doi.org/10.1016/S0257-8972\(96\)03039-3](https://doi.org/10.1016/S0257-8972(96)03039-3).
- [23] D. Seo, K. Ogawa, Y. Suzuki, K. Ichimura, T. Shoji, S. Murata, Comparative study on oxidation behavior of selected MCrAlY coatings by elemental concentration profile analysis, *Appl. Surf. Sci.* 255 (2008) 2581–2590, <https://doi.org/10.1016/j.apsusc.2008.07.141>.
- [24] N. Vialas, D. Monceau, Substrate effect on the high-temperature oxidation behavior of a Pt-modified aluminide coating. Part I: influence of the initial chemical composition of the coating surface, *Oxid. Met.* 66 (2006) 155–189, <https://doi.org/10.1007/s11085-006-9024-z>.
- [25] F. Tang, L. Ajdelsztajn, G.E. Kim, V. Provenzano, J.M. Schoenung, Effects of surface oxidation during HVOF processing on the primary stage oxidation of a CoNiCrAlY coating, *Surf. Coat. Technol.* 185 (2004) 228–233, <https://doi.org/10.1016/j.surfcoat.2003.11.020>.
- [26] M. Shibata, S. Kuroda, H. Murakami, M. Ode, M. Watanabe, Y. Sakamoto, Comparison of microstructure and oxidation behavior of CoNiCrAlY bond coatings prepared by different thermal spray processes, *Mater. Trans.* 47 (2006) 1638–1642, <https://doi.org/10.2320/matertrans.47.1638>.
- [27] A. Fossati, M. Di Ferdinando, A. Lavacchi, U. Bardi, C. Giolli, A. Scrivani, Improvement of the isothermal oxidation resistance of CoNiCrAlY coating sprayed by high velocity oxygen fuel, *Surf. Coat. Technol.* 204 (2010) 3723–3728, <https://doi.org/10.1016/j.surfcoat.2010.04.059>.
- [28] T. Mori, S. Kuroda, H. Murakami, H. Katanoda, Y. Sakamoto, S. Newman, Effects of initial oxidation on β phase depletion and oxidation of CoNiCrAlY bond coatings fabricated by warm spray and HVOF processes, *Surf. Coat. Technol.* 221 (2013) 59–69, <https://doi.org/10.1016/j.surfcoat.2013.01.028>.
- [29] A. Fossati, M. Di Ferdinando, U. Bardi, A. Scrivani, C. Giolli, Influence of surface finishing on the oxidation behaviour of VPS MCrAlY coatings, *J. Therm. Spray Technol.* 21 (2012) 314–324, <https://doi.org/10.1007/s11666-011-9705-2>.
- [30] Y. Li, C.J. Li, Q.A. Zhang, L.K. Xing, G.J. Yang, Effect of chemical compositions and surface morphologies of MCrAlY coating on its isothermal oxidation behavior, *J. Therm. Spray Technol.* 20 (2011) 121–131, <https://doi.org/10.1007/s11666-010-9590-0>.
- [31] W. Brandl, D. Toma, J. Kruger, H.J. Grabke, G. Matthaus, The oxidation behaviour of HVOF thermal-sprayed MCrAlY coatings, *Surf. Coat. Technol.* 94–95 (1997) 21–26.
- [32] E. Essuman, G.H. Meier, J. Zurek, M. Hansel, L. Singheiser, T. Norby, W. J. Quadackers, Effect of oxygen partial pressure on the oxidation behaviour of an yttria dispersion strengthened NiCr-base alloy, *J. Mater. Sci.* 43 (2008) 5591–5598, <https://doi.org/10.1007/s10853-008-2795-7>.
- [33] Z.Y. Liu, W. Gao, K. Dahm, F.H. Wang, The effect of coating grain size on the selective oxidation behaviour of Ni-Cr-Al alloy, *Scr. Mater.* 37 (1997) 1551–1558, [https://doi.org/10.1016/S1359-6462\(97\)00291-1](https://doi.org/10.1016/S1359-6462(97)00291-1).

- [34] F. Wang, The effect of nanocrystallization on the selective oxidation and adhesion of Al₂O₃ scales, *Oxid. Met.* 48 (1997) 215–224.
- [35] Z.Y. Liu, W. Gao, Oxidation behaviour of microcrystalline Ni-Cr-Al alloy coatings at 900 degrees C, *Scr. Mater.* 38 (1998) 877–885, [https://doi.org/10.1016/S1359-6462\(97\)00576-9](https://doi.org/10.1016/S1359-6462(97)00576-9).
- [36] Z.Y. Liu, W. Gao, K.L. Dahm, F.H. Wang, Oxidation behaviour of sputter-deposited Ni-Cr-Al micro-crystalline coatings, *Acta Mater.* 46 (1998) 1691–1700, [https://doi.org/10.1016/S1359-6454\(97\)00346-7](https://doi.org/10.1016/S1359-6454(97)00346-7).
- [37] D. Mercier, C. Kaplin, G. Goodall, G. Kim, M. Brochu, Parameters influencing the oxidation behavior of cryomilled CoNiCrAlY, *Surf. Coat. Technol.* 205 (2010) 2546–2553, <https://doi.org/10.1016/j.surfcoat.2010.10.008>.
- [38] Q. Zhang, C.J. Li, C.X. Li, G.J. Yang, S.C. Lui, Study of oxidation behavior of nanostructured NiCrAlY bond coatings deposited by cold spraying, *Surf. Coat. Technol.* 202 (2008) 3378–3384, <https://doi.org/10.1016/j.surfcoat.2007.12.028>.
- [39] Y. Li, C.J. Li, G.J. Yang, L.K. Xing, Thermal fatigue behavior of thermal barrier coatings with the MCrAlY bond coats by cold spraying and low-pressure plasma spraying, *Surf. Coat. Technol.* 205 (2010) 2225–2233, <https://doi.org/10.1016/j.surfcoat.2010.08.144>.
- [40] P. Richer, A. Zuniga, M. Yandouzi, B. Jodoin, CoNiCrAlY microstructural changes induced during cold gas dynamic spraying, *Surf. Coat. Technol.* 203 (2008) 364–371, <https://doi.org/10.1016/j.surfcoat.2008.09.014>.
- [41] P. Richer, M. Yandouzi, L. Beauvais, B. Jodoin, Oxidation behaviour of CoNiCrAlY bond coats produced by plasma, HVOF and cold gas dynamic spraying, *Surf. Coat. Technol.* 204 (2010) 3962–3974, <https://doi.org/10.1016/j.surfcoat.2010.03.043>.
- [42] A. Manap, A. Nakano, K. Ogawa, The protectiveness of thermally grown oxides on cold sprayed CoNiCrAlY bond coat in thermal barrier coating, *J. Therm. Spray Technol.* 21 (2012) 586–596, <https://doi.org/10.1007/s11666-012-9749-y>.
- [43] K.M. Doleker, A.C. Karaoglanli, Comparison of oxidation behavior of shot-peened plasma spray coatings with cold gas dynamic spray coatings, *Oxid. Met.* 88 (2017) 121–132, <https://doi.org/10.1007/s11085-016-9691-3>.
- [44] A.C. Karaoglanli, A. Turk, Isothermal oxidation behavior and kinetics of thermal barrier coatings produced by cold gas dynamic spray technique, *Surf. Coat. Technol.* 318 (2017) 72–81, <https://doi.org/10.1016/j.surfcoat.2016.12.021>.
- [45] W.R. Chen, E. Irissou, X. Wu, J.G. Legoux, B.R. Marple, The oxidation behavior of TBC with cold spray CoNiCrAlY bond coat, *J. Therm. Spray Technol.* 20 (2011) 132–138, <https://doi.org/10.1007/s11666-010-9601-1>.
- [46] V. Crespo, I.G. Cano, S. Dosta, J.M. Guilemany, The influence of feedstock powders on the CGS deposition efficiency of bond coats for TBCs, *J. Alloys Compd.* 622 (2015) 394–401, <https://doi.org/10.1016/j.jallcom.2014.09.216>.
- [47] A. Bonadei, T. Marrocco, Cold sprayed MCrAlY + X coating for gas turbine blades and vanes, *Surf. Coat. Technol.* 242 (2014) 200–206, <https://doi.org/10.1016/j.surfcoat.2013.08.019>.
- [48] D.L. Guo, D. MacDonald, L. Zhao, B. Jodoin, Cold spray MCrAlY coatings on single-crystal superalloy using nitrogen: properties and economics, *J. Therm. Spray Technol.* 29 (2020) 1628–1642, <https://doi.org/10.1007/s11666-020-01058-x>.
- [49] D. Guo, Y. Wang, R. Fernandez, L. Zhao, B. Jodoin, Cold spray for production of in-situ nanocrystalline MCrAlY coatings – Part I: Process analysis and microstructure characterization, *Surf. Coat. Technol.* 409 (2021), 126854, <https://doi.org/10.1016/j.surfcoat.2021.126854>.
- [50] B.C. Wilson, J.A. Hickman, G.E. Fuchs, The effect of solution heat treatment on a single-crystal Ni-based superalloy, *Jom-Us* 55 (2003) 35–40, <https://doi.org/10.1007/s11837-003-0158-z>.
- [51] Y. Chen, X. Zhao, P. Xiao, Effect of microstructure on early oxidation of MCrAlY coatings, *Acta Mater.* 159 (2018) 150–162, <https://doi.org/10.1016/j.actamat.2018.08.018>.
- [52] F. Wu, H. Murakami, A. Suzuki, Development of an iridium-tantalum modified aluminide coating as a diffusion barrier on nickel-base single crystal superalloy TMS-75, *Surf. Coat. Technol.* 168 (2003) 62–69, [https://doi.org/10.1016/S0257-8972\(03\)00009-4](https://doi.org/10.1016/S0257-8972(03)00009-4).
- [53] C. Borchers, T. Stoltenhoff, M. Hahn, M. Schulze, H. Assadi, C. Suryanarayana, F. Gartner, T. Klassen, Strain-induced phase transformation of MCrAlY, *Adv. Eng. Mater.* 17 (2015) 723–731, <https://doi.org/10.1002/adem.201400174>.
- [54] R. Prescott, M.J. Graham, The formation of aluminum-oxide scales on high-temperature alloys, *Oxid. Met.* 38 (1992) 233–254, <https://doi.org/10.1007/Bf00666913>.
- [55] P.S. Santos, H.S. Santos, S.P. Toledo, Standard transition aluminas. Electron microscopy studies, *Mater. Res.* 3 (2000) 104–114.
- [56] F.H. Stott, The oxidation of alumina-forming alloys, in: *High Temperature Corrosion and Protection of Materials* 4(251–254), 1997, pp. 19–32.
- [57] G.C. Rybicki, J.L. Smialek, Effect of the θ - α -Al₂O₃ transformation on the oxidation behavior of β -NiAl+Zr, *Oxid. Met.* 31 (1989) 275–304.
- [58] C.T. Sims, A contemporary view of nickel-base superalloys, *Jom-Us* 18 (1966) 1119–1130, <https://doi.org/10.1007/BF03378505>.
- [59] A.S. Wilson, Formation and effect of topologically close-packed phases in nickel-base superalloys, *Mater. Sci. Tech.* 33 (9) (2017) 1108–1118, <https://doi.org/10.1080/02670836.2016.1187335>.
- [60] X.P. Tan, H.U. Hong, B.G. Choi, I.S. Kim, C.Y. Jo, T. Jin, Z.Q. Hu, Characterization of topologically close-packed phases in secondary reaction zone in a coated CMSX-4 single crystal Ni-based superalloy, *J. Mater. Sci.* 48 (2013) 1085–1089, <https://doi.org/10.1007/s10853-012-6840-1>.
- [61] K. Kim, P.A. Withey, Microstructural investigation of the formation and development of topologically close-packed phases in a 3rd generation nickel-base single crystal superalloy, *Adv. Eng. Mater.* 19 (2017) 1700041, <https://doi.org/10.1002/adem.201700041>.
- [62] D. Delaunay, A.M. Huntz, Mechanisms of adherence of alumina scale developed during high-temperature oxidation of Fe-Ni-Cr-Al-Y alloys, *J. Mater. Sci.* 17 (1982) 2027–2036, <https://doi.org/10.1007/Bf00540420>.
- [63] A. Gil, V. Shemet, R. Vassen, M. Subanovic, J. Toscano, D. Naumenko, L. Singheiser, W.J. Quadakkers, Effect of surface condition on the oxidation behaviour of MCrAlY coatings, *Surf. Coat. Technol.* 201 (2006) 3824–3828, <https://doi.org/10.1016/j.surfcoat.2006.07.252>.
- [64] D.P. Whittle, J. Stringer, Improvements in high-temperature oxidation resistance by additions of reactive elements or oxide dispersions, *Philos T R Soc A* 295 (1980) 309–332.
- [65] J.G. Smeggil, Some comments on the role of yttrium in protective oxide scale adherence, *Mater. Sci. Eng.* 87 (1987) 261–265, [https://doi.org/10.1016/0025-5416\(87\)90387-9](https://doi.org/10.1016/0025-5416(87)90387-9).
- [66] R. Krishnamurthy, D. Srolovitz, Stress distributions in growing oxide films, *Acta Mater.* 51 (2003) 2171–2190.
- [67] M. Baker, J. Rosler, G. Heinze, A parametric study of the stress state of thermal barrier coatings Part II: cooling stresses, *Acta Mater.* 53 (2005) 469–476, <https://doi.org/10.1016/j.actamat.2004.10.004>.
- [68] A.G. Evans, D.R. Clarke, C.G. Levi, The influence of oxides on the performance of advanced gas turbines, *J. Eur. Ceram. Soc.* 28 (2008) 1405–1419.
- [69] M.Y. He, A.G. Evans, J.W. Hutchinson, Effects of morphology on the decohesion of compressed thin films, *Mater. Sci. Eng. A* 245 (1998) 168–181, [https://doi.org/10.1016/S0921-5093\(97\)00848-4](https://doi.org/10.1016/S0921-5093(97)00848-4).
- [70] C.H. Hsueh, J.A. Haynes, M.J. Lance, P.F. Becher, M.K. Ferber, E.R. Fuller, S. A. Langer, W.C. Carter, W.R. Cannon, Effects of interface roughness on residual stresses in thermal barrier coatings, *J. Am. Ceram. Soc.* 82 (1999) 1073–1075.
- [71] H.E. Evans, Oxidation failure of TBC systems: an assessment of mechanisms, *Surf. Coat. Technol.* 206 (2011) 1512–1521, <https://doi.org/10.1016/j.surfcoat.2011.05.053>.
- [72] B.A. Pint, Experimental observations in support of the dynamic-segregation theory to explain the reactive-element effect, *Oxid. Met.* 45 (1996) 1–37, <https://doi.org/10.1007/bf01046818>.
- [73] A. Atkinson, Wagner theory and short circuit diffusion, *Mater Sci Tech Ser* 4 (1988) 1046–1051, <https://doi.org/10.1179/mst.1988.4.12.1046>.
- [74] L. Ajdelsztajn, J.A. Picas, G.E. Kim, F.L. Bastian, J. Schoenung, V. Provenzano, Oxidation behavior of HVOF sprayed nanocrystalline NiCrAlY powder, *Mat Sci Eng A-Struct* 338 (2002) 33–43.
- [75] F. Tang, L. Ajdelsztajn, J.M. Schoenung, Influence of cryomilling on the morphology and composition of the oxide scales formed on HVOF CoNiCrAlY coatings, *Oxid. Met.* 61 (2004) 219–238.
- [76] D. Rensch, M. Schorr, M. Schütze, The role that bond coat depletion of aluminum has on the lifetime of APS-TBC under oxidizing conditions, *Mater. Corros.* 59 (2008) 547–555, <https://doi.org/10.1002/maco.200804137>.
- [77] P.M. Zhang, K. Yuan, R.L. Peng, X.H. Li, S. Johansson, Long-term oxidation of MCrAlY coatings at 1000 °C and an Al-activity based coating life criterion, *Surf. Coat. Technol.* 332 (2017) 12–21, <https://doi.org/10.1016/j.surfcoat.2017.09.086>.
- [78] N. Birks, G.H. Meier, F.S. Pettit, Mechanisms of oxidation, in: N. Birks (Ed.), *Introduction to the High Temperature Oxidation of Metals*, Cambridge University Press, Cambridge, 2006, pp. 39–74, <https://doi.org/10.1017/CBO9781139163903.005>.
- [79] H.E. Evans, A.T. Donaldson, T.C. Gilmour, Mechanisms of breakaway oxidation and application to a Chromia-forming steel, *Oxid. Met.* 52 (1999) 379–402, <https://doi.org/10.1023/A:1018855914737>.
- [80] A. Atkinson, Diffusion along grain boundaries and dislocations in oxides, alkali halides and carbides, *Solid State Ionics* 12 (1984) 309–320, [https://doi.org/10.1016/0167-2738\(84\)90160-7](https://doi.org/10.1016/0167-2738(84)90160-7).
- [81] H.-C. Yu, A.V.D. Ven, K. Thornton, Theory of grain boundary diffusion induced by the Kirkendall effect, *Appl. Phys. Lett.* 93 (2008) 091908, <https://doi.org/10.1063/1.2978161>.
- [82] Y. Zou, W. Qin, E. Irissou, J.G. Legoux, S. Yue, J.A. Szpunar, Dynamic recrystallization in the particle/particle interfacial region of cold-sprayed nickel coating: Electron backscatter diffraction characterization, *Scr. Mater.* 61 (2009) 899–902, <https://doi.org/10.1016/j.scriptamat.2009.07.020>.
- [83] E.W. Hart, On the role of dislocations in bulk diffusion, *Acta Metall. Mater.* 5 (1957) 597, [https://doi.org/10.1016/0001-6160\(57\)90127-X](https://doi.org/10.1016/0001-6160(57)90127-X).
- [84] A. Atkinson, R.I. Taylor, A.E. Hughes, A quantitative demonstration of the grain boundary diffusion mechanism for the oxidation of metals, *Philosophical Magazine A* 45 (1982) 823–833, <https://doi.org/10.1080/01418618208239905>.
- [85] R.C. Reed, R.T. Wu, M.S. Hook, C.M.F. Rae, R.G. Wing, On oxidation behaviour of platinum aluminide coated nickel based superalloy CMSX-4, *Mater Sci Tech Ser* 25 (2009) 276–286, <https://doi.org/10.1179/174328408x361481>.
- [86] H. Peng, H.B. Guo, J. He, S.K. Gong, Microscale lamellar NiCoCrAlY coating with improved oxidation resistance, *Surf. Coat. Technol.* 207 (2012) 110–116, <https://doi.org/10.1016/j.surfcoat.2012.06.034>.
- [87] A. Hesnawi, H.F. Li, Z.H. Zhou, S.K. Gong, H.B. Xu, Effect of surface condition during pre-oxidation treatment on isothermal oxidation behavior of MCrAlY bond coat prepared by EB-PVD, *Surf. Coat. Technol.* 201 (2007) 6793–6796.
- [88] S. Saeidi, K.T. Voisey, D.G. McCartney, The effect of heat treatment on the oxidation behavior of HVOF and VPS CoNiCrAlY coatings, *J. Therm. Spray Technol.* 18 (2009) 209–216, <https://doi.org/10.1007/s11666-009-9311-8>.
- [89] L.Y. Ni, Z.L. Wu, C.G. Zhou, Effects of surface modification on isothermal oxidation behavior of HVOF-sprayed NiCrAlY coatings, *Prog. Nat. Sci.* 21 (2011) 173–179.

