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Development of Conventional and Nanocrystalline Bond Coats by Cold Gas Dynamic Spraying for Aerospace Thermal Barrier Coatings

By

Patrick Richer

Thesis submitted to the Department of Mechanical Engineering in
conformity with the requirements for the degree of Doctorate of
Science (Engineering)

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Abstract

Gas turbine engines are considered to be among the most hostile operating environments for conventional material systems. Increasing demands for higher engine performance and durability of components have led to the development of thermal barrier coating (TBC) systems. Typical TBC systems consist of two coating layers: an insulating ceramic top coat for thermal protection and an underlying metallic bond coat for improved adhesion of the top coat and better chemical protection against high temperature oxidation and hot corrosion. However, current use of these coating systems is limited due to their premature failure which is associated to cracking and delaminating of the ceramic top coat. It is generally accepted that the primary mechanism responsible for TBC failure is attributed to oxidation of the bond coat which results in the formation of an oxide scale at the interface between the bond coat and ceramic top coat and eventually causes cracking and delamination of the top coat. Better understanding and control of the bond coat oxidation dynamics is therefore of primary importance for the development of TBC systems with improved performance.

The bond coat is commonly manufactured by thermal spray techniques: the bond coat material, initially in powder form, is heated beyond its melting point, projected onto the surface to be coated and finally re-solidified upon cooling to form a coating. It has been demonstrated that certain microstructural features of the bond coat that are detrimental to its oxidation behaviour originate from thermally induced effects encountered during thermal spraying. Therefore, it is expected that improved bond coat oxidation behaviour could be achieved if the deposition process did not involve significant heating of the material.

Recent developments in the surface and coatings industry have given rise to a new coating technology known as Cold Gas Dynamic Spraying (CGDS). As its name implies, this process does not rely on thermal energy for the formation of coatings, but rather on kinetic energy: particles are accelerated above a critical velocity and plastically deform upon impact on the substrate to adhere and form a coating. Due to the absence of significant heating of the sprayed material, this work aims to manufacture bond coats using the CGDS deposition technique and investigate whether improved oxidation behaviour can be achieved.

The present thesis provides a description of the experimental approaches considered for the development of CGDS bond coats with improved oxidation behaviour. Given the complexity of TBC systems due to the various interactions between the multiple coating layers, this work strictly concentrates on the bond coat layer without the presence of the superalloy substrate or ceramic top coat, thereby allowing the thorough characterization of the bond coat oxidation behaviour as a function of the initial powder microstructure and different deposition techniques. As such, the objectives of this work are to demonstrate the feasibility of manufacturing bond coats using the CGDS technique, optimize the deposition process for the materials considered, verify whether the CGDS process induces microstructural changes in the deposited material and finally evaluate and compare the oxidation behaviour of CGDS bond coats with those of thermal sprayed bond coats.

Results of this work show that bond coatings with conventional and nanocrystalline microstructures were successfully manufactured by the CGDS system developed at the University of Ottawa Cold Spray Laboratory. Optimal spraying parameters were also identified and coatings with low levels of porosity were successfully deposited using this technique. Investigation of the original feedstock powder and resulting coating microstructures revealed that significant microstructural transformations had occurred throughout the CGDS deposition process as a result of extensive plastic deformation of the particles. Isothermal oxidation testing was also carried out on both the conventional and nanocrystalline CGDS coatings. For comparison purposes, thermal spray coatings were also manufactured (using the air plasma spray and high velocity oxy-fuel processes) and subjected to oxidation testing. Results showed that low temperature processing of bond coat materials is beneficial to their oxidation behaviour as it results in coatings with low porosity and limited oxide content, thereby leading to lower oxide growth rates. Furthermore, the CGDS process was observed to produce coatings characterized with fine grain structures (either by means of a grain refinement process of the conventional material or by preserving the fine grain structure of the nanocrystalline material) which was also shown to be beneficial to the oxidation behaviour. Results from this work therefore demonstrate that potentially significant improvements to TBC performance could be achieved by manufacturing bond coats using the CGDS deposition technique.

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List of Symbols

Nomenclature

A	Cross-sectional flow area of the nozzle	q_L	Laminar heat flux
A_p	Cross-sectional area of the particle	q_T	Turbulent heat flux
a_p	Acceleration of a particle	R	Specific gas constant
c	Speed of sound	S_{ij}	Stress tensor
C_D	Drag coefficient	t	Time
$C_{\varepsilon 1}$	Closing coefficient	T	Gas temperature
$C_{\varepsilon 2}$	Closing coefficient	u	Axial velocity
C_μ	Closing coefficient	u_p	Particle velocity
C_p	Gas heat capacitance at constant pressure	v	Radial velocity
C_v	Gas heat capacitance at constant volume	x	Independent space coordinate
E	Specific internal energy	ρ	Gas density
F_D	Drag force on a particle	λ	First viscosity coefficient
H	Specific enthalpy	μ	Second viscosity coefficient
k	Specific turbulent kinetic energy	μ_T	Turbulent viscosity
M	Mach number	ε	Specific dissipation of turbulent energy
$\dot{m}$	Mass flow rate	σ_k	Closing coefficient
m_p	Particle mass	σ_ε	Closing coefficient
P	Gas pressure	τ_{ij}	Shear stress tensor
Pr_T	Turbulent Prandtl number	ν	Kinematic viscosity
		γ	Specific heat ratio

Subscripts and Superscripts

0	Flow stagnation properties
$*$	Nozzle throat conditions
e	Nozzle exit area conditions
B	Chamber discharge conditions
p	Particle conditions
i, j, k	Vectorial coordinates

Chemical compounds

Al_2O_3	Aluminium oxide, also known as alumina. Forms the thermally grown oxide on the surface of the bond coat upon oxidation. Formation of alumina in preference to other oxides is desirable as it has a slow growth rate and improves TBC performance.
$\alpha-Al_2O_3$	This is the most desirable type of oxide to form in the thermally grown oxide during oxidation of the bond coat. Due to its low diffusivity of oxygen and stability at elevated temperatures, it reduces the subsequent rate of oxidation.
<i>AMDRY 9951</i>	Commercially available CoNiCrAlY powder from Sulzer Metco with a fine particle size distribution (5-37 μ m).
<i>AMDRY 9954</i>	Commercially available CoNiCrAlY powder from Sulzer Metco with a coarse particle size distribution (11-62 μ m).
$\beta-NiAl$	Intermetallic precipitate phase in a MCrAlY bond coat material composed of NiAl with a bcc crystal lattice. This phase is Al-rich and acts as an aluminum reservoir for the formation
<i>CoNiCrAlY</i>	Alloy composed of Cobalt, Nickel, Chrome, Aluminum, and Yttrium commonly used as a bond coat material.
<i>MCrAlY</i>	Family of alloys commonly used as a bond coat material where M stands for Ni, Co or both.
<i>NiO</i>	Nickel oxide that can form in the thermally grown oxide. Characterized with a rapid growth rate, this oxide is detrimental to TBC performance and is thus undesirable.
$(Ni,Co)(Al,Cr)_2O_4$	Spinel-type oxides such as $NiCr_2O_4$, $NiAl_2O_4$, $CoAl_2O_4$, $CoCr_2O_4$ and $NiCo_2O_4$, or a substitutional solid solution of $(Ni,Co)(Al,Cr)_2O_4$. Characterized with rapid growth rates, these oxide are detrimental to TBC performance and are thus undesirable.
θ or $\gamma-Al_2O_3$	Metastable alumina phases formed in the thermally grown oxide during oxidation of the bond coat. Usually the result of rapid heating rates. These phases have been observed to transform into $\alpha-Al_2O_3$ after prolonged high temperature exposure.
γ -Matrix	Dominant phase in a MCrAlY bond coat material that forms a matrix in which β -NiAl precipitates are formed. Typically composed of a Co-Ni-Cr solid solution with a fcc crystal lattice.
YSZ	Ytria stabilized zirconia. Ceramic material commonly used as the ceramic top coat in thermal barrier coatings.

Chapter 1 - Introduction

1.1 Background

The hot sections of gas turbine engines are considered to be among the most hostile operating environments for material systems. Repeated exposure to high operating temperatures, intensive loading conditions and corrosive/erosive media has led to important design challenges in the gas turbine industry. Additionally, increasing demands for higher performance has led to increasingly rigorous operating conditions. One of the most important variables in the design process of a gas turbine engine is the selection of an appropriate turbine inlet temperature (TIT). Simple thermodynamic modelling shows a significant improvement of engine performance with increasing TIT, thus fuelling the desire for higher operating temperatures. Unfortunately, higher operating temperatures also result in increased thermal stresses, more severe oxidation and corrosion conditions as well as decreased material properties, which all combine to reduce the life of gas turbine engines. Typically, the maintenance costs associated with the replacement of damaged components as well as general safety issues overshadow the performance benefits of operating at higher TIT.

In an attempt to develop engine components capable of withstanding and operating at higher temperatures, researchers have explored various approaches and numerous new technologies. As a result, the average TIT in gas turbine engines has increased over the last twenty years from the range of 1200K-1300K up to 1700K-1800K [1]. This has been made possible in part due to the development of numerous high-temperature resistant nickel-based superalloys which have allowed turbine blades and nozzle vanes to withstand higher loads at temperatures above 1000°C. Most of the research work performed on superalloys has focused on increasing their strength and mechanical properties at elevated temperatures by means of composition refinement, directional grain growth and single crystal alloy development [2, 3]. Despite significant advances, further improvement by means of superalloy development appears unlikely given that they already operate at nearly 90% of their melting temperature [4].

In addition to the use of such superalloys, sophisticated cooling techniques have been developed to further reduce the surface temperature of engine components, thus allowing for a greater TIT. Integration of such cooling techniques in turbine blade design has allowed the blade surface temperature to be maintained nearly 400°C lower than the gas temperature [1]. It should however be noted that the cooling air is typically drawn from the compressor discharge and therefore does not contribute to the production of work in the turbine. Additionally, the use of extensive cooling also leads to higher compressor work requirements given that more cooling air must be compressed. Multiple blade cooling configurations have been developed to help reduce the significance of these drawbacks; however they are all inevitably restricted by similar limitations. As a result, despite important contributions to engine innovation, component cooling technologies have matured and further improvement to engine performance by means of surface cooling has been mostly exhausted.

Another approach to be considered for increased durability and performance of hot-engine components is the use of protective coatings. Coatings in general have been applied as a thin layer (typically less than 500µm) to a wide range of surfaces in numerous applications in an attempt to enhance key surface properties. Coatings can be used to protect a mechanical component from wear, corrosion, oxidation, thermal degradation or any other undesirable surface phenomena [5]. Coatings have also been used for dimensional restoration, lubrication films, abrasive reactivity, seals, biomedical activity and electromagnetic properties control [6]. As such, coatings can be viewed as a solution to many engineering problems, and given their flexibility, broad range of applicability and cost-effectiveness, it is no surprise that the field of coatings and surface technology has become an important worldwide industry. For example, the global thermal spray market in 2004 was estimated at \$5.2 billion, and 60% of the overall market for coating technologies originated from the turbine industry [6].

In the case of gas turbine engine components, the key surface properties to be enhanced are thermal protection from the high temperature environment as well as oxidation and hot-corrosion resistance. The application of protective coatings on the surface of superalloy components in gas turbine engines can be traced back to the 1960s when diffusion aluminide coatings were first introduced [1]. This technology relied on the formation of a coating by means of a chemical reaction and diffusion of metallic constituents on the surface of the part

to be coated. Meanwhile, other coating technologies were evolving such as plasma spray and physical vapour deposition, which allowed the formation of overlay coatings and opened up new possibilities for improved performance. Overlay coatings are defined as materials that are added to an existing surface (called substrate) by a process that prevents mixing between the coating and substrate, thus preserving the composition of the base material [5]. Overlay coatings were first applied on turbine blades in the 1980s and had the advantage of allowing for a better control of the coating composition, thickness and combination of physical-chemical and mechanical properties [1].

A new stage of progress in the field of turbine blade protection was achieved when the first thermal barrier coating (TBC) systems were introduced. These coating systems are deposited on the superalloy engine component and feature two distinct coating layers: the outermost layer is a ceramic top coat that provides thermal protection while the innermost layer is a metallic bond coat that promotes bonding between the ceramic top coat and underlying superalloy. The bond coat is also designed to promote chemical protection to the superalloy engine components: the ceramic top coat is porous and allows oxygen from the hot combustion gases to diffuse across its thickness, thus offering little protection from oxidation and/or hot-corrosion. TBC systems are considered state-of-the-art technology in the aerospace industry and have been the focus of numerous studies and research projects for many years. The application of the bond coat material as a stand-alone protective overlay coating for improved oxidation and corrosion resistance has also become common on components of gas turbine engines that do not specifically require the ceramic top coat for thermal protection.

TBC systems and overlay bond coats are typically manufactured by thermal spraying techniques such as plasma spraying and high-velocity oxy-fuel (HVOF). In thermal spraying, coatings are manufactured at relative high rates by depositing liquid droplets or semi molten particles of the coating material on a substrate. The coating feedstock material is initially in the form of powder, wires or rods, and melting of the material is achieved by means of a heat source such as a plasma jet, electric arc or flame. The molten material is then atomized and/or propelled toward the substrate by process gases flowing through a nozzle (Figure 1.1a). When the particles strike the substrate, they flatten and form splats which rapidly solidify, thus forming a coating (Figure 1.1b). Thermal spraying can be used to deposit a wide range

of materials such as pure metals and alloys, ceramics, ceramic-metal composites (cermets), polymers and nanomaterials [5].