- [90] D. Mercier, B.D. Gauntt, M. Brochu, Thermal stability and oxidation behavior of nanostructured NiCoCrAlY coatings, *Surf. Coat. Technol.* 205 (2011) 4162–4168, <https://doi.org/10.1016/j.surfcoat.2011.03.005>.
- [91] C. Kaplin, M. Brochu, The effect of grain size on the oxidation of NiCoCrAlY, *Appl. Surf. Sci.* 301 (2014) 258–263, <https://doi.org/10.1016/j.apsusc.2014.02.056>.
- [92] P. Richer, *Development of Conventional and nanocrystalline Bond Coats by Cold Gas Dynamic Spraying for Aerospace Thermal Barrier Coatings*, University of Ottawa, 2010.

Chapter 7 Processing Adjustment of Cold Spray NiCoCrAlTaY Coatings on Single-Crystal Superalloys

Previous chapters show that it is feasible to use the CS technique and nitrogen as the process gas to produce desirable and potentially cost-competitive NiCoCrAlTaY coatings on the CMSX-4 single-crystal superalloy (Chapter 5) and to achieve nanocrystalline NiCoCrAlTaY coatings with enhanced oxidation performance while using conventional powders of large grain size (Chapter 6). This chapter presents the study that explores different processing sequences of superalloy substrate heat treatments and CS deposition of the NiCoCrAlTaY coatings. As previously discussed in Section 3.5, the objectives of this study are to investigate the effect of superalloy substrate conditions on the CS coating deposition as well as the effect of processing sequences on the isothermal oxidation performance of the resulting NiCoCrAlTaY coatings.

7.1 Superalloy Heat Treatments and Cold Spray Deposition

Ni-base superalloys usually require three sequential heat treatments to develop the cuboidal γ/γ' microstructure that imparts their superior thermomechanical and creep strength at high temperatures [2, 173, 178]. A solution heat treatment (SHT) is first performed to homogenize the microstructure and to reduce any elemental segregation. This is followed by a primary ageing (PA) to develop the cuboidal γ/γ' microstructure. Finally, a secondary ageing (SA) is carried out to further promote finer γ' precipitates in the γ channel of the γ/γ' microstructure developed during the PA treatment [179]. Figure 7.1 shows the microstructures of the CMSX-4 substrates following the sequential heat treatments. Details of the heat treatment conditions are provided in Table 4.3.

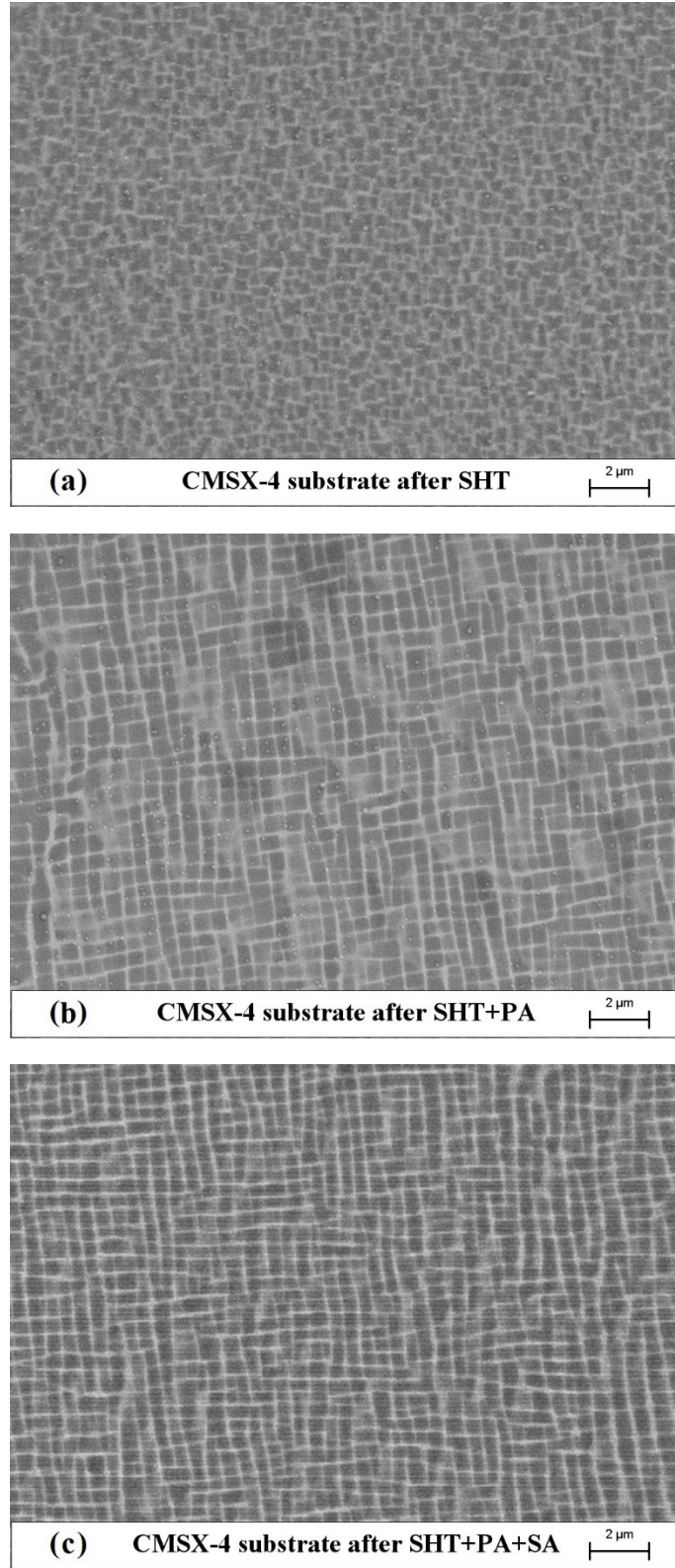


Figure 7.1 BSE images showing the microstructures of the CMSX-4 superalloy substrates after (a) SHT, (b) SHT+PA, and (c) SHT+PA+SA

The CMSX-4 substrate after SHT (hereafter referred to as SHT substrate) shows a microstructure consisting of an irregularly sized and shaped γ' -Ni₃Al phase (dark grey in Fig. 7.1a) residing in a γ solid solution matrix. In contrast, the γ' phase in the CMSX-4 substrates after PA (referred to as SHT+PA substrate) and SA (referred to as SHT+PA+SA substrate) has coarsened and become more regular in terms of size and shape, as seen in Figs. 7.1b and 7.1c, resulting in the cuboidal γ/γ' microstructure. However, the differences in the substrate microstructures between the ageing treatments (PA and SA) are not obvious at the examined magnification (5000X). This is attributed to the significantly smaller sizes of the secondary γ' phase, as shown in Fig. 7.2.

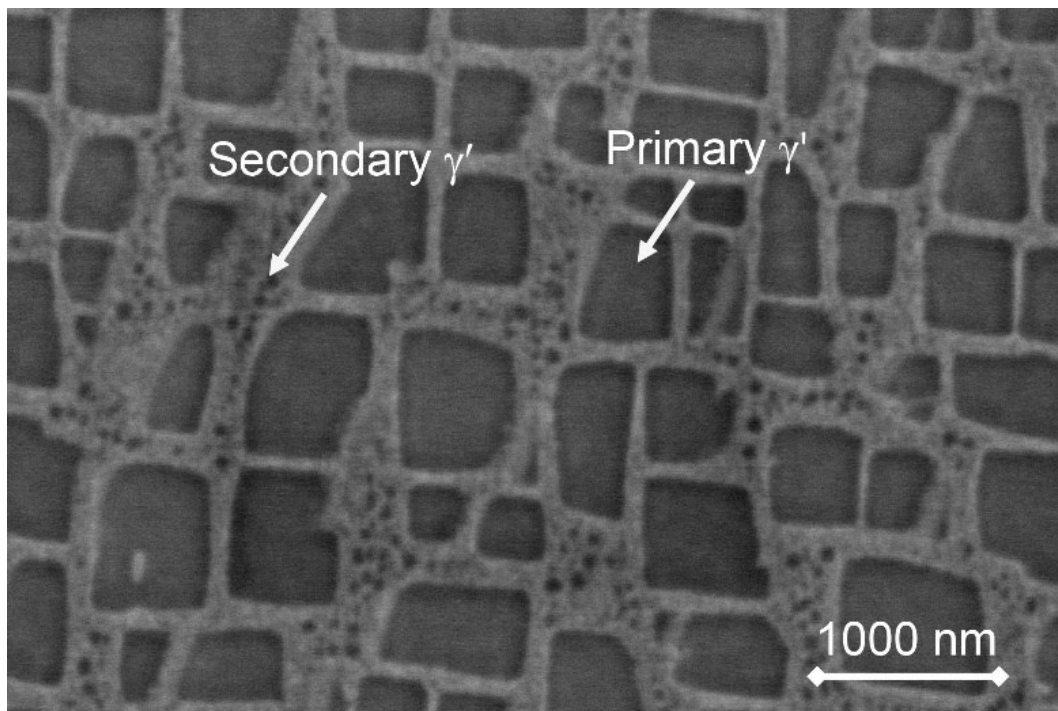


Figure 7.2 BSE image showing the primary γ' phase and the secondary γ' phase within the γ -matrix channel. Reprinted from Ref. [179] with permission from Elsevier.

Despite the noticeable differences in the substrate microstructure, the microhardness is similar for all the CMSX-4 substrates following the different heat treatments, as shown in Table 7.1. This may be due to overlapping effects of regular γ' precipitation and γ' coarsening. Precipitation of the primary and secondary regular γ' phase increases the coherence of the γ/γ' interface, which in turn strengthens the superalloy, whereas γ' coarsening decreases the γ/γ' coherence reducing the superalloy strength/hardness.

Table 7.1 Microhardness of CMSX-4 substrates under different heat treatment conditions and characteristics of CS NiCoCrAlTaY Coatings deposited on the substrates

CMSX-4 Substrate		CS NiCoCrAlTaY Coatings		
Conditions	Hardness (HV _{0.3})	Hardness (HV _{0.3})	Porosity (%)	Thickness (μm)
SHT	443 ± 8	703 ± 17	< 0.5	58.5 ± 4.8
SHT+PA	431 ± 10	721 ± 15	< 0.5	46.4 ± 4.9
SHT+PA+SA	438 ± 10	720 ± 19	< 0.5	48.5 ± 4.6

Coating depositions on the CMSX-4 substrates following different heat treatments were carried out using the CS technique and nitrogen as the process gas. The same spray parameters were used as those listed in Table 5.1. Figure 7.3 presents the resulting coating microstructures on the differently heat-treated substrates.

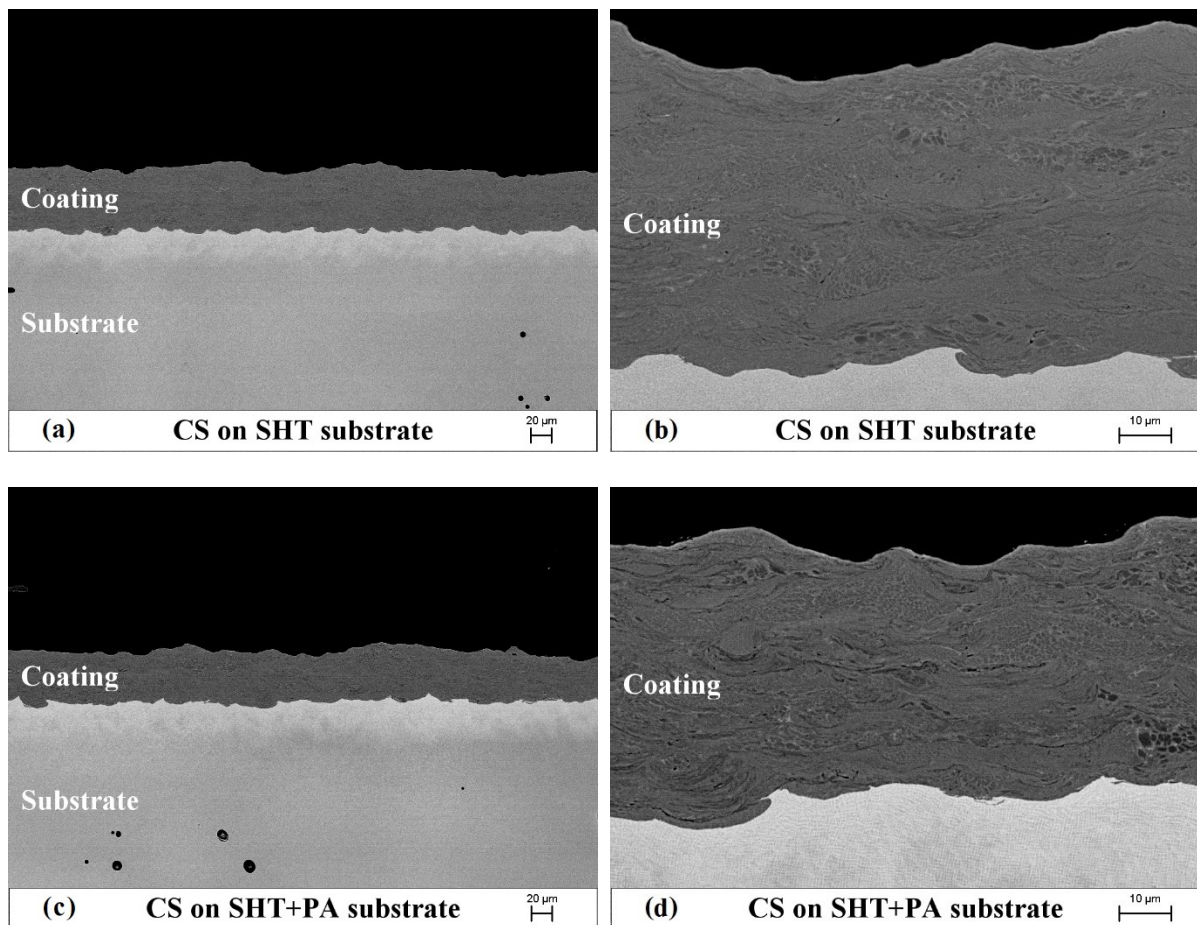


Figure 7.3 CS coating deposition on CMSX-4 substrates with different heat treatments: (a) SHT, (b) SHT+PA, and (c) SHT+PA+SA (continued on the next page)

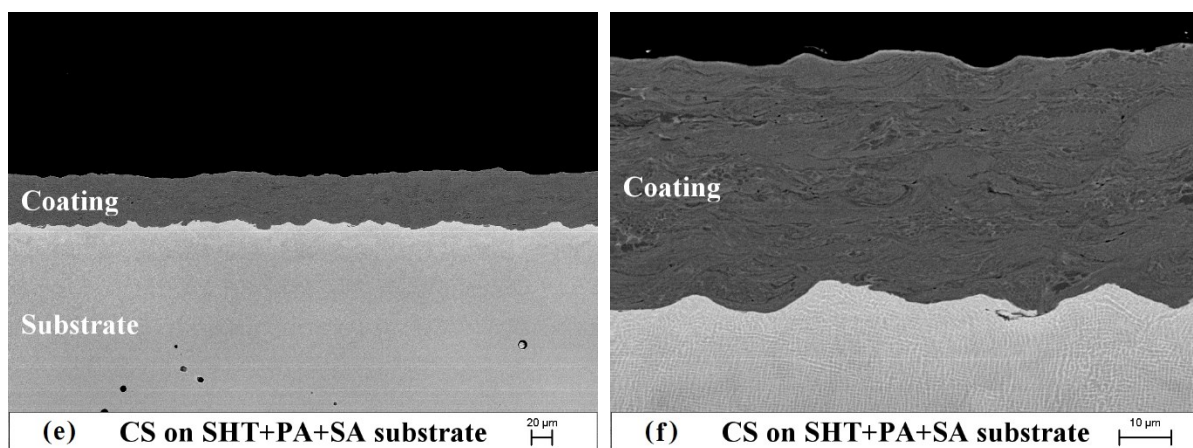


Figure 7.3 (continued) CS coating deposition on CMSX-4 substrates with different heat treatments: (a) SHT, (b) SHT+PA, and (c) SHT+PA+SA

In all three cases, the particles were deformed extensively during the CS deposition, such that the spherical particle morphology and particle boundaries were not distinguishable in the coatings. A summary of the coating characteristics, i.e., microhardness, porosity, and thickness, is also provided in Table 7.1. The NiCoCrAlTaY coatings are dense (porosity < 0.5 %) with similar hardness (720 HV_{0.3}) and coating thickness (approximately 50 μm). As these coatings were deposited using the same spray parameters, a similar coating thickness, therefore, represents a similar deposition efficiency (DE) of the feedstock powder on the different substrates. These results suggest that the different substrate conditions did not have a significant effect on the CS coating deposition mechanisms, and similar particle deformation behaviour (as that previously shown in Figs. 2 and 3 of Section 6.1) is expected on the three CMSX-4 substrates. As such, it is postulated that the resulting NiCoCrAlTaY coatings are also nanocrystalline, as previously demonstrated in Fig. 6 of Section 6.1, despite the different heat treatment history of the CMSX-4 substrates.

However, part of the required superalloy heat treatments is missing for two of the CMSX-4 substrates involved. Namely, the coated SHT sample would need a PA and a SA, while the coated SHT+PA sample would need a SA. These necessary heat treatments for the CMSX-4 substrates were performed after the CS coating depositions. Although this achieves the requirements for the superalloy substrates, it inevitably induces some microstructural changes in the coatings as well as at the coating-substrate interface during the heat treatments. Figure 7.4 presents the microstructures of the coated SHT samples after PA and PA+SA, respectively.

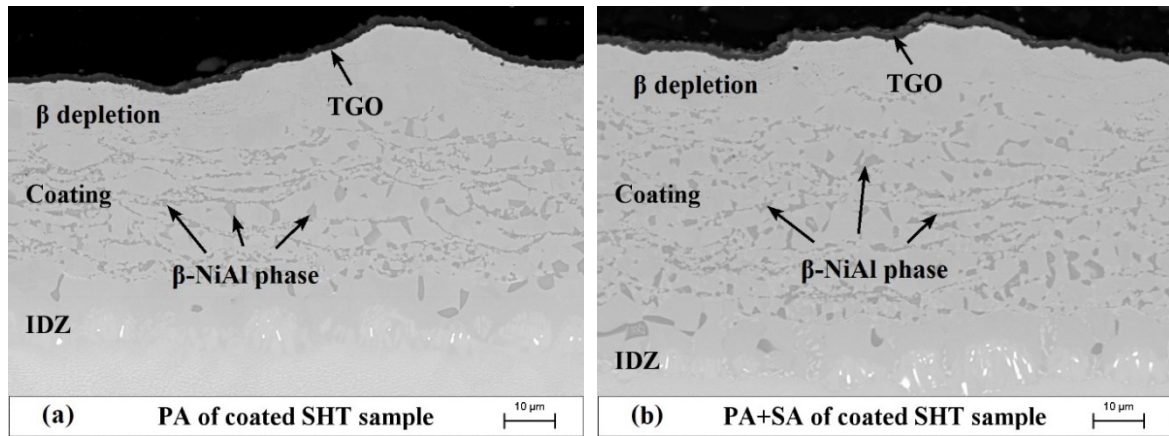


Figure 7.4 BSE images showing the microstructures of coated SHT samples after ageing: (a) PA and (b) PA+SA.

After PA of the coated SHT sample, a thermally grown oxide (TGO) layer was developed on the NiCoCrAlTaY coatings, which in turn resulted in a β -NiAl depletion zone close to the coating surface. At the coating-substrate interface, an inter-diffusion zone (IDZ) was formed during the thermal exposure due to the coating and substrate composition difference. These microstructural features are similar to what has been observed from the short-term isothermal oxidation of the CS NiCoCrAlTaY coatings presented in Fig. 6 of Section 6.2. This can be explained by the similar conditions of the PA (1140 °C for 6 h) and the short-term isothermal oxidation (1100°C, up to 5 h). Upon further ageing, i.e., SA at 870 °C for 20 h, the coated SHT sample did not experience major microstructural changes.

Figure 7.5 shows the microstructure of the coated SHT+PA sample after SA.

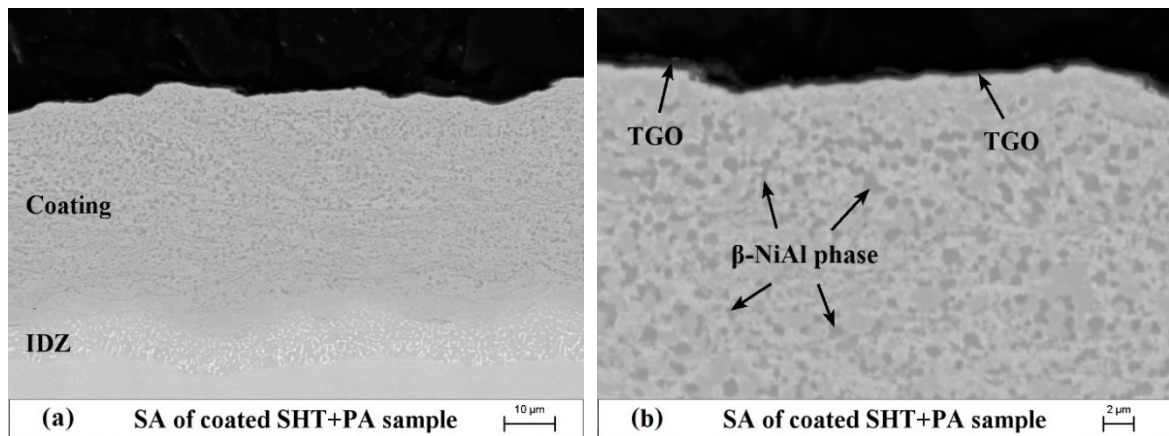


Figure 7.5 BSE images showing the microstructure of coated SHT+PA sample after SA: (a) overview and (b) high magnification revealing the presence of a thin TGO layer.

The microstructure was significantly different when compared to that observed for the coated SHT sample after performing the PA and PA+SA. The re-precipitation of the β -NiAl phase was much finer and more uniform in the NiCoCrAlTaY coatings of the coated SHT+PA sample after SA. This is markedly different from the discrete β phase distribution observed in the NiCoCrAlTaY coatings after thermal exposure at a higher temperature (e.g., Figs. 5 and 6 in Section 6.2, and Fig. 7.4). Furthermore, the IDZ observed at the coating-substrate interface after SA of the coated SHT+PA sample (Fig. 7.5a) was much evident with well-defined boundaries and a range of approximately 10 - 15 μ m. These obvious distinctions between the SHT and SHT+PA samples may be rationalized by the variation of the ageing temperatures. The SA was performed at 870°C, which is considerably lower than the PA temperature (1140°C). As such, much lower diffusion rates and shorter-range atomic diffusion are expected during the SA, thus resulting in a fine β phase due to localized adjustment and precipitation. A similar scenario likely occurred at the coating-substrate interface, leading to the evident IDZ as a result of short-range diffusion.

From this perspective, the microstructure shown in Fig. 7.5 may not be stable since large-scale equilibrium has not been established. Upon exposure to a higher temperature or longer duration at the low temperature, the microstructure observed in Fig. 7.5 would further evolve as enhanced diffusion occurs. For the same reason, i.e., lack of sufficient diffusion, it may seem that a continuous TGO layer has not been developed on the NiCoCrAlTaY coatings after SA of the coated SHT+PA sample. However, the close-up image (Fig. 7.5b) reveals the presence of a much thinner TGO scale on the coating surface. This also resulted in a less obvious depletion of the β phase below the coating surface compared to that of the coated SHT sample after the ageing treatments (Fig. 7.4).

7.2 Isothermal Oxidation Performance

The variation in the relative order of CS coating deposition with respect to required superalloy heat treatments essentially established three different processing sequences, as shown in Fig. 7.6.

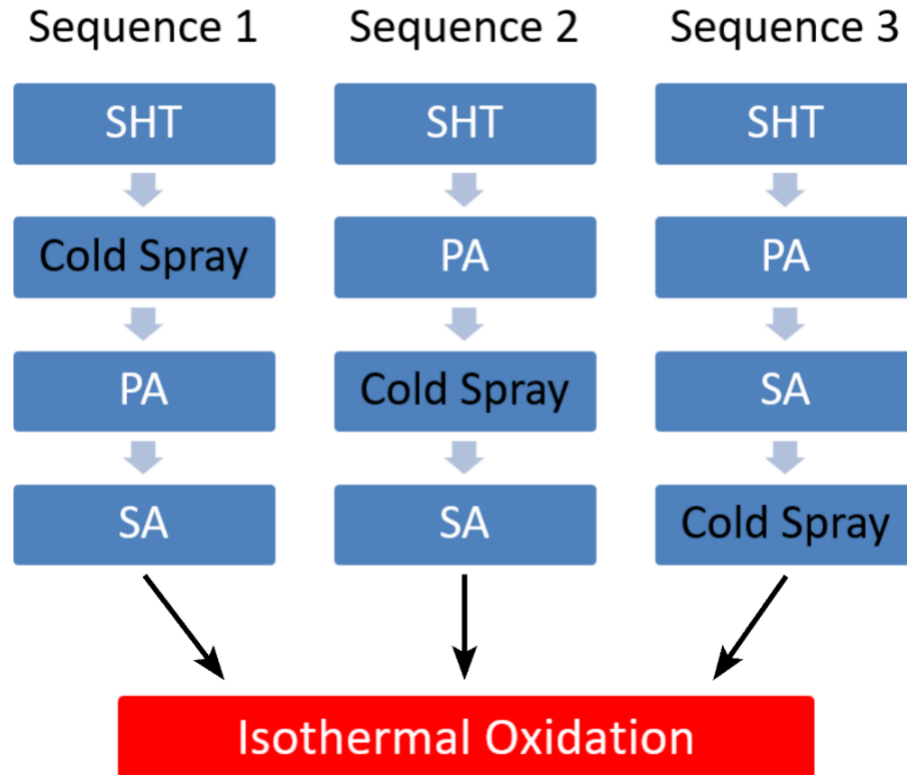


Figure 7.6 Flowchart showing three different sequences of superalloy heat treatments and CS coating deposition

Aside from being required for the superalloy substrate, the PA+SA in Sequence 1 and the SA in Sequence 2 also act as post-deposition heat treatments for the CS NiCoCrAlTaY coatings. Previous studies show that pre-oxidation of MCrAlY coatings may be beneficial to their subsequent oxidation performance due to the promotion of a homogeneous microstructure and an initial TGO scale [112, 113, 174]. In this context, the coated samples heat treatment, i.e., PA and SA of the coated SHT sample (Fig. 7.4) and SA of the coated SHT+PA sample (Fig. 7.5), may serve as the pre-oxidation treatment of the NiCoCrAlTaY coatings for microstructure homogenization and initial TGO formation. As such, the NiCoCrAlTaY coatings produced from Sequences 1 or 2 could potentially perform better than that produced from Sequence 3 in terms of oxidation performance.