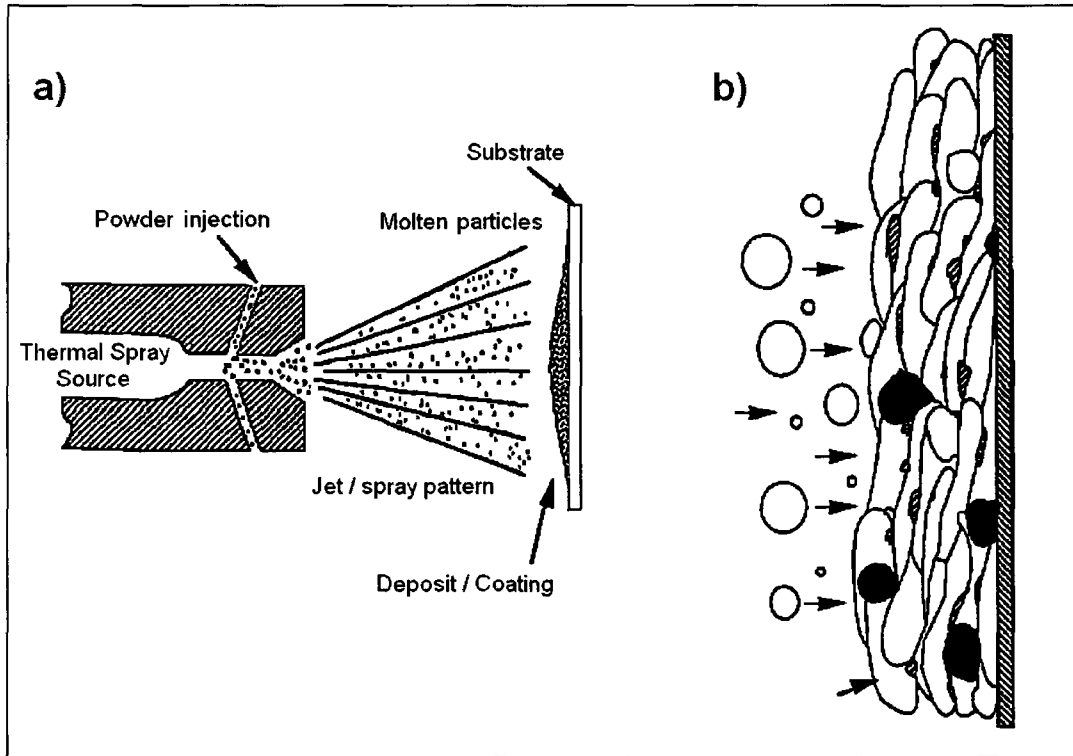


Figure 1.1: Schematic representation of (a) the thermal spray coating process and (b) the formation of a coating by means of material splats resulting from the impact of molten particles on the substrate (adapted from [5])

The physical, chemical and mechanical properties of any coating are strongly dependant on its microstructure. Typically, coatings that exhibit low oxide content and are free of visible defects such as cracks and porosity offer the best mechanical and chemical properties and are therefore desirable. Although thermal spraying offers excellent flexibility for the manufacturing of coatings, it has also been observed to introduce certain defects in the coatings microstructure. Firstly, contraction of the deposited splats upon solidification can lead to increased porosity and the occurrence of tensile residual stresses, which can impede the coating's resistance to fatigue. Secondly, the high process temperatures tend to favour oxidation of the sprayed material, thus resulting in the inclusion of oxides in the coating known as oxide stringers. The presence of such oxides in the coating microstructure can

cause increased hardness, embrittlement, and loss of cohesive strength of the coating. Oxide stringers can also become nucleation sites for further oxidation in high temperature applications and are therefore often viewed as detrimental to the coating oxidation behaviour. Finally, the melting and solidification of the sprayed material inevitably causes microstructural transformations such as grain growth which limits control of the final coating properties. This is especially problematic for the deposition of materials with very fine grain structures such as nanocrystalline materials. Although the severity of these defects can be minimized by adjusting the spraying parameters, the defects can never be eliminated completely. As a result, thermally sprayed coatings exhibit microstructures and compositions that are, to various extents, different to those of the original feedstock powders. Given that these powders are specifically and carefully designed to achieve optimal material performance, any change with respect to the original powder composition and microstructure during the deposition process can be considered to reduce the coating's effectiveness. Therefore, recent trends in the thermal spray industry have resulted in the development of new coating technologies that aim at mitigating these defects and improve control of the material properties throughout deposition. Emphasis on reducing the process temperature to limit the oxidation levels and increasing particle velocities to promote deformation and reduce porosity has led to the development of a variety of spray techniques known as kinetic spraying.

Kinetic spraying is a relatively new coating technology that relies on the kinetic energy of the sprayed particles as opposed to thermal energy in order to produce a coating. The current most popular kinetic spraying process is known as Cold Gas Dynamic Spraying (CGDS). CGDS is an emerging and promising high rate material deposition process that uses a supersonic gas flow to accelerate powder particles above a material dependant critical velocity. Upon impact, the particles having sufficient kinetic energy deform plastically and adhere to the substrate to produce a coating [7]. As opposed to traditional thermal spraying techniques, the relatively low process temperature in CGDS does not cause significant heating, softening or melting of the feedstock particles and has therefore shown better potential for preserving the sprayed material's microstructure. Additionally, CGDS coatings typically exhibit no thermal shrinkage and very low oxide contents. Given this ability to

better preserve the original feedstock powder microstructure, CGDS has been viewed as a deposition process that offers better control of its coating properties.

As can be expected, TBCs and overlay bond coats are not immune to the influences of defects and microstructural changes introduced by thermal spraying. As will be discussed later, the properties of the bond coat, especially its oxidation behaviour, are critical for its durability as a stand-alone coating as well as for the performance of TBC systems. It has been shown that some of the microstructural changes and oxide inclusions introduced by thermal spraying have a detrimental effect on the bond coat oxidation behaviour, thus leading to premature failure of the coating system and limiting its usefulness. The development of a “prime-reliant” TBC system, where life expectancy of the coating system does not govern that of the turbine blade, has yet to be achieved. As such, the modern day TBC system is mostly used as a protective coating designed to prolong engine life as opposed to a coating designed to withstand higher TIT and improve engine performance and efficiency [4]. In order to produce coatings with improved durability and reliability for higher performance applications, better control of the bond coat microstructure than what is currently available via thermal spray is necessary.

1.2 Motivation of Research and General Objectives

The present study was motivated by the potential of the CGDS process to produce metallic coatings with low oxide contents and better controlled microstructures. Based on TBC research work published in the literature, it appears that bond coats featuring low oxide contents and fine grain microstructures could help improve the durability and performance of TBC systems. Additionally, given that the bond coat is often used as a single protective stand-alone coating layer for improved oxidation and hot-corrosion resistance, this work was also motivated by the opportunity to improve the performance of these types of coatings.

Given the complexity of TBC systems due to the various interactions between the numerous coating layers, it was decided that this work should concentrate solely on the oxidation behaviour of free-standing bond coatings without the presence of the superalloy substrate or ceramic top coat. This approach would allow isolating and thoroughly investigating the

specific influence of the deposition technique and resulting coating microstructures on the bond coat oxidation behaviour. As will be discussed further in subsequent sections, the oxidation behaviour of the bond coat plays a major role on the failure dynamics of TBC systems as well as the effectiveness of stand-alone bond coatings. Therefore, the oxidation behaviour of the bond coat is a specific property that is of prime importance to this field of research. Additionally, bond coats are often subjected to pre-oxidation heat treatments prior to deposition of the ceramic top coat, thus making the specific study of the bond coat oxidation behaviour further relevant. For these reasons, although numerous studies have been focused on the high temperature interactions between the various TBC coating layers, a large number of studies have also concentrated on the approach followed in this work for the specific investigation of the bond coat oxidation behaviour. While it is necessarily expected that the addition of a ceramic top coat on the surface of the bond coat will influence its thermo-mechanical behaviour upon thermal cycling, it is not expected to influence the general trends observed for the bond coat oxidation behaviour. As such, the approach considered in this work has been shown to be a valid investigative method for the assessment of bond coat performance.

With this approach in mind, the work presented in this thesis represents the initial building blocks of a broad ongoing research project that currently seeks to investigate the oxidation behaviour of bond coats manufactured by CGDS and ultimately aims to develop high-performance CGDS bond coats for advanced TBC systems. In order to achieve this objective, a number of specific studies will need to be performed as follows:

- a) Explore the potential of the CGDS process for the deposition of bond coat materials with i) crystalline and ii) nanocrystalline microstructures and verify its feasibility.
- b) Optimize the CGDS deposition process for these bond coat materials by means of coating characterization.
- c) Investigate the ability of CGDS to fully preserve the bond coat material microstructure throughout the deposition process.
- d) Evaluate the oxidation behaviour of the CGDS bond coatings.

- e) Compare the properties and performance of the CGDS bond coats with those of bond coats manufactured by industrial thermal spray techniques such as plasma spraying and HVOF spraying.

1.3 *Outline of the Thesis*

The contents of this thesis have been organized into nine chapters. Chapter 1 presents a general introduction of the background information relevant to the current research project. The motivation for the project and some general objectives are also presented in this chapter.

Chapter 2 provides a detailed account and review of the relevant literature for this research project. A description of the various thermal spray techniques considered in this study is presented as well as a more thorough investigation of the CGDS deposition technique. Finally, a review of TBC systems is presented, including further details on the coating system structure, processing methods and failure mechanisms.

Chapter 3 describes in details the specific objectives of this research work in order to provide the reader with a clear vision and sense of direction for the development of metallic bond coats manufactured by CGDS.

Chapter 4 provides a detailed account of the experimental research approach considered in this study. A description of the selected feedstock materials will be presented, followed by an overview of the CGDS experimental apparatus. The material characterization techniques that were used for microstructural observation and oxidation behaviour assessment will also be examined.

Chapter 5 presents the results obtained for the characterization of the conventional and nanocrystalline feedstock powders considered in this work. Key microstructural features for each powder such as phase content and grain structure are presented and compared.

Chapter 6 explores the feasibility of the deposition of conventional and nanocrystalline MCrAlY powders by means of the CGDS coating technique. Examination of the coating optimization approach, which features experimental and numerical modelling results, is also presented.

Chapter 7 presents a thorough characterization of the various as-sprayed MCrAlY coatings. This includes both conventional and nanocrystalline CGDS coatings as well as conventional coatings manufactured by other thermal spraying techniques. Features such as coating structure, porosity, oxide content, phase content and grain structure are presented and compared for the various deposition techniques. Comparison of the coating microstructures with the original feedstock powder particles is also presented in order to assess whether any microstructural changes have occurred throughout the CGDS deposition process.

Chapter 8 reports the results obtained from the oxidation experiments carried out on the various coating samples. Investigation of the oxide growth rates, oxide scale compositions and morphologies are presented. Findings related to the influence of the coating deposition technique (CGDS vs. thermal spray) and coating microstructure (conventional vs. nanocrystalline) are also discussed in this chapter.

Finally, the conclusion will summarize the findings reported in this thesis and provide closing remarks on the present research work. Recommendations and suggestions for future work are also presented.

Chapter 2 - Review of Relevant Literature

The following chapter presents a detailed review of the literature pertinent to this research project. Firstly, as an introduction to coating technologies in general, an overview of some selected thermal spray processes is presented. Emphasis will be made on processes that are currently used for the manufacturing of TBC systems in the gas turbine industry. Secondly, a detailed investigation of the CGDS coating technology is presented, as it is the predominant coating technique considered in this work. Finally, a review of TBC systems is provided along with a discussion of current limitations.

2.1 Thermal Spray Processes

Thermal spray processes tend to differ from other coating techniques such as electrochemical plating or directed vapour deposition because they are considered to be non-atomistic processes, meaning that they do not deposit material in the form of single ions, atoms or molecules. Instead, thermal spray processes deposit relatively large clusters of material in the form of molten droplets or semi-molten particles on a substrate [5]. In order to heat the deposited material to its melting temperature, various energy sources can be used. As such, thermal spray processes are typically classified into four groups based on the type of energy source used to heat the material and achieve deposition. These groups are plasma spraying, electric arc spraying, combustion spraying and kinetic spraying, as depicted in Figure 2.1. It should be noted that although kinetic spraying does not use a thermal source of energy for material deposition, it is still viewed by many as a derivative of thermal spray processes and has therefore been included in the present discussion. The processes highlighted in grey in Figure 2.1 are of particular interest in this study as they are thermal spray processes currently used in the gas turbine industry for the manufacturing of the ceramic top coat and/or metallic bond coat that form the TBC system. The following subsections will examine these selected thermal spray methods in greater detail and give typical characteristics of their resulting coatings.

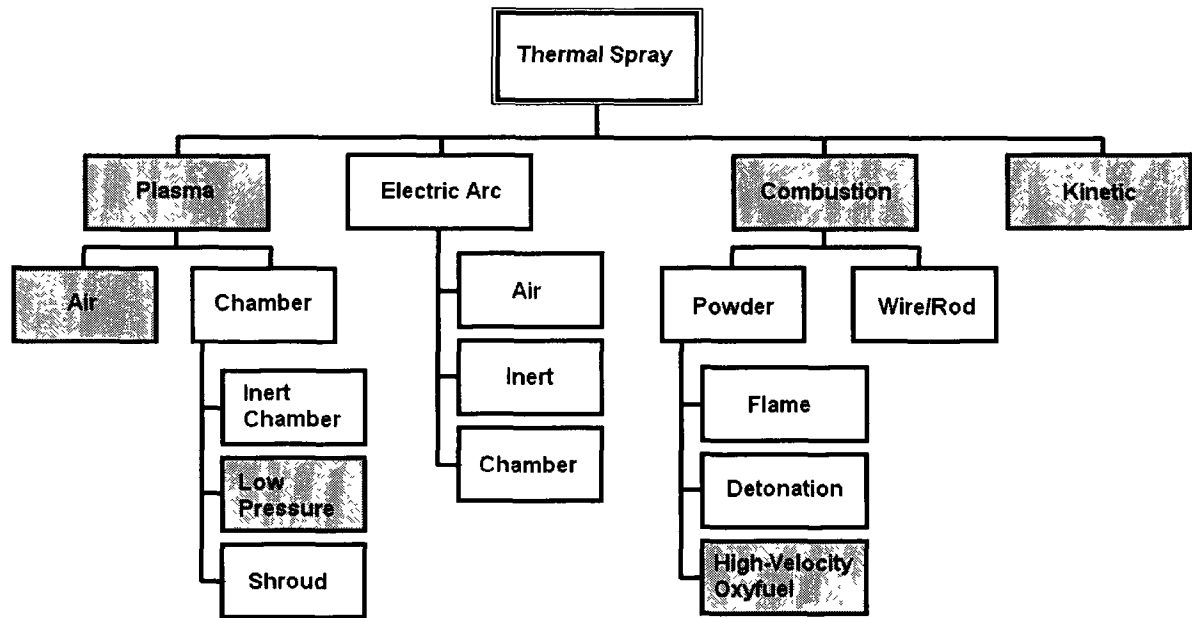


Figure 2.1: Classification of thermal spray processes (adapted from [5])

2.1.1 Plasma Spraying

As its name suggests, the plasma spraying process relies on the thermal energy of a high temperature plasma jet for material deposition. To produce a plasma jet, an electric arc is generated by running a direct current between a water-cooled tungsten cathode and an annular water-cooled copper anode nozzle. A primary gas such as nitrogen or argon is combined to a secondary gas such as hydrogen or helium, and the mixture is then passed through the electric arc where it is heated, dissociated and ionized, to produce a plasma [5, 8, 9]. The plasma jet is typically hottest at the exit of the nozzle anode with temperatures ranging between 5000°C and 25000°C, depending on the gas mixtures and power settings used [9]. The plasma temperature drops off rapidly with increasing distance from the anode nozzle exit, and therefore the feedstock powder particles are usually injected externally near the exit of the nozzle or internally (directly through the nozzle) into the hottest section of the plasma jet. The feedstock particles (typically $\sim 40\mu\text{m}$ in diameter [8]) are then molten in the plasma jet and projected at velocities ranging from 80 to 300 m/s onto the substrate where they rapidly solidify (at a rate of $\sim 10^6\text{K/s}$ [9]) and form a coating. A schematic diagram of a typical plasma torch cross-section is illustrated in Figure 2.2.