Isothermal oxidation performance of the NiCoCrAlTaY coatings following different processing sequences was evaluated at 1100°C for 2 hours, and the resulting microstructures are shown in Fig. 7.7.

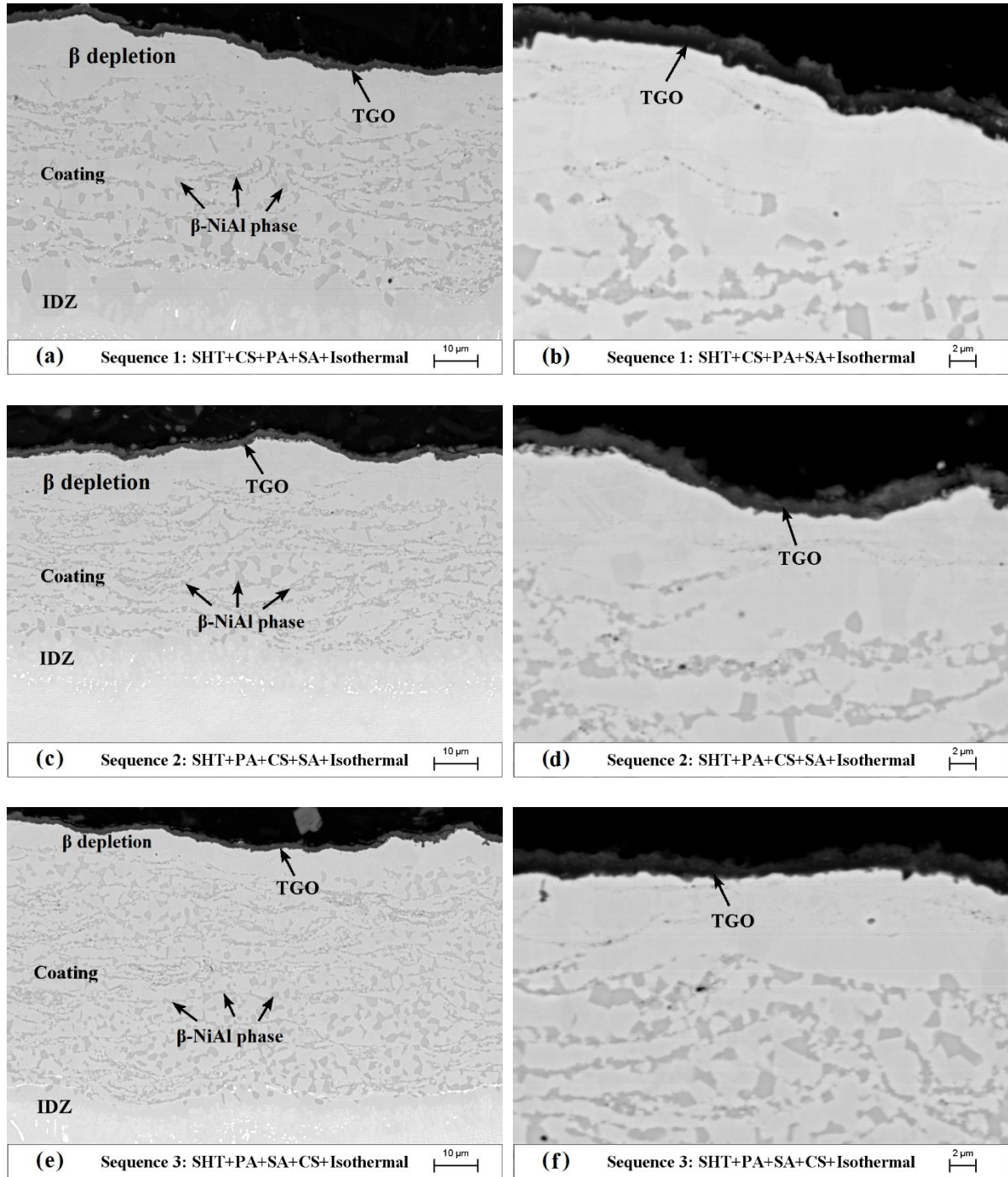


Figure 7.7 BSE images showing the microstructures of NiCoCrAlTaY coatings after 2h oxidation at 1100°C following (a, b) Sequence 1, (c, d) Sequence 2, and (e, f) Sequence 3

For Sequence 1, the coating microstructures before and after the short isothermal oxidation (Fig. 7.4b vs. Fig. 7.7a) are almost identical. This is because the NiCoCrAlTaY coatings

produced from Sequence 1 had already undergone a thermal exposure at a temperature higher than the isothermal oxidation temperature, i.e., the PA at 1140 °C. The microstructure developed during the PA (for example the TGO scale, β depletion, and IDZ) was more likely to achieve equilibrium and therefore stable when exposed to a low temperature during the isothermal oxidation.

However, the conditions are not the same for Sequence 2. The isothermal oxidation temperature (1100°C) is much higher than the SA (870 °C). This incurred further microstructure evolution in the NiCoCrAlTaY coatings (Fig. 7.5a vs. Fig. 7.7c) during the isothermal oxidation, agreeing with previous discussion and postulates. Consequently, an irregular and less uniform distribution of the β phase was found in the bulk coatings; the well-defined IDZ became ambiguous; both the TGO scale and the β depletion further developed and were more apparent. In other words, the resulting microstructure became increasingly similar to that of the NiCoCrAlTaY coatings following Sequence 1.

Sequence 3 did not involve any prior coating treatment before the isothermal oxidation. The CS NiCoCrAlTaY coatings were deposited on the CMSX-4 substrate that underwent all the required superalloy heat treatments (i.e., SHT+PA+SA). The coated samples were then directly exposed to an ambient environment at 1100°C for 2 h. This is the typical processing sequence for manufacturing MCrAlY coatings on nickel-based superalloys and was the one followed in the previous study in Section 6.2, where the detailed characterization of the isothermal oxidation performance of the CS nanocrystalline NiCoCrAlTaY coatings was presented.

The same microstructure shown in Fig. 7.7e as that of Fig. 6c in Section 6.2 confirmed the repeatability of the isothermal oxidation performance of the CS NiCoCrAlTaY coatings. The results and findings obtained in the previous study (Section 6.2) are therefore helpful to interpret the oxidation behaviour of the NiCoCrAlTaY coatings produced from the different processing sequences. First, given the similarity of the TGO characteristics (Figs. 7.7b, 7.7d, and 7.7f), the TGO scales developed on the NiCoCrAlTaY coatings following Sequences 1 and 2 are likely of the same nature as that on the NiCoCrAlTaY coatings of Sequence 3, which had been identified by XRD (Fig. 4 in Section 6.2) as primary α -Al₂O₃ and minor Y₂O₃. This is plausible considering that the as-deposited NiCoCrAlTaY coatings of the three sequences (Fig. 7.3) had similar deposition efficiencies and were likely comprised of nanoscale grains, which

promotes the nucleation and formation of α -Al₂O₃ TGO scale under elevated temperatures [121, 180, 181].

Second, an increasing percentage of the remaining β phase and a decreasing TGO scale thickness (and associated β depletion depth) can be observed in the NiCoCrAlTaY coatings from Sequence 1 to Sequence 2 to Sequence 3 (Figs. 7.7a, 7.7c, and 7.7e). This is attributed to their different exposure durations at elevated temperatures. By the end of isothermal oxidation tests, the NiCoCrAlTaY coatings following Sequence 1 had undergone three thermal exposures: 6 h at 1140 °C, 20 h at 870 °C, and 2 h at 1100°C. In contrast, the coatings in Sequence 2 experienced the two latter heat treatments, whereas the coatings in Sequence 3 only underwent 2h of the isothermal oxidation at 1100°C. Longer thermal exposure of the NiCoCrAlTaY coatings in Sequence 1 not only resulted in TGO growth but also further IDZ development, both of which facilitated the β depletion in the coatings, leading to a relatively lower amount of the remaining β phase.

However, less β phase presence in the NiCoCrAlTaY coatings does not necessarily represent an inferior oxidation behaviour. It was demonstrated in Section 6.2 that the α -Al₂O₃ scale was sustained to the longest duration (500 h) examined, although the β phase was completely depleted between 50 h and 100 h oxidation at 1100°C (Fig. 7 in Section 6.2). Moreover, the TGO growth kinetics decreased rapidly during the early stages of oxidation once a continuous TGO scale was established (Fig. 12 in Section 6.2). In light of these results, the initial TGO scales developed on the NiCoCrAlTaY coatings in Sequences 1 and 2 before isothermal oxidation may help reduce subsequent oxidation rates, potentially further improving the oxidation performance of the CS NiCoCrAlTaY coatings in addition to their nanocrystalline microstructure. Nevertheless, long-term oxidation tests would be required to confirm the processing sequence effects and draw affirmative conclusions.

Chapter 8 Conclusions

Cold spray (CS) has been demonstrated as a promising coating process for manufacturing MCrAlY coatings for gas turbine applications. The general objective of this thesis research was to develop low-cost/high-performance CS NiCoCrAlTaY coatings on a single-crystal nickel-base superalloy (CMSX-4). This was achieved by carrying out several studies that addressed different aspects pertinent to the deposition, characterization, cost analysis, and evaluation of the CS NiCoCrAlTaY coatings.

The feasibility of producing CS NiCoCrAlTaY coatings using nitrogen as the process gas was first verified. Experimental trials were performed using different CS spray parameters, such as gas temperature and pressure, powder preheating temperature, powder feed rate, and traverse speed to determine the spray conditions that yield dense and well adhered NiCoCrAlTaY coatings. Three different materials, i.e., Aluminum alloy 6061, Inconel alloy 625 polycrystalline nickel-base superalloy, and CMSX-4 single-crystal nickel-base superalloy, were used as the substrates to investigate the effect of substrate materials on the CS coating deposition. While dense and thick NiCoCrAlTaY coatings were achieved on Inconel 625 and CMSX-4 substrates, only a thin coating of a few particles was observed on the Al 6061 substrates due to large hardness difference between the powder and the substrate that prevented coating buildup. Substrate surface preparation (grit blasting versus grinding) was found to have a negligible effect on the coating microstructure. However, grit blasting resulted in a noticeable embedment of grit residues at the coating-substrate interface, whereas a clean interface was observed in the CS NiCoCrAlTaY coatings produced on the ground CMSX-4 substrate. The CS coating deposition using different NiCoCrAlTaY powder batches revealed that powder variation can have a significant impact on the coating characteristics and fine-tuning of the spray parameters may be required. To ensure consistency in the CS process and coating quality, the processing of the feedstock powder must be strictly regulated to minimize powder variation between production batches.

Using the spray parameters found, NiCoCrAlTaY coatings were deposited on the CMSX-4 substrates using either nitrogen or helium as the process gas. The resulting coating characteristics and properties were compared, and the economics of the two CS processes were

analyzed. The NiCoCrAlTaY coatings produced using nitrogen showed lower roughness ($R_a = 2.8 \pm 0.8 \mu\text{m}$), lower porosity ($0.1 \pm 0.1 \%$), and higher hardness ($HV_{0.05} = 600 \pm 17$) in comparison to coatings deposited using helium ($R_a = 7.6 \pm 2.7 \mu\text{m}$, porosity = $0.9 \pm 1.0 \%$, and $HV_{0.05} = 507 \pm 39$). This was attributed to enhanced particle impingement as a result of the low deposition efficiency (DE) in the case of CS using nitrogen (0.3%), approximately 40 times lower than that of CS using helium (12.0%). Under low DE conditions, a large number of particles simply bounced off after impact, which promoted plastic deformation of the adhered particles, resulting in a smoothened coating surface and a higher overall deformation in the NiCoCrAlTaY coatings deposited using nitrogen.

While the low DE may be necessary to obtain the desired coating properties with nitrogen, it could dissuade the adoption of nitrogen as the process gas due to significant powder waste and cost increase. To improve the economic viability of CS NiCoCrAlTaY coatings using nitrogen, the concept of powder recycling was introduced and explored. Powder particles that did not adhere during deposition were collected, characterized, and resprayed in subsequent trials. This resulted in coatings similar to the ones achieved from the original feedstock powders. The process economics considering the benefit of powder recycling was analyzed, and it was found that under the set experimental conditions, powder recycling, and local pricing, the process of CS using nitrogen was similar to using helium in final cost - with the largest proportion being gas cost for the helium coatings and labour cost for the nitrogen coatings. These results demonstrated that the use of nitrogen and powder recycling can produce MCrAlY coatings of superior properties than that deposited using helium under the same spray parameters while being potentially cost-competitive.

Dense MCrAlY coatings with low surface roughness have been demonstrated to exhibit desirable performance under a high-temperature oxidizing environment. To further improve the oxidation performance, CS NiCoCrAlTaY coatings with in-situ nanocrystalline microstructure were sought. This was achieved by utilizing a CS process with low spray parameters while using conventional feedstock powders of large grain size. Single-splat and interrupted spray tests revealed that adhered particles experienced extensive plastic deformation during the CS deposition. Scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM) characterization showed that the dense

NiCoCrAlTaY coatings were comprised of extended nanoscale grains as a result of strain-induced grain refinement (or dynamic recrystallization). Under the studied spray conditions, the CS process essentially combines two separate processes of powder nanocrystallization and coating deposition. The fact that a powder milling process is not required prior to CS deposition means that potential powder contamination during milling can be avoided, and the processing time and costs can be reduced for manufacturing nanocrystalline NiCoCrAlTaY coatings.

The oxidation performance of the CS nanocrystalline NiCoCrAlTaY coatings was evaluated under an isothermal condition at 1100°C in air. The microstructural evolution, compositional change, and growth kinetics of thermally grown oxide (TGO) as a function of oxidation time were analyzed. After 1-hour oxidation, a continuous α -Al₂O₃ TGO scale was established on the coating surface. Al consumption by the TGO resulted in a β phase depletion zone in the coating underneath the scale. The TGO scale and β phase depletion grew in thickness with increasing oxidation time. During prolonged oxidation from 25 h to 500 h, the TGO scale experienced localized separation, buckling, cracking, and spallation, attributed to the high cooling rates outside the furnace. While the Al-rich β phase in the coating was completely depleted between 50 h and 100 h oxidation, the Al concentration in the coating subsurface region evolved through three stages and remained above 3.9 wt.% after the longest duration (500 h) examined. The readily available Al in the subsurface region helped sustain the α -Al₂O₃ scale growth throughout the prolonged oxidation, preventing the formation of non-protective mixed or spinel oxides. The TGO growth kinetics deviated from the parabolic rate law and followed a non-parabolic power-law rate of $X = 1.085 t^{0.283}$. The instantaneous rate constants decreased rapidly during the early stages of oxidation, followed by a gradual decrease during the prolonged thermal exposure. A decreasing rate constant represented the desirable scenario of fast scale establishment and slow scale growth. The relatively low TGO growth kinetics suggested an improved oxidation performance of the CS nanocrystalline NiCoCrAlTaY coatings.

Finally, different processing sequences were explored for CS deposition of NiCoCrAlTaY coatings on CMSX-4 single-crystal superalloy substrates. Typical heat treatments, i.e., solution heat treatment (SHT), primary ageing (PA), and secondary ageing (SA), were partly performed on the superalloy substrates, followed by the CS coating deposition. This resulted in three

distinct processing sequences in terms of the relative order of the superalloy heat treatments and the CS deposition. The characteristics of as-deposited NiCoCrAlTaY coatings were similar and independent of the substrate conditions, despite an evident difference in the substrate microstructure. Upon completing all necessary ageing for the superalloy substrates, CS NiCoCrAlTaY coatings following different processing sequences showed evident microstructure variations in terms of γ/β morphology, β content, TGO characteristics, and β depletion magnitude. Nevertheless, the microstructure of the NiCoCrAlTaY coatings after a short isothermal exposure (2h) at 1100°C was similar, featuring a discrete β distribution among the γ matrix, a continuous TGO scale on the coating surface, a β depletion below the coating surface, and an inter-diffusion zone (IDZ) at the coating-substrate interface. The homogeneous coating microstructure developed and the TGO scale promoted during the ageing prior to the isothermal oxidation may help reduce subsequent oxidation rates, potentially further improving the oxidation performance of the CS NiCoCrAlTaY coatings in addition to their nanocrystalline microstructure.

Future Work

The work contained in the present thesis focuses on developing nanocrystalline MCrAlY coatings using the CS technique and examining their isothermal oxidation performance. There is still much work to be done to optimize the manufacturing process and to fully understand the oxidation behaviour of the coatings at elevated temperatures. The following is a list of various topics that could be of interest to future studies.

- The spray parameters used for CS coating deposition in this work were found by focusing on achieving dense nanocrystalline coatings using a NiCoCrAlTaY feedstock powder. It would be interesting to explore how different compositions of MCrAlY powders affect the CS deposition and resulting coating microstructure and properties. It is also important to verify with different CS systems to confirm and promote the manufacturing of nanocrystalline MCrAlY coatings using the CS technique. Furthermore, the CS spray parameters should be optimized to see if a high DE could be achieved while still produce dense nanocrystalline MCrAlY coatings while using commercial powders.
- Recycling the non-deposited MCrAlY powder represents a significant cost reduction for the CS process using nitrogen. The feasibility of powder recycling should be further validated in an industrialized setting with dedicated and automated equipment, where continual operation of multiple cycles of powder recycling and CS deposition should be tested. In addition, a gas blending of nitrogen and helium could be explored to identify balanced spray parameters that result in high deposition efficiency but low overall coating costs while still producing nanocrystalline MCrAlY coatings. Under these situations, the cost model for the CS process should be updated accordingly.
- It was shown in the thesis that a continuous α -Al₂O₃ TGO scale was established on the coating surface after thermal exposure at 1100°C for 1 hour. A shorter oxidation duration, e.g., 5 mins, 10 mins, and 30 mins, should be carried out to characterize the initial TGO formation in terms of microstructure, composition, phase constitution, and growth kinetics. This would provide insight into the initial oxidation behaviour of the CS MCrAlY coatings, e.g., whether transient aluminas or other oxides are formed or

not; Is the decreasing oxidation kinetics related to phase transformation(s) between the transient aluminas and α -Al₂O₃, etc.

- The dislocation density and grain size of the CS MCrAlY coatings should be characterized before thermal exposure and after different oxidation durations. This would require the use of a high-resolution transmission electron microscope (HR-TEM). Given that higher dislocation and grain boundary densities facilitate aluminum diffusion in the coatings, dislocation annihilation and grain growth at elevated temperatures could significantly affect the diffusion rates. Clarification of the dislocation density and grain size changes during the isothermal oxidation would reveal how fast dislocation annihilates and how much grain grows. This will help better understand the isothermal oxidation performance of the CS nanocrystalline MCrAlY coatings.
- Long-term isothermal oxidation tests should be carried out for the CS MCrAlY coatings following different processing sequences. This would reveal whether there is a major difference in terms of long-term coating oxidation performance among the sequences, and which one would be preferred. These results may help to establish the manufacturing procedures for CS MCrAlY coatings on nickel-based superalloys.
- It would be interesting to explore ceramic topcoat deposition on the CS nanocrystalline MCrAlY coatings and evaluate the isothermal oxidation performance of the thermal barrier coating (TBC) system. This should be compared with other TBC systems consisting of conventional bond coats prepared using CS, HVOF, and APS as well as nanocrystalline bond coats prepared using traditional two-step manufacturing processes. The effect of deposition techniques or coating microstructure (porosity, oxide content, grain size) on TGO characteristics and growth kinetics could be examined.
- Lastly, it is equally important to evaluate the performance of the CS MCrAlY coatings or the TBC system under other conditions such as thermal cycling and hot corrosion environment. It would be valuable to reveal the failure mechanism and establish the life prediction model for different coating systems and testing conditions.

Reference

- 1 Donachie, M.J. and S.J. Donachie, *Superalloys: A Technical Guide*. 2nd ed. 2002, Materials Park, Ohio: ASM International.
- 2 Reed, R.C., *The Superalloys: Fundamentals and Applications*. 2006, New York: Cambridge University Press.
- 3 Erickson, G.L., *The development and application of CMSX (R)-10*. Superalloys 1996, 1996: p. 35-44.
- 4 Broomfield, R.W., et al., *Development and turbine engine performance of three advanced rhenium containing superalloys for single crystal and directionally solidified blades and vanes*. Journal of Engineering for Gas Turbines and Power-Transactions of the Asme, 1998. **120**(3): p. 595-608.
- 5 Sato, A., et al., *A 5th generation SC superalloy with balanced high temperature properties and processability*. Superalloys 2008, 2008: p. 131-138.
- 6 Kawagishi, K., et al., *Development of an oxidation-resistant high-strength sixth-generation single-crystal superalloy TMS-238*. Proceedings of Superalloys, 2012: p. 189-195.
- 7 Callister, W.D., *Materials science and engineering: an introduction*. 8th ed. 2010, New York: John Wiley & Sons. xxv, 721, A41, G14, S5, I22 p.
- 8 Kawagishi, K., et al., *The oxidation properties of fourth generation single-crystal nickel-based superalloys*. JOM, 2006. **58**(1): p. 43-46.
- 9 Schulz, U., et al., *Some recent trends in research and technology of advanced thermal barrier coatings*. Aerospace Science and Technology, 2003. **7**(1): p. 73-80.
- 10 Padture, N.P., M. Gell, and E.H. Jordan, *Thermal Barrier Coatings for Gas-Turbine Engine Applications*. Science, 2002. **296**(5566): p. 280-284.
- 11 Strangman, T.E., *Thermal Barrier Coatings for Turbine Airfoils*. Thin Solid Films, 1985. **127**: p. 93-105.
- 12 Sheffler, K.D. and D.K. Gupta, *Current Status and Future Trends in Turbine Application of Thermal Barrier Coatings*. Journal of Engineering for Gas Turbines and Power, 1988. **110**: p. 605-609.

- 13 Miller, R.A., *Thermal barrier coatings for aircraft engines: History and directions*. Journal of Thermal Spray Technology, 1997. **6**(1): p. 35-42.
- 14 Vaßen, R., et al., *Overview on advanced thermal barrier coatings*. Surface & Coatings Technology, 2010. **205**(4): p. 938-942.
- 15 Clarke, D.R., M. Oechsner, and N.P. Padture, *Thermal-barrier coatings for more efficient gas-turbine engines*. Materials Research Society(Mrs) Bulletin, 2012. **37**(10): p. 891-902.
- 16 Brandl, W., et al., *The oxidation behaviour of sprayed MCrAlY coatings*. Surface & Coatings Technology, 1996. **86**(1-3): p. 41-47.
- 17 Seo, D., et al., *Comparative Study on Oxidation Behavior of Selected MCrAlY Coatings by Elemental Concentration Profile Analysis*. Applied Surface Science, 2008. **255**(5): p. 2581-2590.
- 18 Vialas, N. and D. Monceau, *Substrate effect on the high-temperature oxidation behavior of a pt-modified aluminide coating. Part I: Influence of the initial chemical composition of the coating surface*. Oxidation of Metals, 2006. **66**(3-4): p. 155-189.
- 19 Tang, F., et al., *Effects of surface oxidation during HVOF processing on the primary stage oxidation of a CoNiCrAlY coating*. Surface & Coatings Technology, 2004. **185**(2-3): p. 228-233.
- 20 Shibata, M., et al., *Comparison of Microstructure and Oxidation Behavior of CoNiCrAlY Bond Coatings Prepared by Different Thermal Spray Processes*. Materials Transactions, 2006. **47**(7): p. 1638-1642.
- 21 Fossati, A., et al., *Improvement of the Isothermal Oxidation Resistance of CoNiCrAlY Coating Sprayed by High Velocity Oxygen Fuel*. Surface & Coatings Technology, 2010. **204**(21-22): p. 3723-3728.
- 22 Mori, T., et al., *Effects of initial oxidation on β phase depletion and oxidation of CoNiCrAlY bond coatings fabricated by warm spray and HVOF processes*. Surface & Coatings Technology, 2013. **221**: p. 59-69.
- 23 Fossati, A., et al., *Influence of Surface Finishing on the Oxidation Behaviour of VPS MCrAlY Coatings*. Journal of Thermal Spray Technology, 2012. **21**(2): p. 314-324.
- 24 Li, Y., et al., *Effect of Chemical Compositions and Surface Morphologies of MCrAlY Coating on Its Isothermal Oxidation Behavior*. Journal of Thermal Spray Technology, 2011. **20**(1-2): p. 121-131.

- 25 Brandl, W., et al., *The oxidation behaviour of HVOF thermal-sprayed MCrAlY coatings*. Surface & Coatings Technology, 1997. **94-95**(1-3): p. 21-26.
- 26 Essuman, E., et al., *Effect of oxygen partial pressure on the oxidation behaviour of an yttria dispersion strengthened NiCr-base alloy*. Journal of Materials Science, 2008. **43**(16): p. 5591-5598.
- 27 Di Ferdinando, M., et al., *Isothermal oxidation resistance comparison between air plasma sprayed, vacuum plasma sprayed and high velocity oxygen fuel sprayed CoNiCrAlY bond coats*. Surface & Coatings Technology, 2010. **204**(15): p. 2499-2503.
- 28 Toma, D., W. Brandl, and U. Koster, *Studies on the transient stage of oxidation of VPS and HVOF sprayed MCrAlY coatings*. Surface & Coatings Technology, 1999. **120**: p. 8-15.
- 29 Villafuerte, J., *Modern Cold Spray: Materials, Process, and Applications*. 2015: Springer.
- 30 Champagne, V.K., *The Cold Spray Materials Deposition Process: Fundamentals and Applications*. 2007: Taylor & Francis.
- 31 Richer, P., et al., *Oxidation Behaviour of CoNiCrAlY Bond Coats Produced by Plasma, HVOF and Cold Gas Dynamic Spraying*. Surface & Coatings Technology, 2010. **204**(24): p. 3962-3974.
- 32 Manap, A., A. Nakano, and K. Ogawa, *The Protectiveness of Thermally Grown Oxides on Cold Sprayed CoNiCrAlY Bond Coat in Thermal Barrier Coating*. Journal of Thermal Spray Technology, 2012. **21**(3-4): p. 586-596.
- 33 Chen, W.R., et al., *The Oxidation Behavior of TBC with Cold Spray CoNiCrAlY Bond Coat*. Journal of Thermal Spray Technology, 2011. **20**(1-2): p. 132-138.
- 34 Li, Y., et al., *Thermal Fatigue Behavior of Thermal Barrier Coatings With the MCrAlY Bond Coats by Cold Spraying and Low-Pressure Plasma Spraying*. Surface & Coatings Technology, 2010. **205**(7): p. 2225-2233.
- 35 Richer, P., et al., *CoNiCrAlY Microstructural Changes Induced During Cold Gas Dynamic Spraying*. Surface & Coatings Technology, 2008. **203**(3-4): p. 364-371.
- 36 Zhang, Q., et al., *Study of Oxidation Behavior of Nanostructured NiCrAlY Bond Coatings Deposited by Cold Spraying*. Surface & Coatings Technology, 2008. **202**(14): p. 3378-3384.

- 37 Doleker, K.M. and A.C. Karaoglanli, *Comparison of Oxidation Behavior of Shot-Peened Plasma Spray Coatings with Cold Gas Dynamic Spray Coatings*. *Oxidation of Metals*, 2017. **88**(1): p. 121-132.
- 38 Karaoglanli, A.C. and A. Turk, *Isothermal Oxidation Behavior and Kinetics of Thermal Barrier Coatings Produced by Cold Gas Dynamic Spray Technique*. *Surface & Coatings Technology*, 2017. **318**: p. 72-81.
- 39 Crespo, V., et al., *The Influence of Feedstock Powders on the CGS Deposition Efficiency of Bond Coats for TBCs*. *Journal of Alloys and Compounds*, 2015. **622**: p. 394-401.
- 40 Bonadei, A. and T. Marrocco, *Cold Sprayed MCrAlY + X Coating for Gas Turbine Blades and Vanes*. *Surface & Coatings Technology*, 2014. **242**: p. 200-206.
- 41 Dykhuizen, R.C. and M.F. Smith, *Gas Dynamic Principles of Cold Spray*. *Journal of Thermal Spray Technology*, 1998. **7**(2): p. 205-212.
- 42 Gilmore, D.L., et al., *Particle Velocity and Deposition Efficiency in the Cold Spray Process*. *Journal of Thermal Spray Technology*, 1999. **8**(4): p. 576-582.
- 43 Grujicic, M., et al., *Analysis of the Impact Velocity of Powder Particles in the Cold-Gas Dynamic-Spray Process*. *Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing*, 2004. **368**(1-2): p. 222-230.
- 44 Jodoin, B., F. Raletz, and M. Vardelle, *Cold Spray Modeling and Validation Using an Optical Diagnostic Method*. *Surface & Coatings Technology*, 2006. **200**(14-15): p. 4424-4432.
- 45 Assadi, H., et al., *Cold Spraying - A Materials Perspective*. *Acta Materialia*, 2016. **116**: p. 382-407.
- 46 Kumar, S., G. Bae, and C. Lee, *Influence of substrate roughness on bonding mechanism in cold spray*. *Surface & Coatings Technology*, 2016. **304**: p. 592-605.
- 47 Li, Y., et al., *Influence of TGO Composition on the Thermal Shock Lifetime of Thermal Barrier Coatings with Cold-sprayed MCrAlY Bond Coat*. *Journal of Thermal Spray Technology*, 2010. **19**(1-2): p. 168-177.
- 48 Doleker, K.M. and A.C. Karaoglanli, *Comparison of oxidation behavior of YSZ and Gd₂Zr₂O₇ thermal barrier coatings (TBCs)*. *Surface & Coatings Technology*, 2017. **318**: p. 198-207.