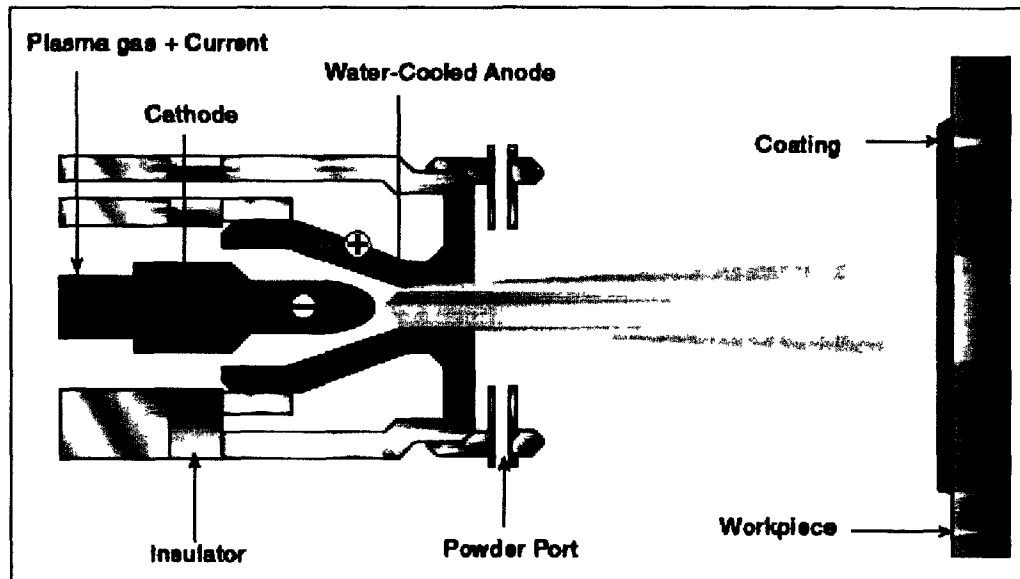


Figure 2.2: Schematic cross-section view of a typical plasma torch [10]

Plasma spraying is considered as the most versatile thermal spraying technique. The high temperature involved in the process makes it suitable for the deposition of many different types of materials including metals and alloys as well as high melting-point ceramics. When the plasma spray deposition process is performed in an environment open to atmospheric air, the process is referred to as Air-Plasma Spraying (APS). This process is relatively inexpensive however it is also most susceptible to the inclusion of oxides and defects in the coatings. As a result, APS is mostly used for the deposition of materials in applications that are less sensitive to oxide and defect content such as ceramics [8]. For more advanced applications, the plasma spray process is performed in a chamber with reduced pressure and controlled inert gas environment. This technique is known as Low-Pressure Plasma Spraying (LPPS) and is typically carried out at chamber pressures ranging between 50 and 200 mbar. The controlled environment allows for reduced oxide contents in the coatings and is therefore used as a deposition technique for more sensitive applications such as bond coat materials for TBCs and biocompatible coatings on medical implants [9]. Although lower oxide content is achieved, the LPPS process still requires melting of the feedstock particles to achieve deposition, and as a result microstructural changes still occur. Other drawbacks of the LPPS method are mostly attributed to equipment complexity and high cost.

2.1.2 High Velocity Oxygen-Fuel Spraying

High Velocity Oxygen-Fuel (HVOF) spraying falls into the category of combustion thermal spray processes since it relies on the chemical reaction between a fuel and oxygen as a source of thermal energy for coating deposition. The HVOF process was developed in 1958 by Union Carbide (now known as Praxair Surface Technologies, Inc.) but was only commercialized in the 1980s. HVOF operates under a continuous regime where a combustion gas and a fuel (usually hydrogen, propylene, propane, acetylene or kerosene) are burnt in an air-cooled or water-cooled combustion chamber. The resulting flame is then fed into a converging/diverging expansion nozzle, also known as the barrel [5]. The hot combustion gases are accelerated in the nozzle at supersonic velocities, leading to jet temperatures of approximately 3000°C and velocity range from 1525m/s to 1825m/s [5, 8]. The feedstock powder particles are injected at the rear of the spray gun in the same axial direction as the flame. Upon exposure to the high temperature and high velocity flame, the particles experience a significant increase in thermal and kinetic energy, thus resulting in partially melted and/or softened high-velocity particles. Coating formation in HVOF is therefore attributed to the combined effect of splat formation and plastic deformation of the particles upon impact with the substrate. Figure 2.3 shows a diagram of a typical HVOF spray gun cross-section.

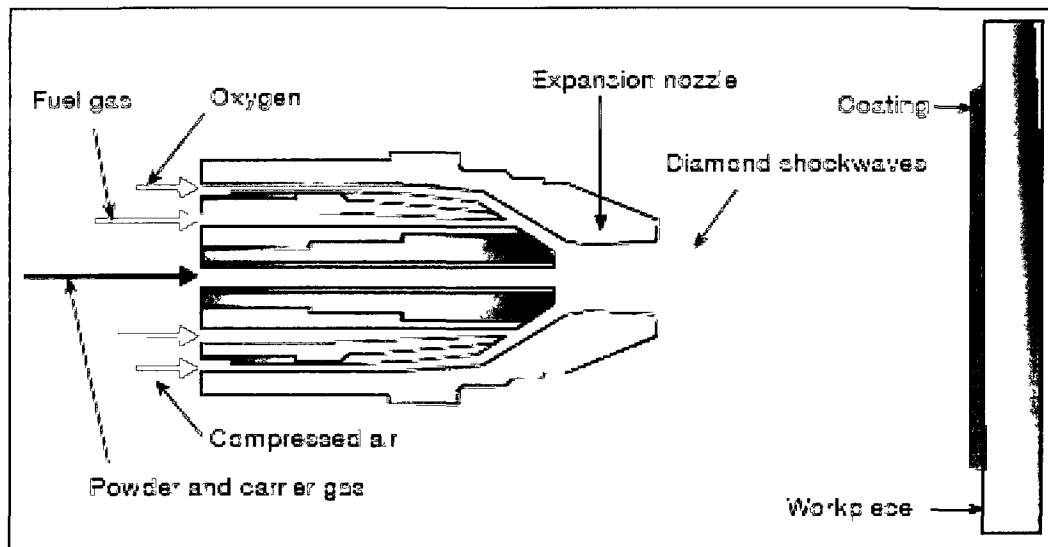


Figure 2.3: Schematic cross-section view of a typical HVOF spray gun [10]

The process temperatures encountered in HVOF are much lower compared to those of plasma spraying and therefore the drawbacks associated with particle melting (microstructural changes, grain growth and high oxide content) are less severe. Additionally, the high gas velocities observed in HVOF are much larger than those observed in other thermal spray techniques, leading to greater particle impact velocities on the substrate. Despite the lower process temperature, this increased impact velocity causes further plastic deformation of the un-melted particles which can lead to improved coating properties such as fewer visible defects and lower porosity. HVOF has been successfully used to deposit dense, hard cermet coatings such as WC-Co as well as metallic coatings such as the bond coat material used in TBCs. Conversely, given its lower processing temperature, material eligibility in HVOF is somewhat less versatile than plasma spraying and therefore cannot be used for the deposition of higher melting point ceramics.

2.1.3 Kinetic Spray Processes

As mentioned previously, kinetic spraying is a subcategory of thermal spray processes that relies on kinetic energy to produce coatings as opposed to thermal energy. Kinetic spray processes include kinetic powder deposition, kinetic spraying, high-velocity powder deposition, and the more popular Cold Gas Dynamic Spraying (CGDS) technique, which will be discussed in greater details in section 2.2. Kinetic spray processes were derived from traditional thermal spray techniques as a result of trends in the industry aiming at reducing process temperatures and increasing process velocities. In kinetic spray processes, only kinetic energy is used to manufacture coatings: solid powder particles are accelerated at high velocities (typically 300 to 1200 m/s [5]) in a supersonic inert gas flow in order to be projected onto the substrate. Although the gas can be preheated up to 700°C [5], the rapid expansion of the gas leads to a considerable temperature decrease within the spray gun and therefore heat transfer to the particles is minimal. As such, coating formation is attributed solely to the severe plastic deformation resulting from the high-velocity impact of the particles on the substrate. Due to the nature of the coating formation mechanism, the use of kinetic spray processes is limited to ductile materials such as pure metals and alloys. Brittle materials such as ceramics generally cannot be deposited using these techniques unless they are included within a ductile metal matrix.

2.1.4 Summary and Comparison of Thermal Spray Processes

The thermal spray processes discussed previously can be best summarized by comparing their general operating features such as temperature and particle velocity. Figure 2.4 shows the range of operating temperatures and particle velocities for various thermal spray processes.

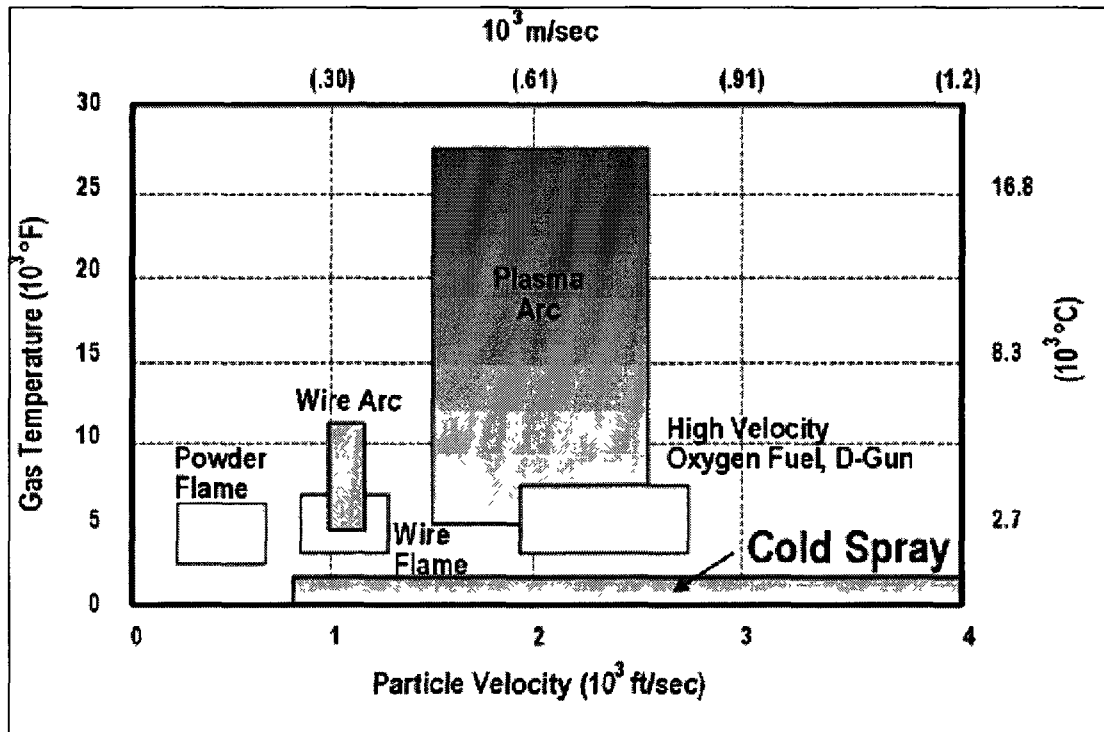


Figure 2.4: Comparison of ranges of particle velocities and gas temperatures for various thermal spray processes [11]

As can be seen in this figure, plasma spraying is characterised as having very high gas temperatures and moderate particles velocities, whereas kinetic spraying (denoted as cold spray on the figure) has very low gas temperatures and very high particle velocities. HVOF finds itself somewhat in between these two processes with a combination of moderately elevated gas temperatures and particle velocities. As a result of these fundamental process differences, some thermal spray techniques are more suitable for the deposition of certain materials. Table 2.1 shows typical operating values as well as material eligibility for the various thermal spray techniques.

Table 2.1: Characteristics of various thermal spray techniques [5, 8]

Spray Technique	Flame Temperature	Particle Velocity	Materials
Plasma	~5000 to 25,000 °C	~80 to 300 m/s	Ceramics and metals
HVOF	~3000 °C	~400 to 800 m/s	Metals, cermets and low-melting point ceramics
Kinetic	Room Temperature	~300 to 1200 m/s	Metals

Given the different operating conditions of the various thermal spray processes, it is expected that their typical coating features and properties will also be different. Coating morphology is strongly dependant on the selected deposition technique, as illustrated in Figure 2.5 which shows typical cross section images of as-sprayed Ni-Al alloy coatings produced by APS, HVOF and CGDS.

Table 2.2 summarizes the typical microstructural features and properties of coatings manufactured by these various thermal spray techniques. It can be seen from this table that all processes can produce coatings with low porosity; however APS and CGDS coatings tend to require more optimization of the spraying parameters in order to achieve high density. It can also be seen that the processes with higher kinetic energy (HVOF and CGDS) lead to compressive residual stresses in the coating which typically improves its mechanical properties. Finally, it can be seen that the low operating temperature and inert environment of the CGDS process tends to minimize the oxide content in the coating. This CGDS feature, in conjunction with its reported ability to retain the properties of the initial particle material [11], makes cold spray an interesting alternative to traditional thermal spraying techniques for the deposition of the metallic bond coat in TBC systems.

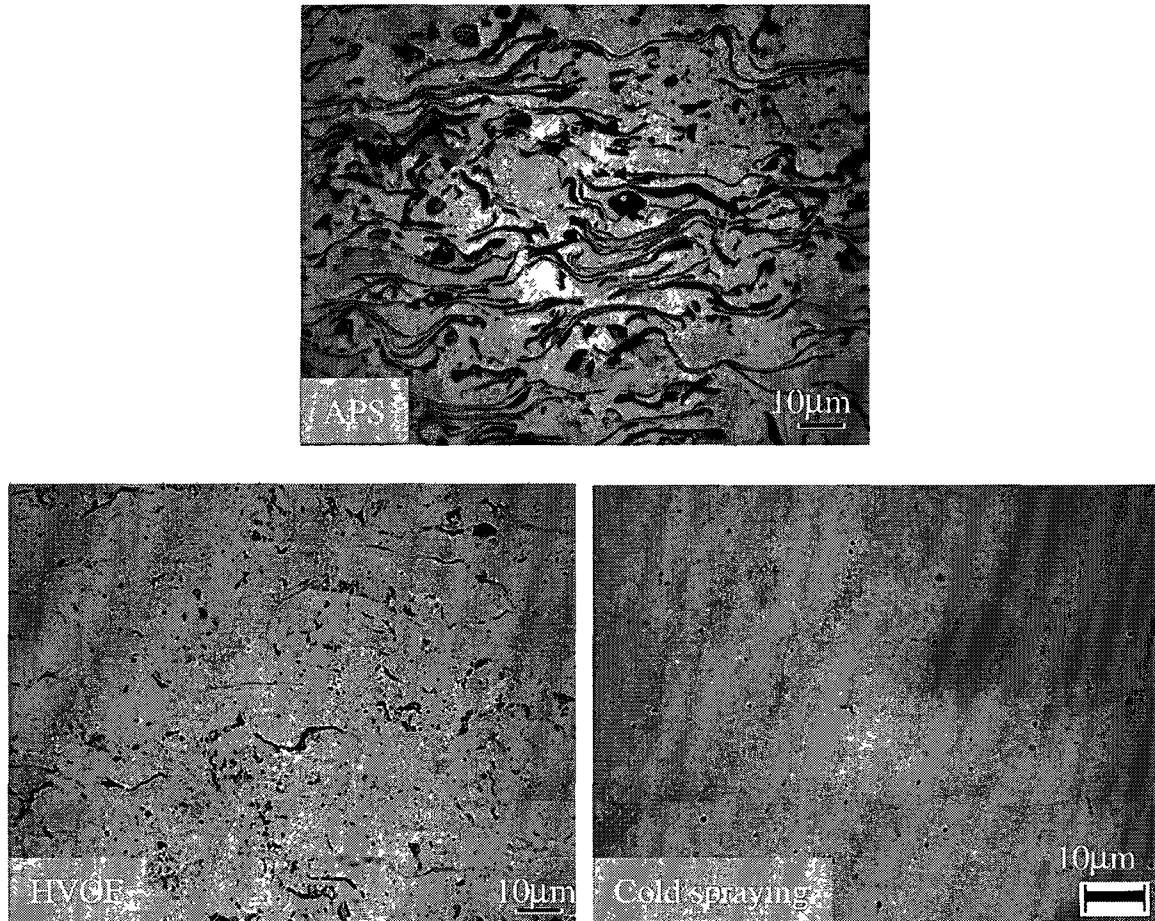


Figure 2.5: Cross-section images of Ni-Al alloy coatings manufactured using air plasma spraying (APS), HVOF spraying and CGDS, (adapted from [12])

Table 2.2: Typical characteristics of various thermal spray techniques [5, 8, 13]

Coating Property	APS	LPPS	HVOF	CGDS
Porosity (%)	1 - 40	1 - 10	0.5 - 5	0.5 – 20
Oxide Content	Moderate-High	Low	Moderate	Minimal
Residual Stresses	Tensile	Tensile	Compressive	Compressive
Adhesion Strength	10-45	>68	Up to 80	20 - 70

2.2 Cold Gas Dynamic Spraying

The current section of this report presents a detailed review of the more popular kinetic spraying technique known as Cold Gas Dynamic Spraying. In particular, discussions pertaining to the historical background, process overview, concept of critical velocity, gas dynamic principles, successfully deposited materials, advantages and limitations, nozzle design considerations and bonding mechanisms of the CGDS technology are presented.