- 49 Feng, S.Q., et al., *Effects of Standoff Distance and Particle Size on Quality of NiCoCrAlY Coating by Cold Spraying*. Applied Science, Materials Science and Information Technologies in Industry, 2014. **513-517**: p. 265-268.
- 50 Borchers, C., et al., *Strain-Induced Phase Transformation of MCrAlY*. Advanced Engineering Materials, 2015. **17**(5): p. 723-731.
- 51 Kalsi, S.B.S., et al., *Evaluation of NiCoCrAlY coatings deposited on superalloy with novel cold spray process*. Surface Engineering, 2015. **31**(11): p. 840-845.
- 52 Xu, Y.X., et al., *Formation of Al₂O₃ diffusion barrier in cold-sprayed NiCoCrAlY/Ni multi-layered coatings on 304SS substrate*. Surface & Coatings Technology, 2016. **307**: p. 603-609.
- 53 Tolpygo, V.K., K.S. Murphy, and D.R. Clarke, *Effect of Hf, Y and C in the underlying superalloy on the rumpling of diffusion aluminide coatings*. Acta Materialia, 2008. **56**(3): p. 489-499.
- 54 Tanno, M., K. Ogawa, and T. Shoji, *Effect of cerium and silicon additions to MCrAlY on the high-temperature oxidation behavior and bond strength of thermal barrier coatings*. Advances in Fracture and Failure Prevention, Pts 1 and 2, 2004. **261-263**: p. 1061-1066.
- 55 Lan, H., et al., *Influence of Aluminum and Rhenium on the Isothermal Oxidation Behavior of CoNiCrAlY Alloys*. Oxidation of Metals, 2011. **75**(1-2): p. 77-92.
- 56 Schütze, M., *Fundamentals of high temperature corrosion*, in *Materials Science and Technology: A Comprehensive Treatment: Corrosion and Environmental Degradation*, R.W. Cahn, P. Haasen, and E.J. Kramer, Editors. 2000, Wiley: Online. p. 67-130.
- 57 Birks, N., G.H. Meier, and F.S. Pettit, *Mechanisms of oxidation*, in *Introduction to the High Temperature Oxidation of Metals*, N. Birks, Editor. 2006, Cambridge University Press: Cambridge. p. 39-74.
- 58 Stott, F.H., G.C. Wood, and J. Stringer, *The Influence of Alloying Elements on the Development and Maintenance of Protective Scales*. Oxidation of Metals, 1995. **44**(1-2): p. 113-145.
- 59 Smialek, J.L. and N.S. Jacobson, *Oxidation of High Temperature Aerospace Materials*, in *High temperature materials and mechanisms*, Y. Bar-Cohen, Editor. 2014, CRC Press: Boca Raton. p. 95-154.
- 60 Goward, G.W., *Progress in coatings for gas turbine airfoils*. Surface & Coatings

- Technology, 1998. **108**(1-3): p. 73-79.
- 61 Meher-Homji, C.B., *Anselm Franz and the Jumo 004*, in *Mechanical Engineering-CIME*. 1997. p. 88-91.
 - 62 Metco, *Thermal Spray Materials Guide* O. Metco, Editor. 2012.
 - 63 Wagner, C., *Passivity and inhibition during the oxidation of metals at elevated temperatures*. Corrosion Science, 1965. **5**(11): p. 751-764.
 - 64 Christensen, R.J., V.K. Tolpygo, and D.R. Clarke, *The influence of the reactive element yttrium on the stress in alumina scales formed by oxidation*. Acta Materialia, 1997. **45**(4): p. 1761-1766.
 - 65 Tolpygo, V.K., J.R. Dryden, and D.R. Clarke, *Determination of the growth stress and strain in alpha-Al₂O₃ scales during the oxidation of Fe-22Cr-4.8Al-0.3Y alloy*. Acta Materialia, 1998. **46**(3): p. 927-937.
 - 66 Smialek, J.L., *Advances in the oxidation resistance of high-temperature turbine materials*. Surface and Interface Analysis, 2001. **31**(7): p. 582-592.
 - 67 Smeggil, J.G., *Some Comments on the Role of Yttrium in Protective Oxide Scale Adherence*. Materials Science and Engineering, 1987. **87**(1-2): p. 261-265.
 - 68 Sigler, D.R., *The Influence of Sulfur on Adherence of Al₂O₃ Grown on Fe-Cr-Al Alloys*. Oxidation of Metals, 1988. **29**(1-2): p. 23-43.
 - 69 Wiemer, D., H.J. Grabke, and H. Viefhaus, *Investigation on the Influence of Sulfur Segregation on the Adherence of Protective Oxide Layers on High-Temperature Materials*. Fresenius Journal of Analytical Chemistry, 1991. **341**(5-6): p. 402-405.
 - 70 Smeggil, J.G. and A.J. Shuskus, *The oxidation behavior of some FeCrAlY, FeCrAl, and yttrium ion-implanted FeCrAl alloys compared and contrasted*. Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, 1986. **4**(6): p. 2577-2582.
 - 71 Anderson, A.B., S.a. Mehandru, and J.L. Smialek, *Dopant Effect of Yttrium and the Growth and Adherence of Alumina on Nickel-Aluminum Alloys*. Journal of the Electrochemical Society, 1985. **132**(7): p. 1695-1701.
 - 72 Allam, I.M., D.P. Whittle, and J. Stringer, *The oxidation behavior of CoCrAl systems containing active element additions*. Oxidation of Metals, 1978. **12**(1): p. 35-66.
 - 73 Allam, I.M., D.P. Whittle, and J. Stringer, *The role of active elements and oxide*

- dispersions in the development of oxidation-resistant alloys and coatings.* 1979, California Univ., Berkeley (USA). Lawrence Berkeley Lab.
- 74 Hindam, H. and D.P. Whittle, *Peg Formation by Short-Circuit Diffusion in Al₂O₃ Scales Containing Oxide Dispersions.* Journal of the Electrochemical Society, 1982. **129**(5): p. 1147-1149.
 - 75 Hindam, H. and D.P. Whittle, *Mechanism of PEG growth and influence on scale adhesion.* 1982.
 - 76 Golightly, F.A., G.C. Wood, and F.H. Stott, *The early stages of development of α -Al₂O₃ scales on Fe-Cr-Al and Fe-Cr-Al-Y Alloys at high temperature.* Oxidation of Metals, 1980. **14**(3): p. 217-234.
 - 77 Golightly, F., F. Stott, and G. Wood, *The Relationship Between Oxide Grain Morphology and Growth Mechanisms for Fe-Cr-Al and Fe-Cr-Al-Y Alloys.* Journal of the Electrochemical Society, 1979. **126**(6): p. 1035-1042.
 - 78 Golightly, F., F. Stott, and G. Wood, *The influence of yttrium additions on the oxide-scale adhesion to an iron-chromium-aluminum alloy.* Oxidation of Metals, 1976. **10**(3): p. 163-187.
 - 79 Prescott, R. and M.J. Graham, *The Formation of Aluminum-Oxide Scales on High-Temperature Alloys.* Oxidation of Metals, 1992. **38**(3-4): p. 233-254.
 - 80 Khanna, A.S., et al., *Addition of Yttrium, Cerium and Hafnium to Combat the Deleterious Effect of Sulfur Impurity during Oxidation of an Ni-Cr-Al Alloy.* Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing, 1989. **120**: p. 185-191.
 - 81 Nicholls, J.R., *Designing Oxidation-Resistant Coatings.* Journal of the Minerals Metals & Materials Society, 2000. **52**(1): p. 28-35.
 - 82 Nicholls, J.R., et al., *Smart overlay coatings - concept and practice.* Surface & Coatings Technology, 2002. **149**(2-3): p. 236-244.
 - 83 Tien, J. and F. Pettit, *Mechanism of oxide adherence on Fe-25Cr-4Al (Y or Sc) alloys.* Metallurgical Transactions, 1972. **3**(6): p. 1587-1599.
 - 84 Ramanarayanan, T., et al., *The influence of yttrium on oxide scale growth and adherence.* Oxidation of Metals, 1988. **29**(5-6): p. 445-472.

- 85 Young, E.W.A., H.E. Bishop, and J.H.W. De Wit, *On the use of markers and tracers to establish the growth mechanism of alumina scales during high temperature oxidation*. Surface and Interface Analysis, 1986. **9**(3): p. 163-168.
- 86 Reddy, K.P.R., J.L. Smialek, and A.R. Cooper, *18O Tracer studies of Al₂O₃ scale formation on NiCrAl alloys*. Oxidation of Metals, 1982. **17**(5): p. 429-449.
- 87 Young, E.W.A. and J.H.W. Dewit, *The Use of a O-18 Tracer and Rutherford Backscattering Spectrometry to Study the Oxidation Mechanism of NiAl*. Solid State Ionics, 1985. **16**(1-4): p. 39-46.
- 88 Jedliński, J. and S. Mrowec, *The influence of implanted yttrium on the oxidation behaviour of β -NiAl*. materials Science and Engineering, 1987. **87**: p. 281-287.
- 89 Stott, F.H., *The oxidation of alumina-forming alloys*. High Temperature Corrosion and Protection of Materials 4, 1997. **251-254**: p. 19-32.
- 90 Heuer, A.H., et al., *Alumina Scale Formation: A New Perspective*. Journal of the American Ceramic Society, 2011. **94**(S1): p. S146-S153.
- 91 Mistler, R. and R. Coble, *Rate-Determining Species in Diffusion-Controlled Processes in Al₂O₃*. Journal of the American Ceramic Society, 1971. **54**(1): p. 60-61.
- 92 Mistler, R. and R. Coble, *Grain-boundary diffusion and boundary widths in metals and ceramics*. Journal of Applied Physics, 1974. **45**(4): p. 1507-1509.
- 93 Abbasi, K., M. Zahiri, and A. Heuer, *Study of Scale Formation on Al₂O₃-Scale Forming Alloys by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)*. 2017.
- 94 Huntz, A., et al., *Yttrium influence on the alumina growth mechanism on an FeCr23Al5 alloy*. Applied surface science, 1987. **28**(4): p. 345-366.
- 95 Pint, B.A., *Experimental observations in support of the dynamic-segregation theory to explain the reactive-element effect*. Oxidation of Metals, 1996. **45**(1): p. 1-37.
- 96 Schütze, M., *Failure of Oxide Scales on Advanced Materials Due to the Presence of Stresses*. High Temperature Corrosion of Advanced Materials and Protective Coatings, 1992: p. 39-49.
- 97 Jedlinski, J., *Application of O-18(2) exposure-based approach to study the failure mechanisms of oxide scales on alumina formers*. Advanced Materials and Technologies, 2006. **513**: p. 149-163.

- 98 Nagl, M.M. and W.T. Evans, *The Mechanical Failure of Oxide Scales under Tensile or Compressive Load*. Journal of Materials Science, 1993. **28**(23): p. 6247-6260.
- 99 Evans, H.E., *Spallation of Oxide from Stainless Steel Agr Nuclear-Fuel Cladding: Mechanisms and Consequences*. Materials Science and Technology, 1988. **4**(5): p. 415-420.
- 100 Schütze, M., *Plasticity of Protective Oxide Scales*. Materials Science and Technology, 1990. **6**(1): p. 32-38.
- 101 Evans, H.E. and R.C. Lobb, *Conditions for the Initiation of Oxide Scale Cracking and Spallation*. Corrosion Science, 1984. **24**(3): p. 209-222.
- 102 Schütze, M., P.F. Tortorelli, and I.G. Wright, *Development of a Comprehensive Oxide Scale Failure Diagram*. Oxidation of Metals, 2010. **73**(3-4): p. 389-418.
- 103 Smialek, J.L., et al., *Effects of Hydrogen Annealing, Sulfur Segregation and Diffusion on the Cyclic Oxidation Resistance of Superalloys - a Review*. Thin Solid Films, 1994. **253**(1-2): p. 285-292.
- 104 Toma, D., W. Brandl, and U. Koster, *The characteristics of alumina scales formed on HVOF-sprayed MCrAlY coatings*. Oxidation of Metals, 2000. **53**(1-2): p. 125-137.
- 105 Rybicki, G.C. and J.L. Smialek, *Effect of the θ - α -Al₂O₃ transformation on the oxidation behavior of β -NiAl+ Zr*. Oxidation of Metals, 1989. **31**(3-4): p. 275-304.
- 106 Puetz, P., et al., *Characterization of transient oxide formation on CoNiCrAlY after heat treatment in vacuum and air*. Surface & Coatings Technology, 2010. **205**(2): p. 647-657.
- 107 Moseley, P., et al., *The microstructure of the scale formed during the high temperature oxidation of a FeCrAlloy steel*. Corrosion Science, 1984. **24**(6): p. 547-565.
- 108 Pint, B.A., J.R. Martin, and L.W. Hobbs, *18O/SIMS characterization of the growth mechanism of doped and undoped α -Al₂O₃*. Oxidation of Metals, 1993. **39**(3): p. 167-195.
- 109 Rommerskirchen, I., B. Eltester, and H.J. Grabke, *Oxidation of β -FeAl and Fe-Al alloys*. Materials and Corrosion, 1996. **47**(11): p. 646-649.
- 110 Nijdam, T.J., et al., *On the microstructure of the initial oxide grown by controlled annealing and oxidation on a NiCoCrAlY bond coating*. Oxidation of Metals, 2005. **64**(5-6): p. 355-377.

- 111 Matsumoto, M., *Development of plasma-sprayed thermal barrier coatings with low thermal conductivity and high oxidation resistance*. Journal of the Ceramic Society of Japan, 2007. **115**(1338): p. 118-123.
- 112 Chen, W.R., et al., *Pre-oxidation and TGO growth behaviour of an air-plasma-sprayed thermal barrier coating*. Surface & Coatings Technology, 2008. **202**(16): p. 3787-3796.
- 113 Saeidi, S., K.T. Voisey, and D.G. McCartney, *The Effect of Heat Treatment on the Oxidation Behavior of HVOF and VPS CoNiCrAlY Coatings*. Journal of Thermal Spray Technology, 2009. **18**(2): p. 209-216.
- 114 Zhou, C.G., H.B. Xu, and S.K. Gong, *Influence of water vapor on the cyclic-oxidation behavior of a low-pressure plasma-sprayed NiCrAlY coating*. Oxidation of Metals, 2004. **62**(3-4): p. 195-206.
- 115 Saunders, S.R.J., M. Monteiro, and F. Rizzo, *The oxidation behaviour of metals and alloys at high temperatures in atmospheres containing water vapour: A review*. Progress in Materials Science, 2008. **53**(5): p. 775-837.
- 116 Sullivan, M.H. and D.R. Mumm, *Transient stage oxidation of MCrAlY bond coat alloys in high temperature, high water vapor content environments*. Surface & Coatings Technology, 2014. **258**: p. 963-972.
- 117 Pace, M.T., R.C. Thomson, and J. Wells, *Oxidation of MCrAlY Coatings on Ni-Based Superalloys*. Superalloys 2008, 2008: p. 651-660.
- 118 Haynes, J.A., et al., *Impact of superalloy composition, bond coat roughness and water vapor on TBC lifetime with HVOF NiCoCrAlYHfSi bond coatings*. Surface and Coatings Technology, 2013. **237**: p. 65-70.
- 119 Ajdelsztajn, L., et al., *Oxidation behavior of HVOF sprayed nanocrystalline NiCrAlY powder*. Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing, 2002. **338**(1-2): p. 33-43.
- 120 Tang, F., L. Ajdelsztajn, and J.M. Schoenung, *Influence of cryomilling on the morphology and composition of the oxide scales formed on HVOF CoNiCrAlY coatings*. Oxidation of Metals, 2004. **61**(3-4): p. 219-238.
- 121 Wang, F., *The effect of nanocrystallization on the selective oxidation and adhesion of Al₂O₃ scales*. Oxidation of Metals, 1997. **48**(3-4): p. 215-224.
- 122 Gil, A., et al., *Effect of Surface Condition on the Oxidation Behaviour of MCrAlY*