2.2.1 Historical Background

The origins of the modern day CGDS coating technique can be credited to a group of scientists in the mid 1980s who were conducting experiments in a supersonic wind tunnel at the Institute of Theoretical and Applied Mechanics of the Siberian Branch of the Russian Academy of Sciences in Novosibirsk, Russia [7]. The researchers were performing experimental and theoretical work on the interaction of a two-phase supersonic flow with the surface of immersed bodies. During their experiments, they observed that as the flow velocity increased, the fine tracer particles in the supersonic flow would no longer erode the body but rather adhere upon impact to the immersed object, which resulted in the discovery of what they referred to as the “cold spray” phenomenon [14]. Following this discovery, work was performed to develop tools and devices capable of accelerating powder particles in a high-pressure gas flow at temperatures well below their melting point in order to form thick and dense coatings on a surface, which led to the formulation of a first US patent for the technology in 1994 [7]. Since then, the number of patents issued and research papers published on the CGDS coating technology has grown exponentially [14]. After several years of research and development activities on the topic, many commercial systems have emerged and are now available from many equipment manufacturers in various forms, mainly categorized as low-pressure and high-pressure systems [14] while many in-house systems have been developed and used by various academic laboratories to pursue fundamental and explorative work on the process [15-17].

2.2.2 Process Overview

A typical CGDS system is schematically illustrated in Figure 2.6. In CGDS, a primary high-pressure gas supply (typically helium or nitrogen) is used to generate the main or driving flow that will be used to accelerate the powder particles. The driving flow can be heated by means of an electric gas heater, thus allowing operation at temperatures ranging from room temperature up to 700°C. The purpose of heating the gas is not to heat or soften the powder particles, but rather to achieve greater gas velocities and consequently higher particle velocities. The driving flow is then fed into a converging/diverging de-Laval type nozzle where it expands and accelerates to supersonic speeds by converting thermal energy into kinetic energy [5, 11, 18]. The gas velocity at the exit of the nozzle is a function of the nozzle geometry, gas type, and gas stagnation conditions (pressure and temperature).

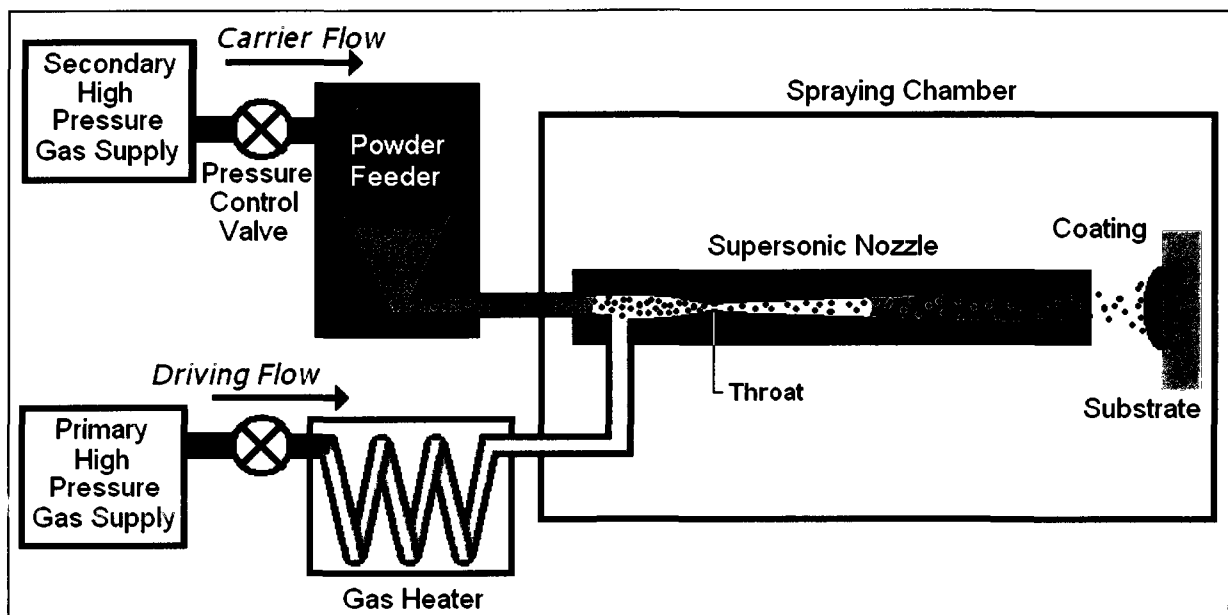


Figure 2.6: Diagram of a typical CGDS system [19]

Meanwhile, a secondary high pressure flow, also known as the carrier flow, is directed to a powder feeder where it entrains the powder particles. Assisted by the carrier flow, the powder particles are injected into the nozzle where they are accelerated by the driving flow. Injection of the powder can occur either axially (upstream of the throat at the inlet of the nozzle), or radially through a sidewall port on the nozzle (downstream of the throat) where the pressure is lower due to expansion of the gas. The particles having acquired sufficient kinetic energy and

momentum transfer from the driving gas will impact the substrate, plastically deform and adhere to the surface to form a coating. The threshold velocity for particle deposition is referred to as the critical velocity, and is the topic of discussion of the following section.

2.2.3 Concept of Particle Critical Velocity

Not all the particles projected on the substrate surface have sufficient kinetic energy to plastically deform and bond to form a coating. In fact, particles having insufficient velocity tend to bounce off the substrate or even erode its surface. The existence of this minimal velocity has led to the formulation of the concept of critical velocity which has been investigated in multiple studies [18, 20-29]. By definition, the critical velocity is the threshold velocity at which a noticeable increase in deposition efficiency is observed. The deposition efficiency is the ratio of the mass deposited on the substrate over the total mass of sprayed powder.

Figure 2.7 shows the deposition efficiency as a function of particle velocity for aluminum, copper and nickel [11]. It can be seen from this figure that deposition of these materials becomes possible when the particle velocities reach 500 to 650 m/s. Sudden increases in the deposition efficiency with increasing particle velocities suggest that the critical velocity has been reached. As such, based on this figure, it can be argued that the critical velocity for copper, nickel and aluminum is of approximately 525 m/s, 575 m/s and 650 m/s respectively.

As expected, the type of material to be deposited has the strongest influence on the critical velocity, and therefore many studies have been focused on that specific issue [18, 20, 22, 24, 25, 29]. However, it is important to recognize that the critical velocity is also a function of other parameters such as powder particle sizes [25-27], particle impact temperature [24, 27,28], powder oxide content [26, 28] and substrate material [21, 23, 29].

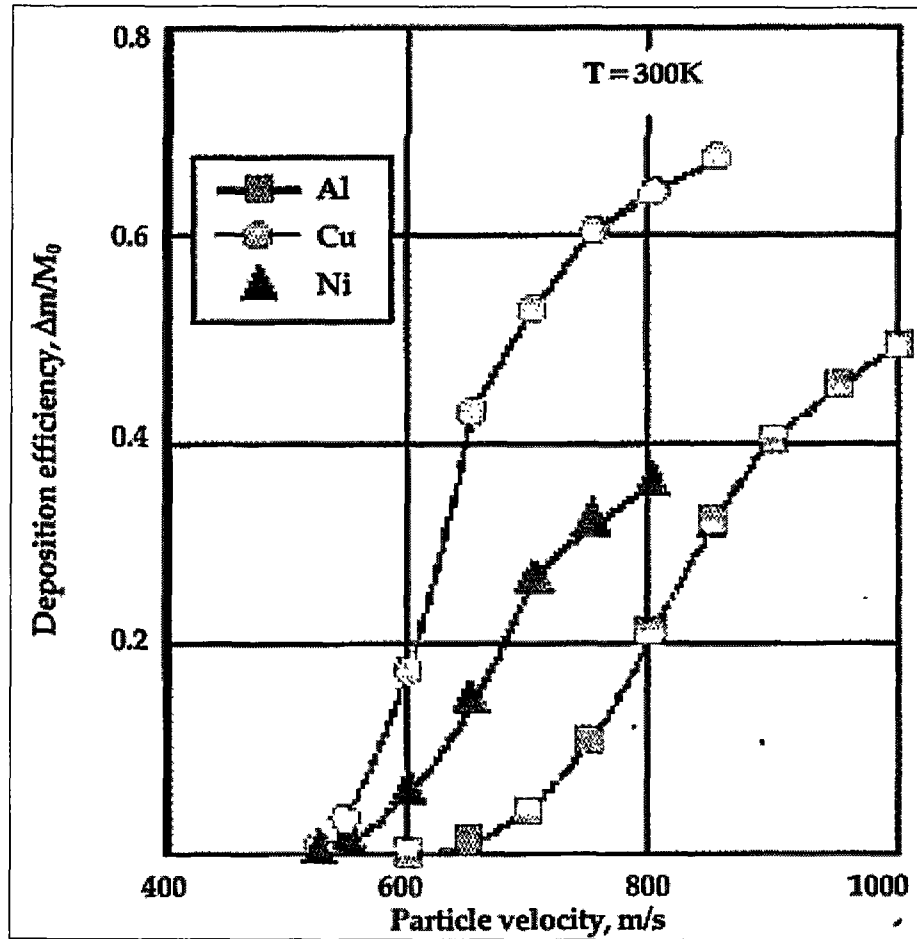


Figure 2.7: Deposition efficiency as a function of particle velocity for Aluminum, Copper and Nickel particles [11]

Figure 2.8 shows the critical velocity of a range of materials based on experimental results as reported by Gärtner *et al.* [18]. In their study, the authors suggested that the different critical velocities were the result of different crystallographic lattice structures, stiffness and density. They also proposed that other material properties such as melting temperature and mechanical strength could influence the critical velocity. It is important to realize that the critical velocity is reached when the impacting particles begin to adhere to the substrate, and this only occurs once sufficient plastic deformation of the particles has been achieved. As such, any property that influences the energy required for plastic deformation of the sprayed material will also have an effect on the critical velocity.

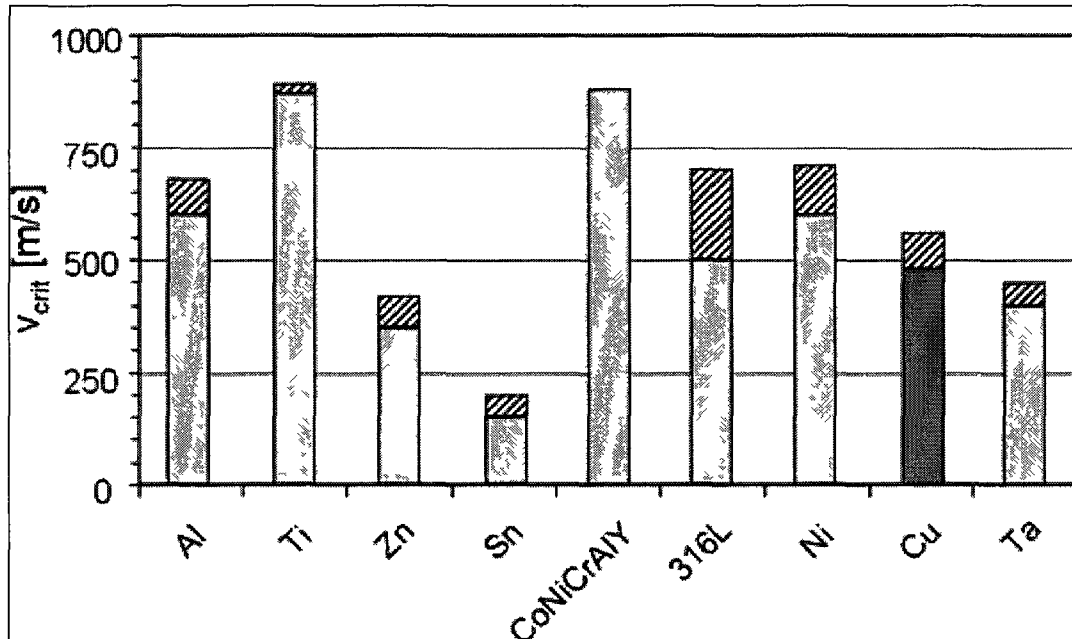


Figure 2.8: Experimentally determined critical velocities for various materials [18]

From Figure 2.8, it is also interesting to note that CoNiCrAlY has a high critical velocity of approximately 850 m/s. CoNiCrAlY is a complex alloy commonly used as a bond coat material in TBC applications, and is therefore of interest for this study. Although Gärtner *et al.* [18] do not specifically discuss the reasons for this material's high critical velocity, it is believed to be attributed to the material's high melting point and complex microstructure (the presence of numerous alloying elements and phases in its microstructure act as strengthening mechanisms, thus requiring more energy to cause plastic deformation).

Particle impact temperature is another important parameter affecting critical velocity. Modelling work has shown that increasing impact temperatures help decrease a material's critical velocity due to thermal softening [25], as illustrated in Figure 2.9. Unfortunately, particle impact temperature is not an easily controlled spraying parameter as it depends strongly on the flow conditions, nozzle geometry, powder preheated temperature, and particle size range. All these parameters will influence heat transfer mechanisms between the gas flow and the powder particles in the nozzle, thus affecting the particle temperature upon impact.