- Coatings*. Surface & Coatings Technology, 2006. **201**(7): p. 3824-3828.
- 123 Scrivani, A., et al., *A comparative study of high velocity oxygen fuel, vacuum plasma spray, and axial plasma spray for the deposition of CoNiCrAlY bond coat alloy*. Journal of Thermal Spray Technology, 2003. **12**(4): p. 504-507.
 - 124 Higuera, V., F.J. Belzunce, and J. Riba, *Influence of the thermal-spray procedure on the properties of a CoNiCrAlY coating*. Surface & Coatings Technology, 2006. **200**(18-19): p. 5550-5556.
 - 125 Chen, W.R., et al., *TGO Growth Behaviour in TBCs With APS and HVOF Bond Coats*. Surface and Coatings Technology, 2008. **202**(12): p. 2677-2683.
 - 126 King, P., M. Yandouzi, and B. Jodoin, *The Physics of Cold Spray*, in *Modern Cold Spray: Materials, Process, and Applications*, J. Villafuerte, Editor. 2015, Springer International Publishing: Cham. p. 31-72.
 - 127 Alkhimov, A.P., et al., *Gas-dynamic spraying method for applying a coating*, in *Patent US 5302414*. 1994.
 - 128 Tokarev, A.O., *Structure of aluminum powder coatings prepared by cold gasdynamic spraying*. Metal Science and Heat Treatment, 1996. **38**(3-4): p. 136-139.
 - 129 Dykhuizen, R.C., et al., *Impact of high velocity cold spray particles*. Journal of Thermal Spray Technology, 1999. **8**(4): p. 559-564.
 - 130 Stoltenhoff, T., H. Kreye, and H.J. Richter, *An analysis of the cold spray process and its coatings*. Journal of Thermal Spray Technology, 2002. **11**(4): p. 542-550.
 - 131 Assadi, H., et al., *Bonding Mechanism in Cold Gas Spraying*. Acta Materialia, 2003. **51**(15): p. 4379-4394.
 - 132 Gärtner, F., et al., *The Cold Spray Process and Its Potential for Industrial Applications*. Journal of Thermal Spray Technology, 2006. **15**(2): p. 223-232.
 - 133 Li, C.J., W.Y. Li, and H.L. Liao, *Examination of the critical velocity for deposition of particles in cold spraying*. Journal of Thermal Spray Technology, 2006. **15**(2): p. 212-222.
 - 134 Julio, V., *Current and Future Applications of Cold Spray Technology*. Metal finishing, 2010.
 - 135 Singh, H., T.S. Sidhu., and S.B.S. Kalsi., *Cold spray technology: future of coating*

- deposition processes*. *Frattura ed Integrità Strutturale*, 22 (2012) 2012. **22**: p. 17.
- 136 Wu, X., et al., *Advanced cold spray technology: Deposition characteristics and potential applications*. *Science China Technological Sciences*, 2012. **55**(2): p. 357-368.
 - 137 Grigoriev, S., et al., *Cold spraying: From process fundamentals towards advanced applications*. *Surface & Coatings Technology*, 2015. **268**: p. 77-84.
 - 138 Xiong, T.Y., et al., *Introduction to a new technology - Cold gas dynamic spray*. *Corrosion Science & Technology Protection (Chinese)*, 2001. **13**(5): p. 267-269.
 - 139 Irissou, E., et al., *Review on Cold Spray Process and Technology: Part I-Intellectual Property*. *Journal of Thermal Spray Technology*, 2008. **17**(4): p. 495-516.
 - 140 Papyrin, A., et al., *Cold Spray Technology*. 2007, Oxford: Elsevier. 1-328.
 - 141 Maev, R.G.L., Volf *Introduction to Low Pressure Gas Dynamic Spray*, in *Technology & Engineering*. 2009.
 - 142 Ajdelsztajn, L., et al., *Cold Spray Deposition of Nanocrystalline Aluminum Alloys*. *Metallurgical and Materials Transactions a-Physical Metallurgy and Materials Science*, 2005. **36A**(3): p. 657-666.
 - 143 Kim, H.J., C.H. Lee, and S.Y. Hwang, *Fabrication of WC-Co coatings by cold spray deposition*. *Surface & Coatings Technology*, 2005. **191**(2-3): p. 335-340.
 - 144 Pattison, J., et al., *Cold Gas Dynamic Manufacturing: A Non-Thermal Approach to Freeform Fabrication*. *International Journal of Machine Tools & Manufacture*, 2007. **47**(3-4): p. 627-634.
 - 145 Wikipedia. *de Laval nozzle*. [cited 2018 April 23]; Available from: https://en.wikipedia.org/wiki/De_Laval_nozzle.
 - 146 Van Steenkiste, T.H., et al., *Kinetic spray coatings*. *Surface & Coatings Technology*, 1999. **111**(1): p. 62-71.
 - 147 Pritchard, P.J., R.W. Fox, and A.T. McDonald, *Fox and McDonald's introduction to fluid mechanics*. 8th ed. 2011, Hoboken, NJ: John Wiley & Sons, Inc. xviii, 875 p.
 - 148 Jodoin, B., *Cold Spray Nozzle Mach Number Limitation*. *Journal of Thermal Spray Technology*, 2002. **11**(4): p. 496-507.
 - 149 Grujicic, M., et al., *Adiabatic shear instability based mechanism for particles/substrate*

- bonding in the cold-gas dynamic-spray process*. Materials & Design, 2004. **25**(8): p. 681-688.
- 150 Schmidt, T., et al., *From Particle Acceleration to Impact and Bonding in Cold Spraying*. Journal of Thermal Spray Technology, 2009. **18**(5-6): p. 794-808.
 - 151 Hussain, T., et al., *Bonding Mechanisms in Cold Spraying: The Contributions of Metallurgical and Mechanical Components*. Journal of Thermal Spray Technology, 2009. **18**(3): p. 364-379.
 - 152 Grujicic, M., et al., *Computational analysis of the interfacial bonding between feed-powder particles and the substrate in the cold-gas dynamic-spray process*. Applied Surface Science, 2003. **219**(3-4): p. 211-227.
 - 153 Varacalle, D.J., et al., *Effect of grit-blasting on substrate roughness and coating adhesion*. Journal of Thermal Spray Technology, 2006. **15**(3): p. 348-355.
 - 154 Samson, T., et al., *Effect of Pulsed Waterjet Surface Preparation on the Adhesion Strength of Cold Gas Dynamic Sprayed Aluminum Coatings*. Journal of Thermal Spray Technology, 2015. **24**(6): p. 984-993.
 - 155 Champagne, V.K., et al., *Interface material mixing formed by the deposition of copper on aluminum by means of the cold spray process*. Journal of Thermal Spray Technology, 2005. **14**(3): p. 330-334.
 - 156 Van Steenkiste, T.H., J.R. Smith, and R.E. Teets, *Aluminum coatings via kinetic spray with relatively large powder particles*. Surface and Coatings Technology, 2002. **154**(2): p. 237-252.
 - 157 Zhang, D., P.H. Shipway, and D.G. McCartney, *Cold gas dynamic spraying of aluminum: The role of substrate characteristics in deposit formation*. Journal of Thermal Spray Technology, 2005. **14**(1): p. 109-116.
 - 158 Chen, C.Y., et al., *On the role of oxide film's cleaning effect into the metallurgical bonding during cold spray*. Materials Letters, 2018. **210**: p. 199-202.
 - 159 Richer, P., *Development of Conventional and Nanocrystalline Bond Coats by Cold Gas Dynamic Spraying for Aerospace Thermal Barrier Coatings*. 2010, University of Ottawa.
 - 160 Roy, J.-M.L., *Development of Cold Gas Dynamic Spray Nozzle and Comparison of Oxidation Performance of Bond Coats for Aerospace Thermal Barrier Coatings at Temperatures of 1000°C and 1100°C*. 2012, University of Ottawa.

- 161 Grunling, H.W., H. Rechtenbacher, and L. Singheiser, *Some practical aspects of corrosion and coatings in utility gas turbines*. High Temperature Corrosion and Protection of Materials, 1997. **251-254**: p. 483-502.
- 162 Wu, F., H. Murakami, and A. Suzuki, *Development of an iridium-tantalum modified aluminide coating as a diffusion barrier on nickel-base single crystal superalloy TMS-75*. Surface & Coatings Technology, 2003. **168**(1): p. 62-69.
- 163 Ichikawa, Y. and K. Ogawa, *Critical Deposition Condition of CoNiCrAlY Cold Spray Based on Particle Deformation Behavior*. Journal of Thermal Spray Technology, 2017. **26**(3): p. 340-349.
- 164 Liu, Z.Y., et al., *Oxidation Behaviour of Sputter-Deposited Ni-Cr-Al Micro-Crystalline Coatings*. Acta Materialia, 1998. **46**(5): p. 1691-1700.
- 165 Iqbal, P., J. Preece, and P. Mendes, *Nanotechnology: The “Top-Down” and “Bottom-Up” Approaches*, in *Supramolecular Chemistry: From Molecules to Nanomaterials*, P.A. Gale and J.W. Steed, Editors. 2012, John Wiley & Sons, Ltd.: Online.
- 166 Koch, C.C., *Top-down synthesis of nanostructured materials: Mechanical and thermal processing methods*. Reviews on Advanced Materials Science, 2003. **5**(2): p. 91-99.
- 167 Yang, L., et al., *Effects of surface finish of single crystal superalloy substrate on cyclic thermal oxidation of its nanocrystalline coating*. Corrosion Science, 2016. **111**: p. 313-324.
- 168 Ma, K.K. and J.M. Schoenung, *Influence of cryomilling on the microstructural features in HVOF-sprayed NiCrAlY bond coats for thermal barrier coatings: Creation of a homogeneous distribution of nanoscale dispersoids*. Philosophical Magazine Letters, 2010. **90**(10): p. 739-751.
- 169 King, P.C., S.H. Zahiri, and M. Jahedi, *Microstructural Refinement within a Cold-Sprayed Copper Particle*. Metallurgical and Materials Transactions A, 2009. **40**(9): p. 2115-2123.
- 170 Zou, Y., et al., *Dynamic recrystallization in the particle/particle interfacial region of cold-sprayed nickel coating: Electron backscatter diffraction characterization*. Scripta Materialia, 2009. **61**(9): p. 899-902.
- 171 Zou, Y., et al., *Microstructure and nanohardness of cold-sprayed coatings: Electron backscattered diffraction and nanoindentation studies*. Scripta Materialia, 2010. **62**(6): p. 395-398.

- 172 Rokni, M.R., C.A. Widener, and V.R. Champagne, *Microstructural Evolution of 6061 Aluminum Gas-Atomized Powder and High-Pressure Cold-Sprayed Deposition*. Journal of Thermal Spray Technology, 2014. **23**(3): p. 514-524.
- 173 Wilson, B.C., J.A. Hickman, and G.E. Fuchs, *The Effect of Solution Heat Treatment on a Single-Crystal Ni-Based Superalloy*. JOM, 2003. **55**(3): p. 35-40.
- 174 Lau, H., et al., *Influence of bondcoat pre-treatment and surface topology on the lifetime of EB-PVD TBCs*. Surface & Coatings Technology, 2003. **165**(3): p. 217-223.
- 175 Guo, D.L., et al., *Cold Spray MCrAlY Coatings on Single-Crystal Superalloy Using Nitrogen: Properties and Economics*. Journal of Thermal Spray Technology, 2020. **29**(7): p. 1628-1642.
- 176 Guo, D., et al., *Cold spray for production of in-situ nanocrystalline MCrAlY coatings – Part I: Process analysis and microstructure characterization*. Surface and Coatings Technology, 2021. **409**: p. 126854.
- 177 Guo, D., L. Zhao, and B. Jodoin, *Cold spray for production of in-situ nanocrystalline MCrAlY coatings – Part II: Isothermal oxidation performance*. Surface and Coatings Technology, 2021. **409**: p. 126828.
- 178 Harris, K., et al., *Development of the Rhenium Containing Superalloys CMSX-4(R) and CM 186 LC(R) for Single-Crystal Blade and Directionally Solidified Vane Applications in Advanced Turbine-Engines*. Superalloys 1992, 1992: p. 297-306.
- 179 Gilles, R., et al., *Investigations of early stage precipitation in a tungsten-rich nickel-base superalloy using SAXS and SANS*. Journal of Alloys and Compounds, 2014. **612**: p. 90-97.
- 180 Liu, Z.Y., et al., *The effect of coating grain size on the selective oxidation behaviour of Ni-Cr-Al alloy*. Scripta Materialia, 1997. **37**(10): p. 1551-1558.
- 181 Liu, Z.Y. and W. Gao, *Oxidation behaviour of microcrystalline Ni-Cr-Al alloy coatings at 900 degrees C*. Scripta Materialia, 1998. **38**(6): p. 877-885.

Appendix

To avoid lengthy and heavy methodology details and improve the text readability, some equipment used in the thesis work was not shown in Chapter 4 and instead was provided here. These include the equipment and apparatus for metallographic sample preparation, oxidation test, powder reclamation, and materials characterization.

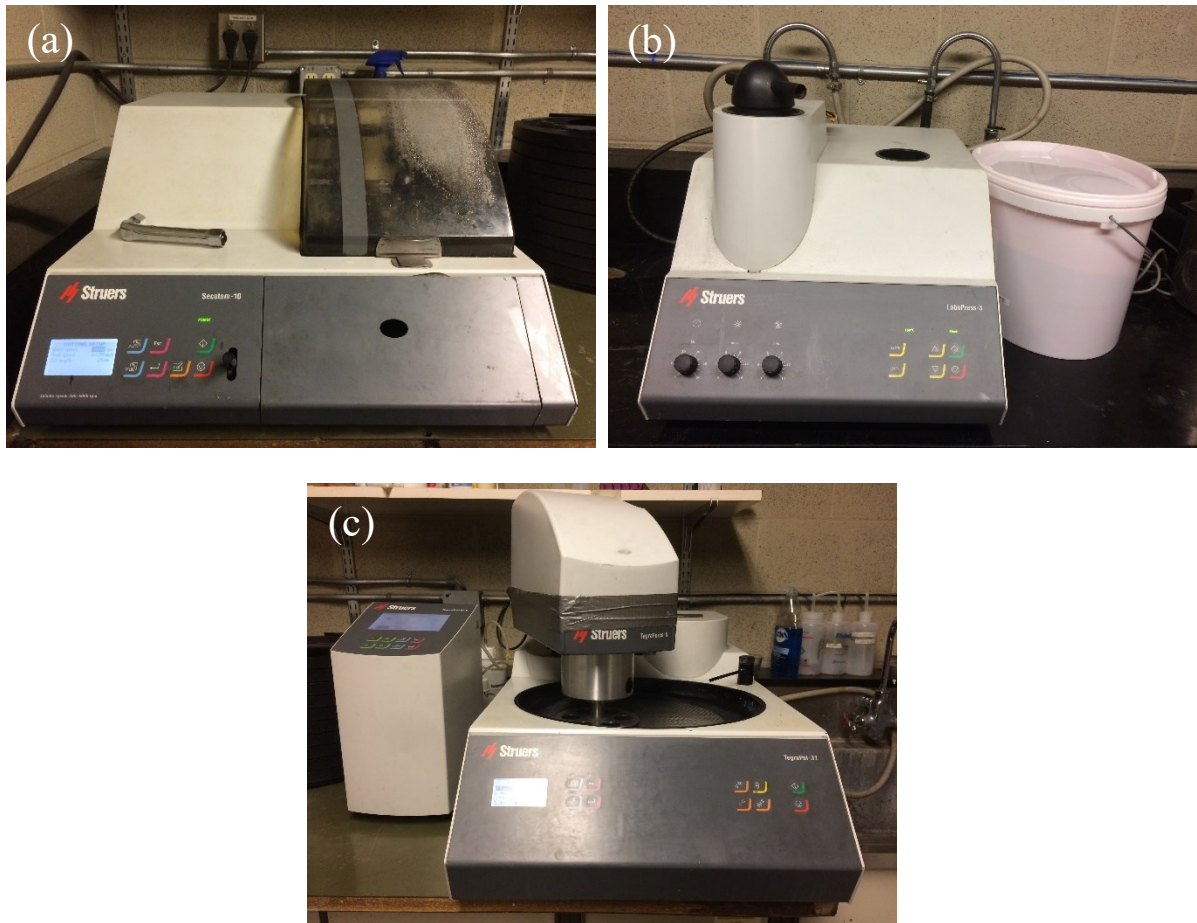


Figure A.1 Metallographic sample preparation equipment: (a) sectioning (Struers Secotom-10), (b) mounting (Struers LaboPress-3), and (c) grinding and polishing (Struers TegraPol-31, TegraForce-5, and TegraDoser-5).