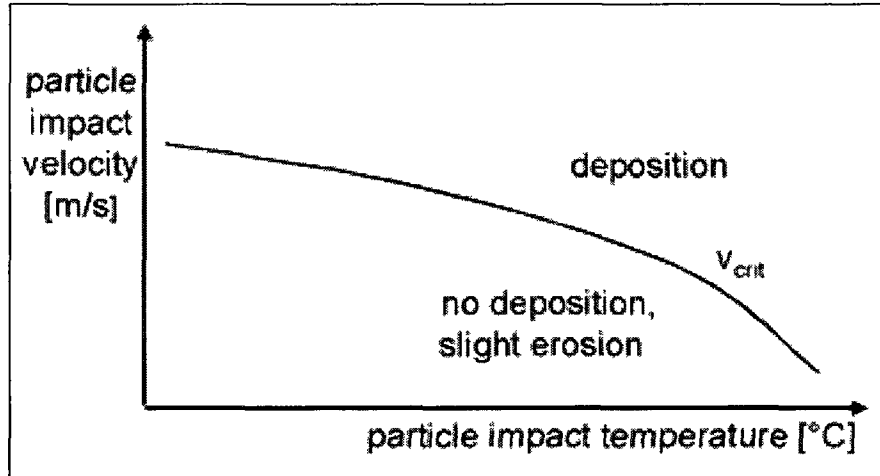


Figure 2.9: Critical particle velocity as a function of impact temperature (adapted from [27])

Modeling work performed by Stoltenhoff *et al.* [24] looked at the influence of the gas stagnation temperature on the particle temperature as it exits the nozzle. Results showed that a copper particle with a diameter of $15\mu\text{m}$ initially at room temperature would be heated up to only 200°C when a gas stagnation temperature of up to 500°C was used. This increase in particle temperature is not overly significant when compared to the high gas stagnation temperature and is attributed to the rapid decrease of the gas temperature in the nozzle as a result of its expansion to supersonic velocities, as will be discussed in further detail in section 2.2.4. Additionally, the short exposure time of the particles in the hot region of the nozzle flow restricts heat transfer and prevents important particle temperature increases. Similar findings were reported by Van Steenkiste *et al.* for a broader range of particle sizes [29]. Even though some increase in particle temperature is observed due to heat transfer with the gas, it is important to note that the sprayed material never reaches its melting or softening temperature. As such, increasing the gas stagnation temperature can assist in reducing the critical velocity, but only marginally. However, increasing the gas temperature does contribute significantly to increasing the gas velocity and consequently particle velocities, as discussed in section 2.2.4.

Stoltenhoff *et al.* [24] also investigated the influence of particle size on particle impact temperature and critical velocity. Modelling results showed that fine particles were much more sensitive to heat transfer from the gas flow and therefore the increase in particle

temperature could be more significant. Conversely, larger particles were less subject to increases in particle temperature. Influence of the particle size on the impact temperature was also investigated by Schmidt *et al.* [27] where a powder preheating chamber was added to the CGDS apparatus. Results showed a more significant increase in particle impact temperature for particle sizes greater than 20 μ m, and therefore lower critical velocities were achieved for this particle size range. Alternatively, the smaller particles experienced more heat transfer with the gas flow and gave up some of the heat acquired in the preheating chamber, thus making the preheating process obsolete for finer particles. Research work performed on the influences of particle size and particle impact temperature on the critical velocity shows that both parameters are strongly interrelated. As such, when presenting critical velocity data, it is important to also specify the particle size range and stagnation temperature.

Particle oxide content is another parameter to be considered with respect to critical velocity. It has been reported that the relatively high critical velocity for aluminum is attributed to the presence of an alumina (Al_2O_3) surface oxide film that forms naturally upon exposure of aluminum to oxygen [26]. It was argued that for deposition of aluminum to occur, the impact energy must be sufficiently large to disrupt and break down this oxide film in addition to providing sufficient plastic deformation of the particle. Li *et al.* [28] also showed that the critical velocity of copper particles increased significantly with an increase in particle oxide content. In general, oxides contained within a sprayed material restrict deformation mechanisms and therefore increase its critical velocity.

Finally, studies have been carried out to investigate the effect of the substrate material on the critical velocity, however these studies have reported conflicting results. Gilmore *et al.* [21] evaluated the deposition efficiency of copper particles deposited onto both aluminum and copper substrates and showed that the deposition efficiency was somewhat affected by the use of different substrate materials. The modeling work performed by Grujicic *et al.* [23] also predicted different deformation mechanisms for coatings produced on copper and on aluminum substrates. Conversely, Van Steenkiste *et al.* [29] examined the thickness of copper, iron and aluminum coatings as a function of various substrate materials such as aluminum, brass, copper and steel. Findings from this study suggested that the effects of the substrate material on the coating thickness and critical velocity were negligible. It is

important to realize that the substrate material and its properties only influence the deposition efficiency of a few initial layers of deposited material. The following incoming particles will impact on the previously deposited layer of material which has its own set of properties, and therefore the deposition mechanisms of the initial layers of material is different to that of subsequent layers. The inability to specifically recognize this occurrence in the literature may be the reason for the conflicting results.

In summary, cold sprayed particles need to be accelerated in the nozzle above their material specific critical velocity for any coating deposition to occur. Although this critical velocity can be adjusted by varying certain spraying parameters such as stagnation temperature and particle size distribution, it appears more appropriate to concentrate efforts on the design of a nozzle capable of accelerating the particles well above the given critical velocity. As such, the following section is dedicated to presenting the relevant gas dynamic principles and nozzle design considerations in CGDS.

2.2.4 Gas Dynamic Principles in CGDS

The present section of this report will examine the fundamental gas dynamic principles that are relevant to the CGDS deposition technique. The most important component of any CGDS system is the nozzle in which the gas flow is accelerated to supersonic velocities in order to propel the powder particles onto the substrate. Therefore, clear understanding of the compressible fluid mechanics involved in the process is critical for proper nozzle and CGDS system design. This section will present appropriate gas dynamics assumptions and simplifications, introductory compressible flow concepts, flow in a variable area nozzle, gas stagnation properties, flow behaviour in a converging/diverging nozzle and important nozzle design considerations.

2.2.4.1 Assumptions for Gas Dynamic Principles in CGDS

The complex compressible fluid mechanics involved in CGDS can be simplified significantly with the application of various adequate assumptions. Firstly, CGDS typically uses inert gases such as nitrogen or helium to generate the main driving flow, and therefore it is a correct assumption to consider these fluids as calorically perfect gases with no interaction

between the gas particles. Secondly, models have been developed successfully to represent the flow behaviour in a CGDS nozzle as a one-dimensional, steady-state isentropic flow [29-31]. Validation of these models has shown small discrepancies with experimental results that fall within acceptable engineering constraints. The one-dimensional assumption supposes that the flow conditions and fluid properties are uniform throughout a given cross-section in the nozzle. It also suggests that the rate of change of fluid properties normal to the streamline direction (nozzle radial direction) are negligible compared to those along the streamline direction (nozzle longitudinal axis). The steady-state assumption supposes that the CGDS process is operating at equilibrium conditions; therefore changes in flow conditions with respect to time are neglected. Finally, the isentropic flow condition encompasses two important underlying assumptions. The flow is first said to be inviscid, and therefore the absence of losses due to viscous effects in the nozzle results in a reversible gas expansion process. Also, heat losses through the nozzle are considered minimal and the process is thus said to be adiabatic. When the adiabatic and reversible assumptions are applied to the second law of thermodynamics, the process is found to be isentropic. When these simplifications are applied to the conservation equations such as continuity, momentum and energy, relatively simple expressions that quantify the compressible flow behaviour can be obtained. Although the assumptions unavoidably introduce errors when computing the flow behaviour, they allow for a simple and sufficiently accurate first approximation of the CGDS nozzle flow.

2.2.4.2 *Introductory Compressible Flow Concepts*

Compressible flows imply that a change of fluid density $\Delta\rho$ occurs due to a change in pressure ΔP . Therefore, the rate of change of density with respect to pressure is an important parameter and is closely related to sound. Sound is an infinitesimal pressure wave that causes a small increase in pressure ∂P , density $\partial\rho$ and velocity ∂u as it propagates through a fluid medium at the speed of sound c . Applying continuity and conservation of momentum to such an infinitesimal pressure wave leads to the following results:

$$\frac{\partial\rho}{\rho} = \frac{\partial u}{c} \quad (\text{Eq. 2.1})$$

and

$$c^2 = \left(\frac{\partial P}{\partial \rho} \right)_s \quad (\text{Eq. 2.2})$$

Equation 2.2 shows that the speed of sound is directly linked to the rate of change of pressure with respect to density, and is therefore an important parameter in compressible flows. It can be observed that a fluid characterized by a high speed of sound implies that a large pressure needs to be applied in order to produce a given change in density $d\rho$. As such, a fluid with a high speed of sound is said to be less compressible than a fluid with a low speed of sound. In the case of a perfect gas undergoing an isentropic evolution, equation 2.2 can be reworked to yield the following result:

$$c = \sqrt{\gamma RT} \quad (\text{Eq. 2.3})$$

where γ is the specific heat ratio (C_p/C_v), R is the specific gas constant and T is the fluid temperature. Equation 2.3 shows that for a perfect gas, the speed of sound is determined exclusively by the type of gas and temperature. Table 2.3 shows the speed of sound of various perfect gases at standard atmospheric conditions and room temperature. It is interesting to note the very high speed of sound in helium which results from its low molecular weight (high gas constant) and monatomic nature (high specific heat ratio).

Table 2.3: Speed of sound in different fluids at standard pressure and temperature

Fluid	Speed of Sound
Air	346 m/s
Nitrogen	351 m/s
Helium	1016 m/s

The importance of compressibility effects in fluid flow calculations depend on the magnitude of the flow velocity with respect to the speed of sound. This is quantified using the Mach number (M) which is given by the following expression:

$$M = \frac{u}{c} = \frac{u}{\sqrt{\gamma RT}} \quad (\text{Eq.2.4})$$

A flow with a low Mach number ($M < 0.3$) is considered incompressible and is thus not subject to changes in density with changes in pressure. Subsonic flow represents the range of flow velocities where compressibility effects are present but velocities remain below the speed of sound ($0.3 < M < 1$). Sonic flow occurs when the flow speed matches exactly that of the speed of sound ($M = 1$). Finally, supersonic flow is defined as a compressible flow with velocity greater than that of sound ($M > 1$).

The Mach number and speed of sound are important fundamental concepts of compressible flows. As seen in the following section, the Mach number helps to understand the basic differences that exist between the behaviour of subsonic and supersonic flows in a variable area nozzle.

2.2.4.3 Flow in a Variable Area Nozzle

In CGDS, the flow is accelerated to supersonic velocities by means of a converging/diverging nozzle. Therefore, understanding of the isentropic flow behaviour in a variable area nozzle for both the subsonic and supersonic flow regimes is important. Three governing equations must be considered in order to investigate this flow behaviour: continuity, conservation of energy and the second law of thermodynamics. From these conservation equations, the following equality can be demonstrated:

$$\frac{du}{u}(1 - M^2) = -\frac{dA}{A} \quad (\text{Eq. 2.5})$$

Equation 2.5 shows the relationship between changes in the flow velocity du and changes in the area dA of a variable area nozzle. Most importantly, this equation shows that the flow behaviour in a variable area nozzle is strongly dependant on compressibility effects measured by the Mach number. For subsonic flow ($M < 1$), it can be seen that du and dA will be of opposite sign. This is the traditional fluid behaviour found in incompressible flows where the velocity increases in a nozzle with reducing area and decreases in a diffuser with increasing area. Conversely, for supersonic flow ($M > 1$), the flow behaviour changes completely.

Equation 2.5 predicts that a supersonic flow will further accelerate in a nozzle with increasing area and decelerate in a nozzle with decreasing area. In summary, the response of a flow to a specific area change is exactly the opposite for subsonic and supersonic flows, as shown in Figure 2.10.

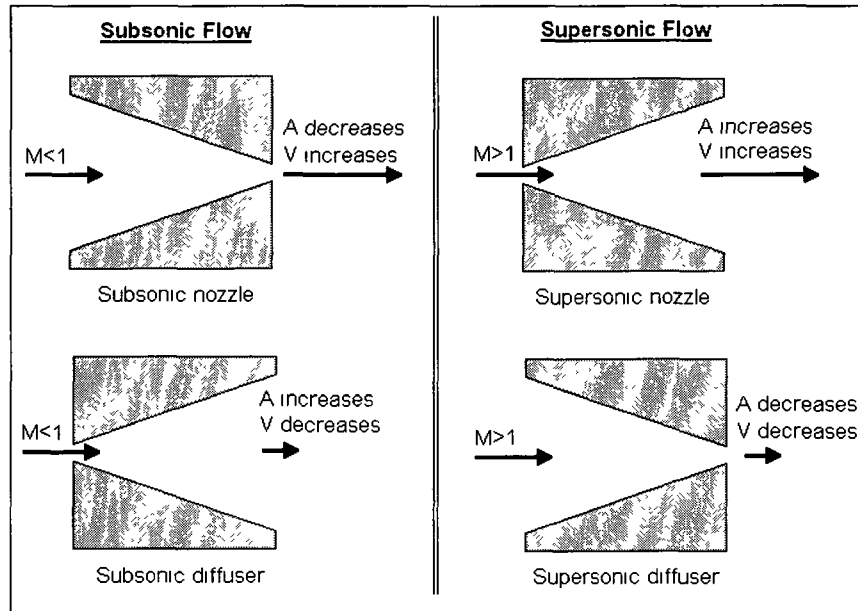


Figure 2.10: Representation of differences in flow behaviour for subsonic and supersonic flows in a variable area nozzle

Further examination of equation 2.5 and the different predicted flow behaviours reveals that a specific type of nozzle geometry is required to accelerate a flow from low subsonic velocities to supersonic velocities. The flow must first be accelerated in the subsonic regime, and therefore a nozzle with a converging section is required. Given the proper gas inlet conditions, this geometry will allow the flow to reach the speed of sound ($M=1$), at which point the flow is said to be choked and its behaviour changes to that of the supersonic regime. Then, a nozzle with a diverging section is required to further accelerate the flow to supersonic velocities. The result is a nozzle with a converging section at the inlet and then a diverging section at the outlet, as depicted in Figure 2.11. Therefore, nozzles capable of accelerating flows to supersonic velocities such as those used in CGDS are referred to as converging/diverging nozzles. The location of the minimum cross-sectional area in a converging/diverging nozzle is known as the throat and is characterized as having a local Mach number of 1 (velocity equal to the speed of sound) for supersonic nozzle flow.

However, it is important to note that the flow does not always reach Mach 1 at the throat. This is because the flow behaviour also depends on the gas stagnation pressure, which is the topic discussed in the following section.

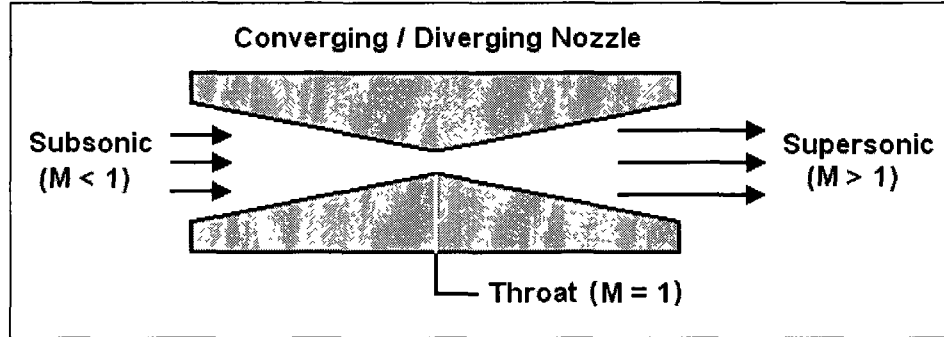


Figure 2.11: Schematic of the nozzle geometry required for the acceleration of a gas to supersonic velocities

2.2.4.4 Gas Stagnation Properties

The state of zero velocity in an isentropic evolution is called the isentropic stagnation state. As such, the gas stagnation properties represent the properties of the flow when it is decelerated isentropically to zero velocity. The flow stagnation properties are of particular interest when considering the expansion of a gas in a converging/ diverging nozzle. As a gas expands in the nozzle, energy is converted from pressure and thermal energy (thus enthalpy) into kinetic energy, and therefore the gas pressure and temperature decrease accordingly. In the case of a calorically perfect gas following an isentropic expansion, the flow pressure and temperature can be determined based on the Mach number and the stagnation properties (identified with the subscript o) as follows:

$$\frac{T_o}{T} = 1 + \frac{\gamma - 1}{2} M^2 \quad (\text{Eq. 2.6})$$

and

$$\frac{P_o}{P} = \left(1 + \frac{\gamma - 1}{2} M^2 \right)^{\frac{\gamma}{\gamma - 1}} \quad (\text{Eq. 2.7})$$

These relationships can be used in different ways to determine flow properties at any location in a variable area nozzle. For instance, if the Mach number at a given location in the nozzle and the gas stagnation properties are known, it is possible to determine the local pressure and temperature. Conversely, knowing the local pressure or temperature at a given location in the nozzle as well as the gas stagnation properties allows for the evaluation of the local Mach number.

Equation 2.7 also shows that if it is desired to accelerate a flow to a specific Mach number, an appropriate pressure ratio P_0/P must be available. For example, if air ($\gamma=1.4$) must be accelerated to a Mach number of 3 at the nozzle exit, then the required stagnation pressure will be approximately 36.7 times larger than the nozzle discharge pressure. The relationship between the stagnation pressure, nozzle discharge pressure and flow behaviour in a converging/diverging nozzle is examined more closely in the following section.

2.2.4.5 Compressible Isentropic Flow in a Converging/Diverging Nozzle

The behaviour of a flow in a converging/diverging nozzle is best represented by considering the effect of varying the pressure ratio between the stagnation pressure P_0 and the chamber pressure where the flow discharges, also known as back pressure P_B . The different flow behaviours along the axis of a converging/diverging nozzle resulting from increasing the pressure ratio (achieved by decreasing P_B) are shown in Figure 2.12. Case a) represents the situation where the back pressure is equal to the stagnation pressure ($P_B=P_0$) and the trivial result where there is no flow through the nozzle. As the back pressure is reduced, a flow is generated in the nozzle as shown in case b). However, the pressure ratio is insufficient to choke the nozzle ($M<1$ at the throat), and therefore after being accelerated in the converging section of the nozzle, the flow begins to decelerate in the diverging section. The flow thus remains subsonic throughout the nozzle and exits the nozzle with a pressure equal to the back pressure. Further decreasing the back pressure results in the flow behaviour shown in case c). In this situation, the pressure ratio is large enough to choke the nozzle and therefore the flow reaches the speed of sound ($M=1$) at the throat. However, the pressure ratio is too low to sustain supersonic flow in the diverging section. The flow thus reverts to the subsonic regime, decelerates in the diverging section and exits the nozzle at a pressure equal to P_B . If

the back pressure is lowered further, the pressure ratio becomes large enough to choke the nozzle and sustain supersonic flow for a portion of the diverging section, but not for the entire diverging section length, as shown in case d). This results in an abrupt deceleration of the flow within the nozzle diverging section by means of a compressive shockwave inside the nozzle. The flow reverts to subsonic conditions and exits the nozzle with a pressure equal to the back pressure. Cases e), f) and g) are all characterized as having a pressure ratio sufficiently large to choke the nozzle and sustain the supersonic flow throughout the entire length of the diverging section of the nozzle. In case e), the gas flow has been expanded to a nozzle exit pressure lower than the back pressure. As the flow exits the nozzle, it seeks to readjust itself to match the equilibrium back pressure and achieves this by means of a series of oblique shockwaves and expansion waves. This type of nozzle flow is said to be over-expanded. Case f) represents the ideal isentropic situation where the flow is supersonic throughout the diverging region of the nozzle and exits without the occurrence of shockwaves. The nozzle exit pressure is equal to the back pressure, and as a result the pressure ratio P_0/P_B is said to be matched to the specific nozzle geometry. Finally, case g) represents the situation where the back pressure is even lower than the ideal back pressure in case f). Once again, the flow is choked at the throat and accelerated to supersonic velocities throughout the diverging section of the nozzle, however upon exiting the nozzle it must readjust and further expand to reach the equilibrium back pressure. This is achieved via a series of expansion waves and oblique shockwaves, similarly to an over-expanded flow but in the opposite order. This type of nozzle flow is referred to as an under-expanded flow.

It is interesting to point out that in cases c) to g), the flow conditions in the converging section of the nozzle remain the same. For all these cases, the pressure ratio is sufficiently large to choke the nozzle, meaning that information with respect to downstream conditions (pressure waves propagating at the speed of sound) cannot travel upstream of the throat to adjust the flow.

Most nozzle designs for use in the CGDS process aim to generate a matched flow like the one shown in case f). This situation is considered ideal because of the supersonic velocity throughout the diverging section of the nozzle as well as the absence of strong disturbances in the flow both inside and outside the nozzle. The high velocities are necessary to accelerate

the particles, whereas disturbances such as shockwaves can impede particle flow. CGDS nozzles are therefore designed with a geometry that will achieve the desired nozzle exit velocities while operating at a specific pressure ratio to generate a matched flow. CGDS nozzle design considerations are presented in the following section.

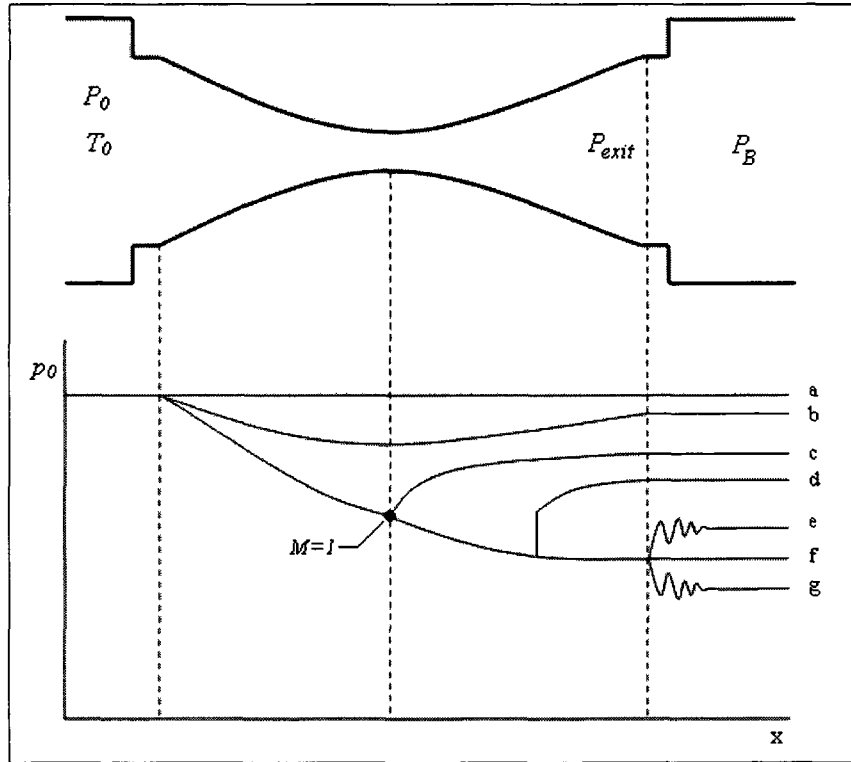


Figure 2.12: Flow behaviour in a converging/diverging nozzle as a function of the pressure ratio P_0/P_B (adapted from [32])

2.2.4.6 CGDS Nozzle Design Considerations

The previous sections have outlined the general flow behaviour in a variable area nozzle as well as the influence of the pressure ratio on the flow characteristics in a converging/diverging nozzle. However, the relationships presented thus far have not defined the behaviour of the flow with respect to the nozzle geometry, which is critical in the nozzle design process. The geometry of a converging/diverging nozzle can be expressed using the non-dimensional nozzle area ratio A/A^* , where A is the area at a given location in the nozzle and A^* is the nozzle throat area. The relationship between the nozzle area ratio and the local Mach number is given by the following expression:

$$\frac{A}{A^*} = \frac{1}{M} \left[\left(\frac{2}{\gamma + 1} \right) \left(1 + \frac{\gamma - 1}{2} M^2 \right) \right]^{\frac{\gamma + 1}{2(\gamma - 1)}} \quad (\text{Eq. 2.8})$$

From equation 2.8, it can be seen that the nozzle area ratio is a function of the Mach number squared. As such, given a specific nozzle area ratio, there are two possible solutions for the Mach number: one for subsonic flow and one for supersonic flow. As discussed in the previous section, the pressure ratio determines whether the flow will be subsonic or supersonic in the diverging section of the nozzle. Therefore, equation 2.8 can be used to predict the Mach number at the exit of a nozzle by considering the nozzle exit area ratio A_e/A^* . Substituting the exit Mach number into equation 2.7 then allows the computation of the pressure ratio required to achieve matched flow conditions.

The exit Mach number can also be used in equation 2.6 to evaluate the gas exit temperature (for a given stagnation temperature), which can in turn be used to calculate the nozzle exit velocity using equation 2.4. Closer inspection of equations 2.4 and 2.6 helps to understand the relationship between the gas stagnation temperature and the exit gas velocity. For a nozzle with a fixed geometry, the exit Mach number (assuming an isentropic flow) is predefined based on equation 2.8. Increasing the gas stagnation temperature will then result in an increase of the nozzle exit gas temperature, thus increasing the local speed of sound and consequently enhancing the gas velocity at the nozzle exit.

However, some restrictions need to be taken into account throughout the CGDS nozzle design process. Although these restrictions impose limits on the nozzle design possibilities, they also are useful in fixing certain unknown variables for the design process. Firstly, the chamber in which the nozzle discharges the flow is typically at atmospheric pressure, thus providing a lower limit for the back pressure. Also, due to safety concerns and industrial equipment pressure ratings, an upper limit exists for the maximum available stagnation pressure. These physical restrictions establish somewhat of a practical range of pressure ratios that can be used for the CGDS nozzle design process. Secondly, the CGDS deposition technique is often criticized for its relatively large gas consumption, which can become rather expensive, especially when helium is used as the process gas. As such, restrictions with regard to the mass flow rate in the nozzle must often be respected. The mass flow rate in the nozzle can be

obtained as the product of the density ρ , velocity u and area A , as shown in the following equation:

$$\dot{m} = \rho u A \quad (\text{Eq. 2.9})$$

In the case of a choked nozzle, the mass flow rate can be evaluated easily by considering equation 2.9 at the nozzle throat where the Mach number is known to be equal to 1. Substitution of the perfect gas law as well as equations 2.6 and 2.7 into equation 2.9 yields the following result:

$$\dot{m} = P_o A^* \sqrt{\frac{\gamma}{RT_o} \left(\frac{2}{\gamma + 1} \right)^{\frac{\gamma+1}{\gamma-1}}} \quad (\text{Eq. 2.10})$$

Equation 2.10 provides a simple expression to evaluate the mass flow rate in a choked nozzle based on the gas properties, nozzle throat area and gas stagnation properties. The mass flow rate in a choked converging/diverging nozzle can therefore be scaled directly by adjusting the nozzle throat area. The corresponding desired exit area can then be determined based on the required nozzle area ratio.

Additionally, other off-design considerations related to non-isentropic flow behaviour should be heeded throughout the nozzle design process. The flow behaviour presented thus far was considered to be isentropic; however some irreversibilities due to viscous effects necessarily occur and have been sometimes shown to influence the nozzle flow behaviour. Alkhimov *et al.* [33] showed that boundary layer development along the internal walls of the nozzle resulted in a displacement thickness that influenced the effective nozzle area ratio, thus reducing the actual nozzle exit Mach number to as low as 85% of the original design value. Boundary layer effects were shown to be more important with increasing nozzle length. In another study, Jodoin [34] investigated the influence of the nozzle exit Mach number on the flow behaviour as the supersonic jet impinges on the substrate. When the supersonic flow encounters the substrate, it undergoes a rapid non-isentropic deceleration by means of a strong bow shockwave that forms ahead of the substrate surface. Jodoin's findings suggested that for flows with high Mach numbers and small particles, the strength of this bow shock was

sufficient to slow down the sprayed particles considerably and influence deposition. As such, restrictions with respect to particle size and maximum design nozzle exit Mach number were recommended.

Nozzle design is critical in CGDS because the process relies entirely on the ability of the nozzle to accelerate the powder particles beyond their critical velocity. As such, the method by which the particles are accelerated in the nozzle flow is of interest and therefore constitutes the focus of the following section.

2.2.4.7 Particle Acceleration

The previous sections have extensively discussed the behaviour of a compressible flow inside a converging/diverging nozzle like the ones used in the CGDS technique. However, little has been said about the acceleration of the powder particles in the flow. The present section of the report looks at the interaction of the particles in the supersonic flow.

The acceleration of the powder particles occurs as a result of the drag force acting on its surface due to the surrounding high velocity flow. As a first approximation, the drag force F_D can be expressed by the following expression [30]:

$$F_D = \frac{1}{2} C_D A_p \rho (u - u_p)^2 \quad (\text{Eq. 2.11})$$

where C_D is the drag coefficient, A_p is the projected area of the powder particle, ρ is the density of the flow, and $(u - u_p)$ is the relative velocity of flow with respect to the particle. Combining equation 2.11 with Newton's second law shows the dependence of the particle acceleration a_p on the flow and particle properties:

$$a_p = \frac{1}{2} C_D \frac{A_p}{m_p} \rho (u - u_p)^2 \quad (\text{Eq. 2.12})$$

where m_p is the mass of the particle. Many interesting features related to particle acceleration can be interpreted from equation 2.12. Firstly, it can be seen that particle acceleration is mostly dependant upon the magnitude of the relative flow velocity. This is why proper nozzle

design is critical and higher flow velocities are desirable. Particle acceleration is also dependant on the drag coefficient which shows that the morphology of the particles is important. Jodoin *et al.* [35] observed that a particle with a spherical morphology has a lower drag coefficient than a particle with an irregular morphology due to delayed boundary layer separation, and this can lead to differences in coating quality. The ratio A_p/m_p encompasses a few underlying features related to particle size and material. The projected particle area is a function of its diameter squared, whereas the mass is a function of the particle volume, and therefore is proportional to the particle diameter cubed. This shows that the particle acceleration is in fact inversely proportional to its diameter, and therefore larger particles will be more difficult to accelerate. Also, particles made of a material with a high density will have a larger mass and will also be more difficult to accelerate. Finally, particle acceleration is also dependant on the flow density, which is in turn dependant on the gas stagnation properties. According to the perfect gas law, a greater density can be achieved by increasing the stagnation pressure, which would promote particle acceleration. However, one must recall that increasing the stagnation pressure also increases the pressure ratio in the nozzle which may lead to an underexpanded flow and the presence of oblique shockwaves outside the nozzle. The perfect gas law also predicts a decrease in density when a gas is heated, which should in theory decrease particle acceleration. However, as discussed in section 2.2.4.6, increasing the gas stagnation temperature increases the gas velocity, which has a greater influence on particle acceleration than the resulting changes in density.