Procedures recommended by Struers were used for the sample sectioning and mounting. Typical polishing procedures used comprised a coarse grinding (3-5 mins on MD-Piano120 plate with water, comparable to SiC paper grit 120), a fine grinding (3 mins on MD-Allego

Plate with 9-micron water-based diamond suspension, comparable to SiC paper grit 500), a coarse polishing (3 mins on MD-Mol Plate with 3-micron water-based diamond suspension), and a fine polishing (1 min on MD-Chem Plate with 0.25-micron colloidal silica suspension).



Figure A.2 Laboratory furnace (Lindberg/Blue M™, Thermo Scientific™) for superalloy heat treatments and isothermal oxidation evaluation

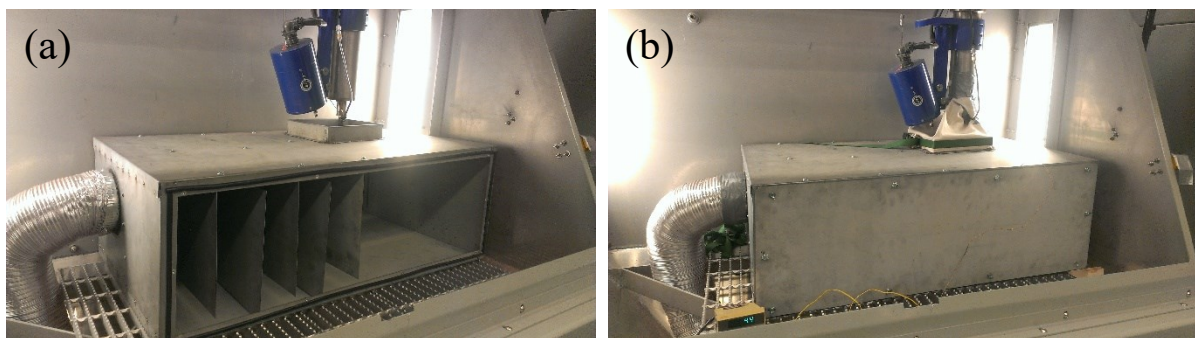


Figure A.3 In-house powder reclamation apparatus: (a) open view without the front panel, and (b) enclosed setup during an actual spray.

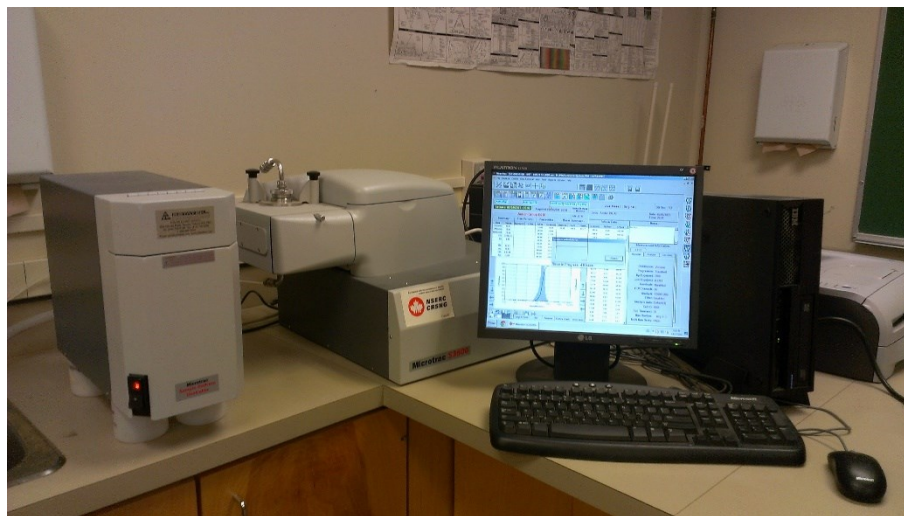


Figure A.4 Laser diffraction analyzer (Microtrac S3500, Nikkiso, Japan) for particle size distribution analysis

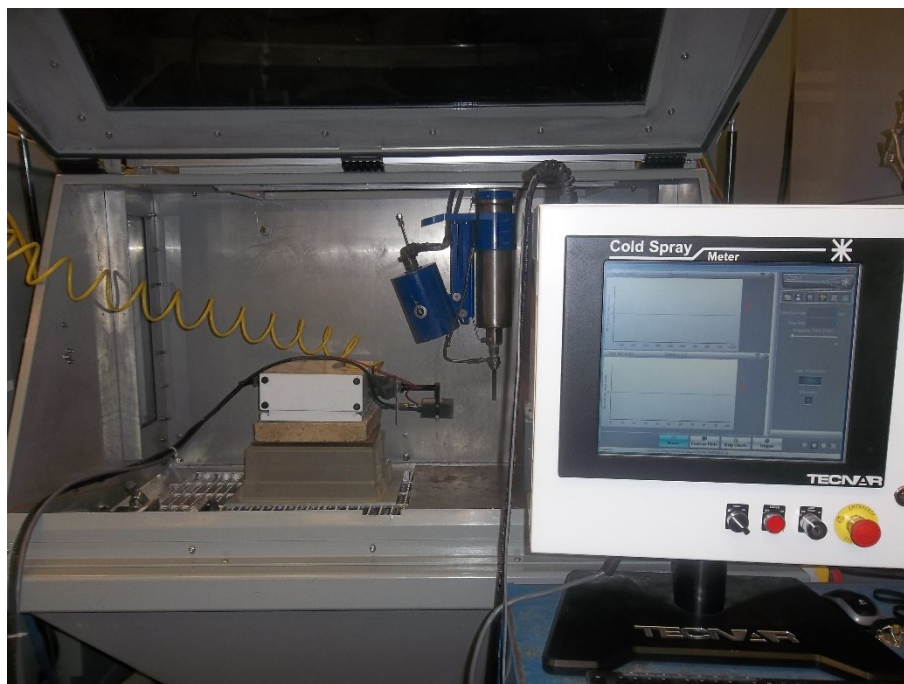


Figure A.5 Laser Doppler velocimetry meter (ColdSprayMeter, Tecnar, Canada) for particle velocity distributions analysis



Figure A.6 Stylus surface roughness tester (SRG-4000, Phase II Plus, USA)

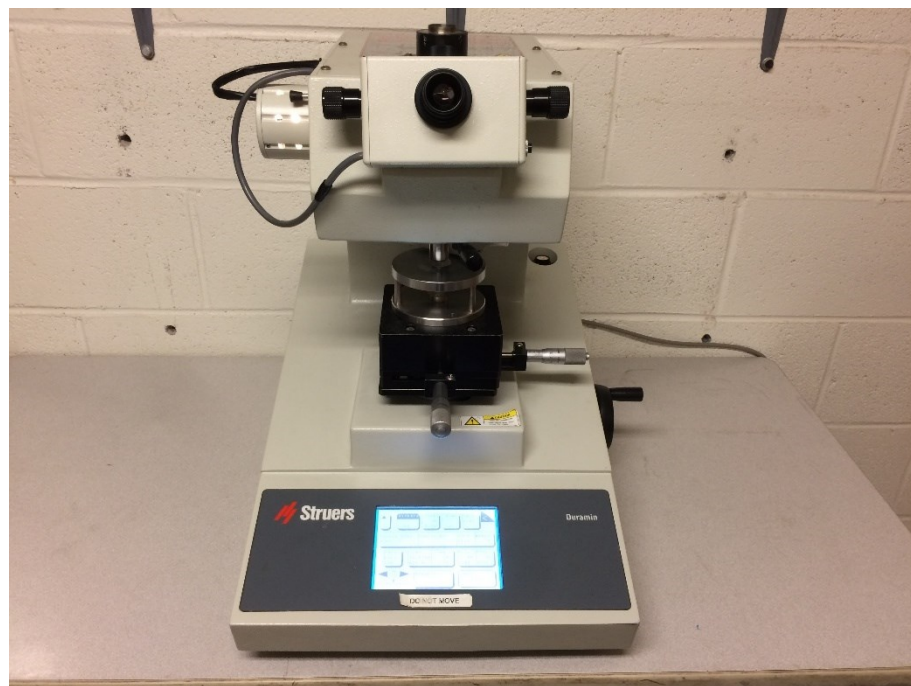


Figure A.7 Vickers Microhardness Tester (Duramin-1, Struers, Denmark)

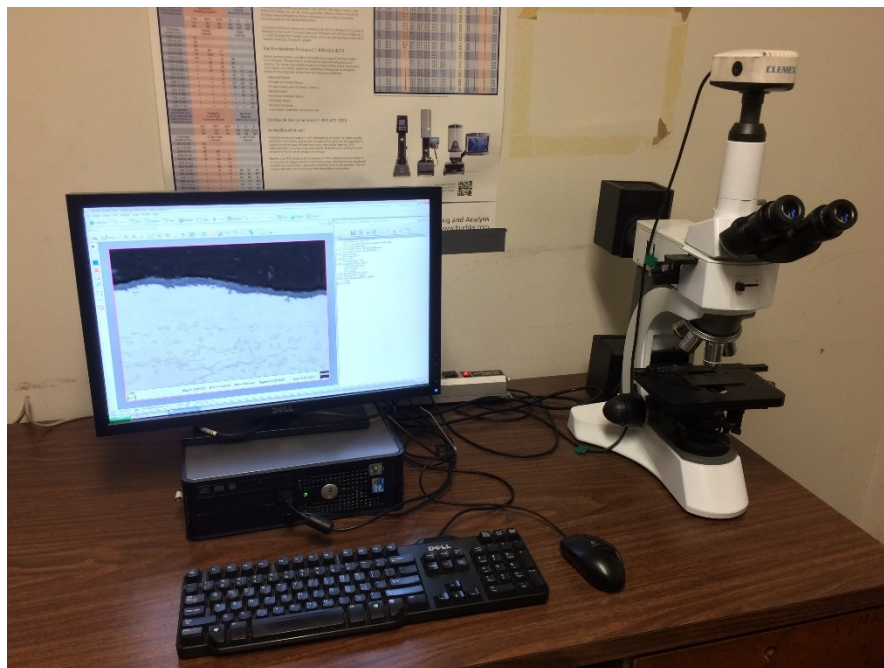


Figure A.8 Optical microscope (NMM-800TRF, Kingdak, China) equipped with digital camera and image analysis software (Vision Lite, Clemex, Canada) for coating porosity and thickness measurement

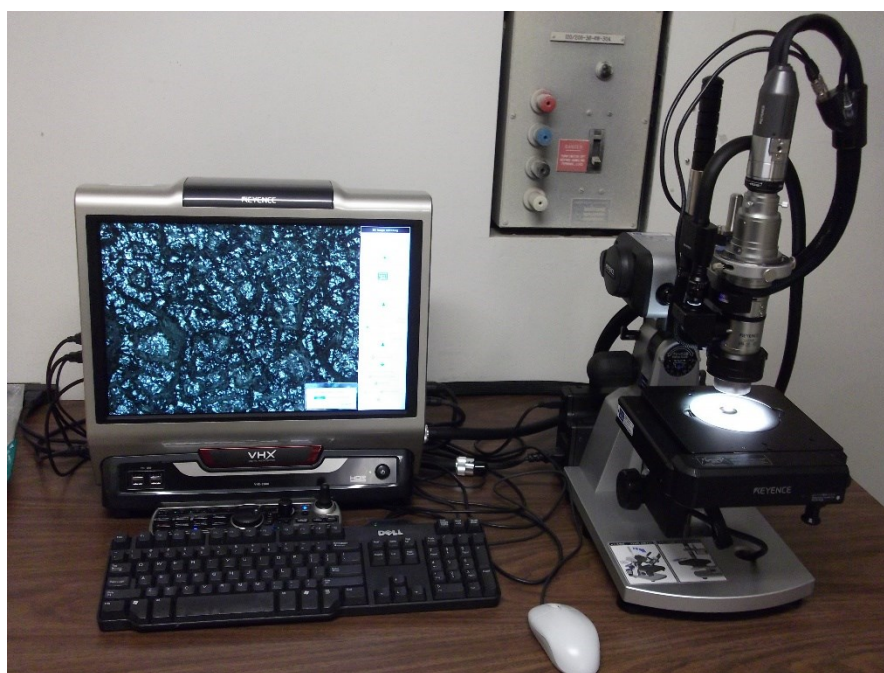


Figure A.9 Three-dimensional optical microscope (VHX-2000, Keyence, Osaka, Japan) for general sample examination



Figure A.10 Scanning electron microscope (SEM) (EVO-MA10, Zeiss, Germany) equipped with energy-dispersive X-ray spectrometer (EDS) (INCA-x-act, Oxford Instruments, UK) for microstructure and chemical composition characterization

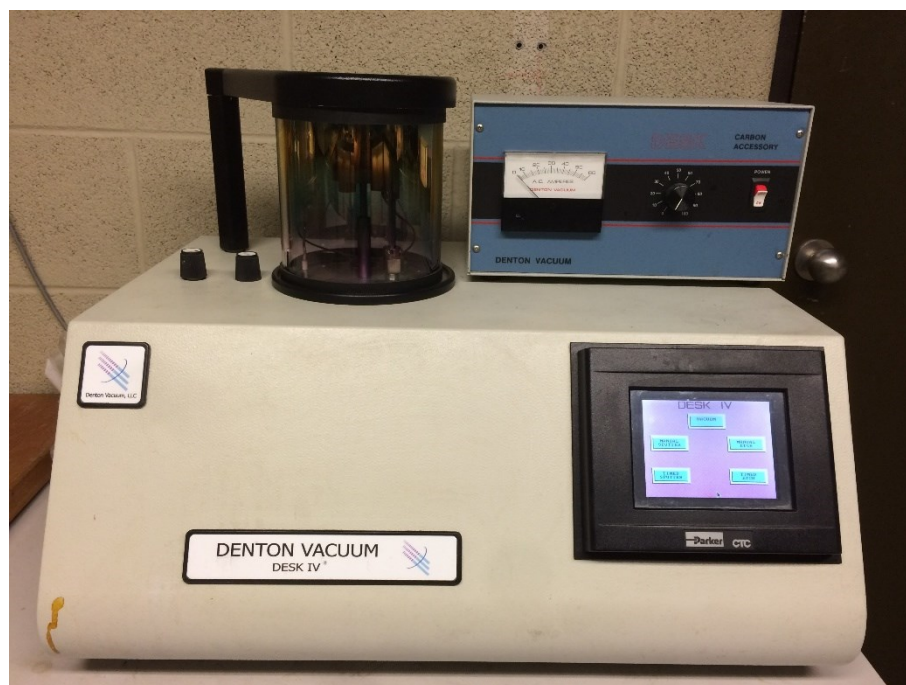


Figure A.11 Gold sputter (Desk IV, Denton Vacuum, Moorestown, USA) for depositing a thin conductive layer on samples prior to SEM examination