Further development of equation 2.12 shows that particle acceleration is also a differential equation with respect to the axial length over which acceleration occurs [30]. Longer nozzles have been shown to accelerate particles to higher velocities due to extended dwell time of the particles in the supersonic flow [24, 30, 36]. As a result, most CGDS nozzles use long diverging sections in order to provide longer exposure of the particles in the high velocity supersonic region of the nozzle.

Gas dynamic principles associated to CGDS are complex and contend with many interrelated parameters and process variables. However, it is critical not to overlook these principles since they ultimately dictate whether a particle will be sufficiently accelerated or not in order to achieve bonding on the substrate and form a coating.

2.2.5 Bonding Mechanisms

The gas dynamic principles discussed in the previous section are important as they provide an understanding of the method by which the powder particles in CGDS are accelerated beyond their critical velocity. The actual bonding mechanisms by which they adhere to the substrate to form a coating are equally important and are thus the focus of the present section of this report.

Investigation of the particle-substrate and particle-particle bonding mechanisms in CGDS has been the focus of numerous studies [22, 23, 26, 38, 40-42]. To date, there is no official consensus with respect to a single, dominant and universal bonding mechanism in CGDS. However, all researchers agree that the impact of high velocity particles on the substrate leads to plastic deformation of the deposited material as well as a significant dissipation of heat. One of the more important sources of disagreement between researchers has to do with the assumption that the amount of heat dissipated upon impact is sufficient to cause localized melting and/or softening of the sprayed particle, thus influencing the bonding mechanism. Papyrin *et al.* [43] modeled the impact of aluminum particles on a rigid substrate at velocities commonly achieved by the CGDS process and showed that localized melting can occur at the particle-substrate interface under certain conditions. However, melting was shown to be limited to a very fine region and as a result it was argued that this would not influence coating properties. Conversely, Dykhuizen *et al.* [40] suggested that particles remain un-molten throughout the deposition process. These differences of opinion have resulted in the formulation of various theories for bonding mechanisms involved in CGDS.

A popular theory with respect to the bonding mechanism in CGDS has been proposed by Dykhuizen *et al.* [40] who suggest that strong similarities exist between the impact phenomena in CGDS and the bonding mechanism observed in explosive welding. In explosive welding, the high velocity impact of two metal plates causes localized softening at the impact point due to heat dissipation and results in the formation of a solid-state (un-molten) metal jet. It is generally accepted that the formation of this metal jet is responsible for breaking up the surface oxides and providing clean and intimate contact between the two surfaces, therefore promoting good bonding between the two plates. The modeling and

experimental work performed by Dykhuizen *et al.* [40] showed evidence of the formation of a jet of material upon particle impact in CGDS, as shown in Figure 2.13, thus supporting their theory. Results of their work also revealed that jetting of both the particle and substrate materials had occurred, and that neither of these materials needed to be molten to provide good bond strength. This proposed bonding mechanism has also been suggested elsewhere: Van Steenkiste *et al.* [26] suggested a similar bonding mechanism where no evidence of melting was observed and large pressures upon impact caused localized plastic flow of material, removed surface oxide films and allowed metallic bonds to form. Also, Zhang *et al.* [38] agreed with the bonding mechanism proposed by Dykhuizen *et al.* however it was further suggested that plastic deformation of the substrate was not required for bonding to occur.

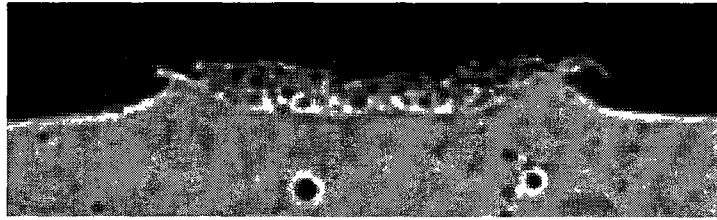


Figure 2.13: Cross-section view of the crater formed by the high velocity impact of a 700m/s copper particle on a stainless steel substrate during CGDS deposition showing evidence of material jetting [40]

Grujicic *et al.* [23] performed numerous computational simulations to further investigate the previously discussed jetting bonding mechanism and determine how the formation of such a jet helps to promote bonding. Their work first showed that the concept of bonding by means of atomic diffusion was insignificant under the dynamic CGDS conditions due to the very short time period ($\sim 20\text{ns}$) over which the jetting interface is subjected to increased temperatures resulting from heat dissipation. For similar reasons, bonding by means of localized melting and re-solidifying of the particle-substrate interface (which was shown to be possible under certain spraying conditions) was also shown to be of minimal importance. The primary bonding mechanism suggested by Grujicic *et al.* [23] further reinforced the theory of the formation of a jetting region capable of promoting intimate contact and adhesion between the materials. In addition, Grujicic also proposed that the formation of micron-scale vortex-like mixing regions or roll-ups in the jetting region could contribute significantly to bonding.

Increased bonding due to the presence of roll-ups is another phenomenon observed in explosive welding that has been used to explain the bonding mechanisms involved in CGDS. Roll-ups occur when two fluid-like materials are subjected to a relative displacement parallel to their interface. The presence of a non-zero curvature perturbation at the interface can result in one fluid flowing over the other, which gives rise to centrifugal forces. Further relative displacement can then lead to the formation of interfacial roll-ups. The evolution of the formation of such roll-ups is represented schematically in Figure 2.14. In the case of CGDS, the interfacial jetting region of the impacting materials can behave as a fluid due to localized heat dissipation and thermal softening, and therefore the formation of roll-ups has been observed experimentally, as shown in Figure 2.15 [15]. Grujicic *et al.* [23] suggested that in addition to the jetting behaviour proposed by Dykhuizen, the formation of these roll-ups in the interfacial region helps to promote bonding by (1) significantly increasing the available contact area between the particle and substrate materials and (2) effectively anchoring the deposited particles to the substrate by means of mechanical interlocking.

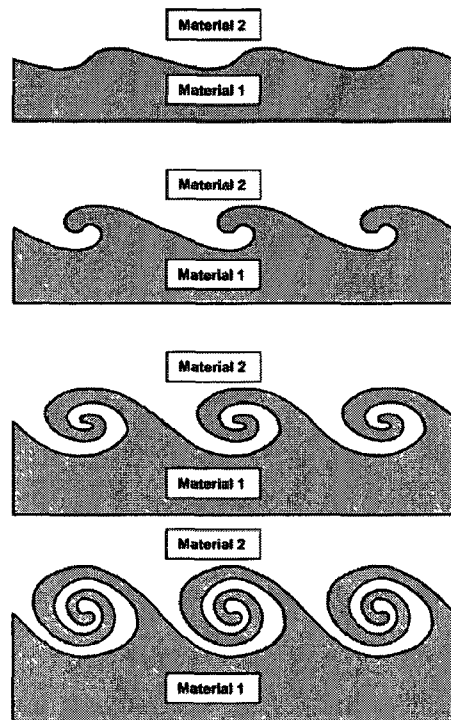


Figure 2.14: Schematic representation of the evolution of vortex-like roll-ups capable of enhancing bonding in CGDS [23]

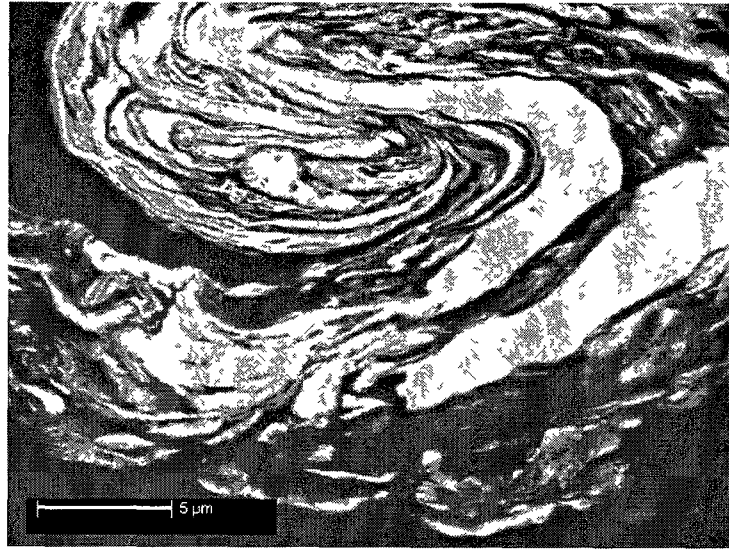


Figure 2.15: Evidence of the existence of roll-ups at the particle-substrate interface of a CGDS coating [15]

The final popular CGDS bonding mechanism theory to be discussed in the present report has been associated with the rapid localized heating and shearing phenomenon known as adiabatic shear instability. The adiabatic shear instability mechanism was originally described in details by Wright [44] and subsequently used to explain the deformation mechanism for particle/particle and particle/substrate bonding during the CGDS process by Assadi *et al.* [22] as well as Grujicic *et al.* [42]. The adiabatic shear instability concept is based on the assumption that localized material softening in the interfacial region occurs due to an adiabatic temperature increase. High strain rates in these regions resulting from high impact velocities lead to shearing instabilities and cause the material deformation mechanism to change from plastic to viscous flow. The assumption that the particle/particle or particle/substrate interaction is adiabatic is based on the fact that the thermal diffusion distance during impact is small due to the short contact time [23], and therefore heat conduction may be neglected during particle impact and deformation.

Assadi *et al.* [22] performed numerical simulations to evaluate the impact behaviour of copper particles at various velocities and observed that when sufficiently high strain rates are encountered (higher impact velocities), the material deformation characteristics are governed by the adiabatic shear instability. Figure 2.16 shows the temporal evolution of the strain, temperature and stress for a copper particle impacting at different velocities. It can be seen

from this figure that when the particle impact velocity is increased from 550 m/s to 580 m/s, the behaviour of the material changes drastically, with significantly higher strains and temperatures, as well as lower stress levels. This change in behaviour differs from the trend observed at lower velocities and suggests that the threshold velocity to trigger the adiabatic shear instability mechanism is of the order of 580 m/s for the given copper particle. This threshold velocity was also shown to correlate closely with the experimentally determined values for the critical velocity of copper particles. These results not only support the claim by Assadi *et al.* [22] suggesting that adiabatic shear instability is an important phenomenon associated to the bonding mechanism in CGDS, but also that this particular shearing behaviour may be closely linked to the prediction of a material's critical velocity.

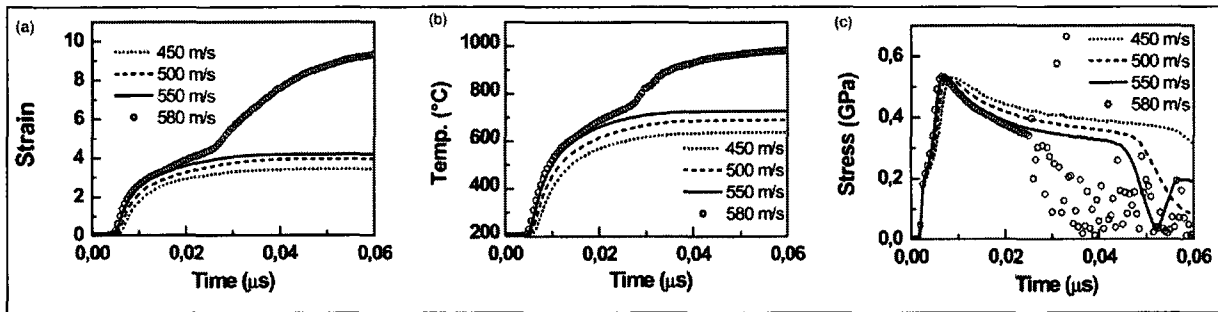


Figure 2.16: Temporal evolution of (a) strain, (b) temperature and (c) stress in the interfacial region of a copper particle impacting at various velocities [22]

The adiabatic shear instability has been shown to lead to the formation of highly deformed jet-like regions in the material which are known as shear bands. Figure 2.17 illustrates the evolution in time of the jet formation as a particle impacts the substrate in CGDS. Shear bands have been observed in various studies that support the theory of adiabatic shear instability as an important bonding mechanism in CGDS [25, 41, 45-47]. Figure 2.18 and Figure 2.19 show various examples of evidence of shear band formation resulting from adiabatic shear instability mechanisms observed in CGDS coatings. It has been proposed that the formation of shear bands helps create intimate contact between clean surfaces and promotes metallurgical bonding at the interfacial surfaces.

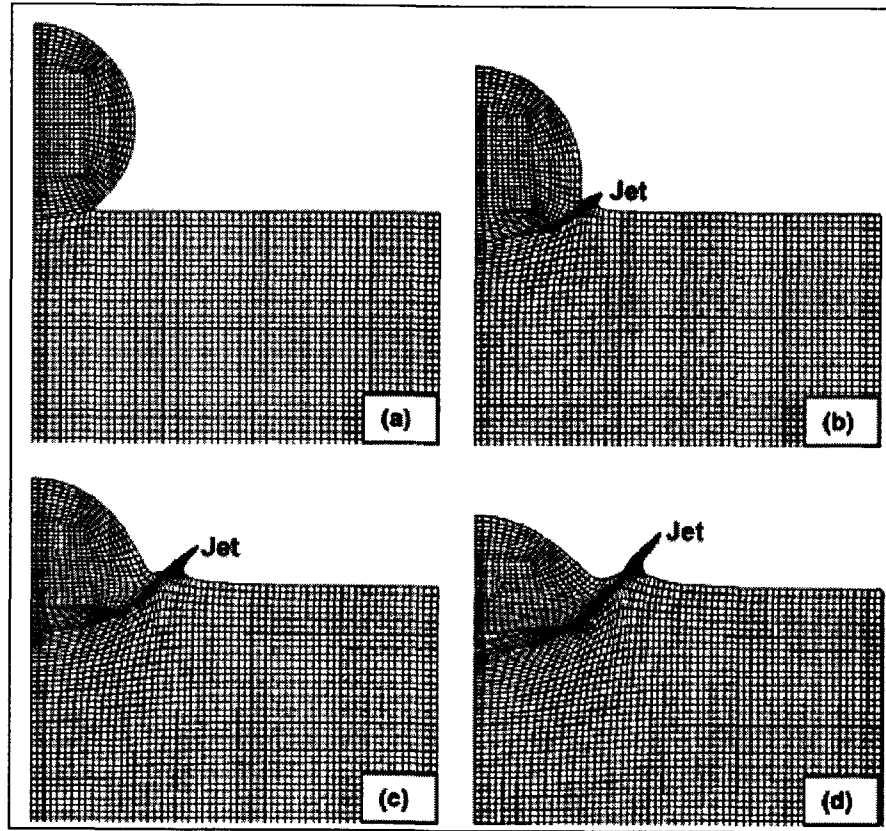


Figure 2.17: Temporal evolution and formation of a jet of material resulting from the creation of shear bands due to adiabatic shear instability during a particle impact in CGDS [42]

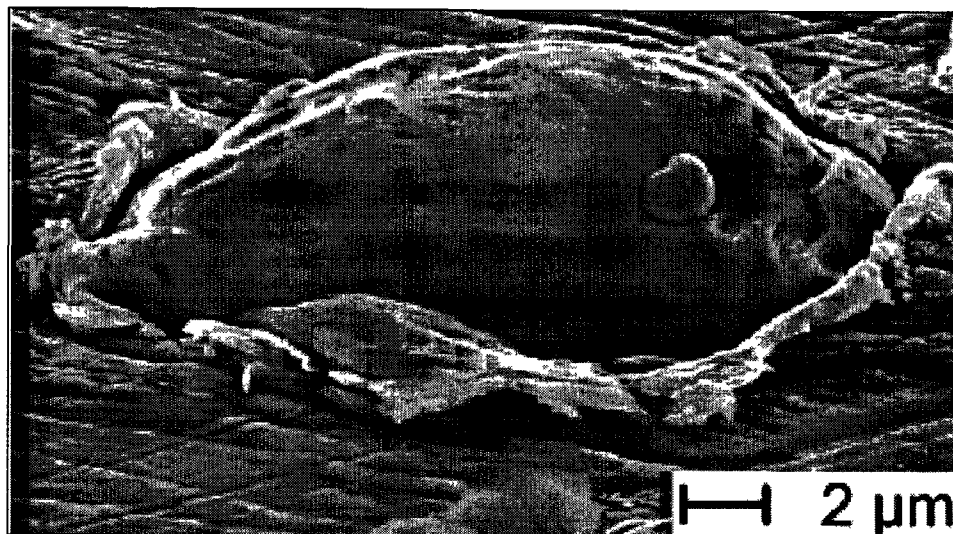


Figure 2.18: Single copper particle impact showing the formation of jets around the particle impacting surfaces (adapted from [22])

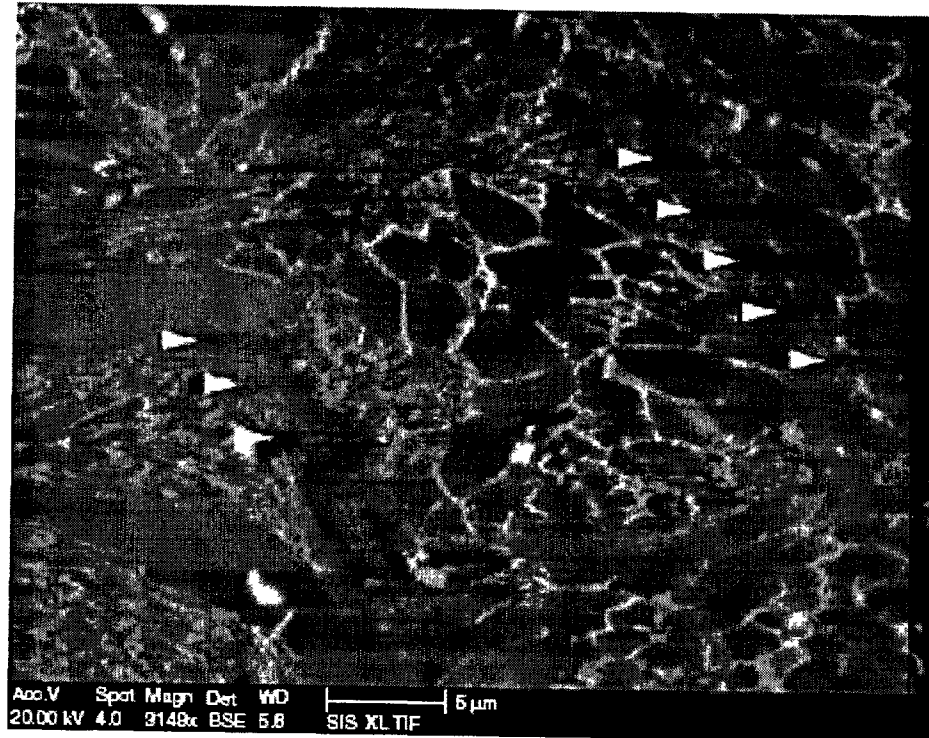


Figure 2.19: Evidence of the presence of shear bands in the microstructure of a Al-2618 coating manufactured by CGDS [45]

The bonding mechanisms involved in CGDS have been investigated in numerous studies however a general widespread consensus has not yet been met. Although some numerical models have predicted that localized melting upon particle impact is possible, there is little experimental evidence to support the theory. Whether bonding is achieved mostly by adhesion, mechanical interlocking, adiabatic shear band formation or a combination of these mechanisms is not known. Despite significant advances, the particle impact dynamics remain difficult to model due to high strain rates, short impact duration and the shortage of material properties data for the given unusual loading conditions. Additionally, validation of the models is complex due to the micron size scale of the interfacial region where bonding occurs.

2.2.6 CGDS Advantages and Limitations

The present section of the report is dedicated to listing the important advantages and limitations of the CGDS technology. Firstly, the CGDS process has been shown to be capable of producing coatings of a variety of materials, such as pure metals like aluminum,

copper, titanium and zinc [26, 48-50]; alloys in conventional [45, 51], nanocrystalline [15, 52, 53] and amorphous [47] forms; cermets in conventional and nanocrystalline forms [16, 54] and metal-matrix composites [55]. Coatings can be formed with a relatively large thickness in a single pass on thin surfaces (<1mm) without damaging the substrate [52]. In addition to coating manufacturing, the versatility of the CGDS process has allowed it to be used in applications such as free-forming and joining of materials [56, 57].

Some general advantages of the CGDS coatings include: 1) a low porosity level attributed to sufficient plastic deformation experienced by the particles upon impact on the substrate and subsequent densification caused by impinging particles on the existing coating [26]; 2) good adherence between the substrate and the coatings attributed to sufficient plastic deformation of the sprayed particles upon impact with the substrate [40]; 3) increased hardness compared to the original feedstock powder as a result of the cold working effect on the original feedstock powder [35] and 4) improved fatigue resistance due to the introduction of compressive residual stresses [58].

The most important advantages of the CGDS process can be attributed to the absence of significant heating of the deposited particles. This CGDS feature, combined with the use of inert propellant gases has been shown to prevent the onset of in-spray particle surface oxidation and reduce the coating oxide content [7]. Also, the low temperature environment has been shown to prevent microstructural changes during spraying, and therefore the material's microstructure and properties can be better preserved and controlled throughout the spraying process [7, 15, 53]. This has been shown to be particularly important for the deposition of nanocrystalline materials, where the fine grain microstructure is easily affected by thermally induced grain growth. In general, thermally and chemically sensitive materials can be deposited using CGDS with minimal material degradation.

The CGDS technique is also necessarily characterized by certain limitations such as restrictions to material eligibility. Given the bonding mechanisms discussed in the previous section, it is important to note that material deposition in CGDS is achieved by means of plastic deformation, and therefore CGDS is only appropriate for ductile materials. Deposition of ceramics is not possible unless they are sprayed within a ductile matrix.

Nozzle clogging or fouling has also been reported in the case of prolonged spraying at elevated stagnation temperatures [59, 60] which impedes the productivity of the CGDS technique. It has been suggested that this problem can be overcome by further optimization of the nozzle design and reduction of the powder flow rate.

Interaction between the gas flow and powder particles in the nozzle has also been shown to be two-sided. While the objective of CGDS is for the gas flow to accelerate the powder particles, the presence of solid particles in the flow also necessarily causes some disturbance of the fluid behaviour due to particle loading effect. Flow saturation resulting from high powder feedrates has been observed to impede the development of the gas flow in the nozzle and reduce coating quality [61]. However, this effect was shown to be negligible when using powder flow rates that fall within normal operating conditions. While this may suggest that the CGDS process has a limited material deposition rate that would make it less attractive from an industrial productivity perspective, the use of normal powder flow rates in CGDS still allows for the production of thick coatings (in some cases thicker than 1mm) for a single pass, which is in fact much larger than other thermal spray deposition techniques.

Finally, it is worth mentioning that although CGDS is considered to be the deposition technique with the most potential for preserving a material's microstructure, some studies have shown evidence of grain refinement in the coating microstructure [41, 50, 62, 63]. In these studies, grain refinement was observed at the interface of impacting surfaces, and therefore the large plastic deformations associated with the creation of shear bands were said to be responsible for the microstructural changes.

2.3 Bond Coats and Thermal Barrier Coatings

The current section of this report will present a detailed review of bond coats and thermal barrier coatings in general. More specifically, information will be provided to discuss the typical TBC structure, coating processing methods, failure mechanisms and reported attempts and recommendations for improving TBC performance. Although in some cases the bond coat can be used as a stand-alone coating layer for improved oxidation and hot-corrosion resistance, it is presented in the following section as an integral part of TBC systems for conciseness purposes.

2.3.1 TBC Overview

Thermal barrier coating systems are used to protect hot components of gas turbine engines such as nozzle vanes and turbine blades in order to achieve prolonged engine life. The levels of protection offered by TBC systems are twofold. Firstly, TBCs provide thermal protection from the hot combustion gases in order to limit the operating temperature of the superalloy components for structural considerations. Secondly, TBCs offer protection against chemical attacks such as oxidation and hot-corrosion which occur at elevated temperatures and can cause rapid degradation of the unprotected turbine blade. In order to meet these multifunctional requirements, it appears that no single coating material composition is available. As such, manufacturing of TBCs involves the deposition of two distinct superimposed coating layers: the first is a metallic bond coat applied on the superalloy substrate, while the second is a low thermal conductivity ceramic top coat. Upon exposure to high gas temperatures, the ceramic top coat acts as an insulation layer to reduce the underlying blade surface temperature. State-of-the-art ceramics used as top coats in TBCs have been shown to be capable of producing a temperature drop of up to 170°C across a small coating thickness (150µm) [4]. Figure 2.20 shows the evolution of temperature across the section of a TBC system. Although the ceramic top coat provides good thermal protection for the underlying turbine blade, its porous microstructure allows for the diffusion of oxygen across its thickness, and therefore the turbine blade remains vulnerable to oxidation damage. The temperature drop in the ceramic top coat provides some relief as the oxidation becomes less detrimental at lower temperatures; however oxidation of the turbine blade remains

problematic. To address this issue, the bond coat is carefully designed to act as a protective layer against oxidation and hot-corrosion. In addition, as its name suggests, the bond coat is used to promote adhesion between the ceramic top coat and substrate superalloy and improve coating longevity. Further details with respect to the structure and materials typically found in TBC systems are presented in the following section.

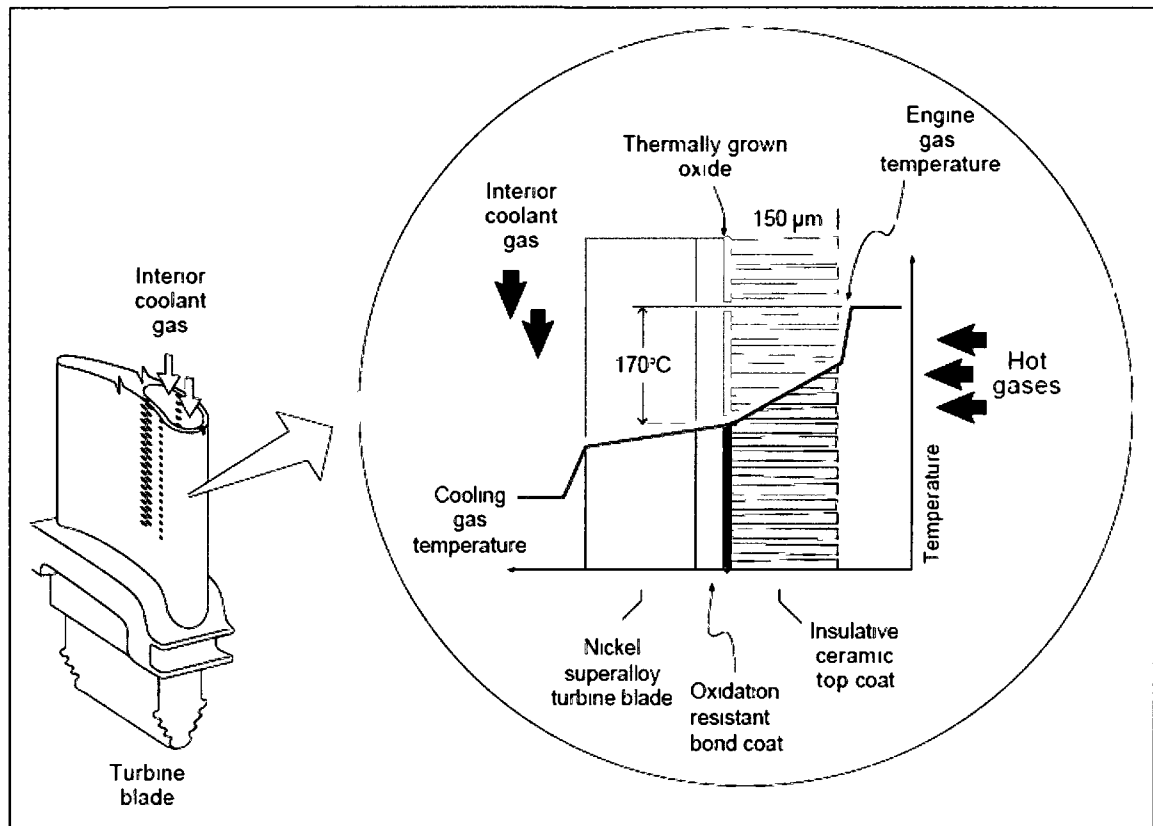


Figure 2.20: Schematic view of the temperature distribution inside the cross-section of a TBC system applied to the surface of a turbine blade (adapted from [4])

2.3.2 TBC Structure and Materials

The present section of the report will discuss the typical structure of TBC systems as well as the common materials used in the industry for their manufacturing. As discussed previously, TBC systems are typically manufactured by the deposition of two superimposed coating layers: the metallic bond coat and the ceramic top coat. Upon exposure to high temperatures and thermal cycling, oxygen diffuses through the porous ceramic top coat and reacts with the metallic constituents of the bond coat to naturally form a thin oxide layer known as the

thermally grown oxide (TGO). This oxide layer forms at the interface between the bond coat and top coat, and has been shown to play an important role in TBC performance. The typical structure of a TBC is presented in Figure 2.21.

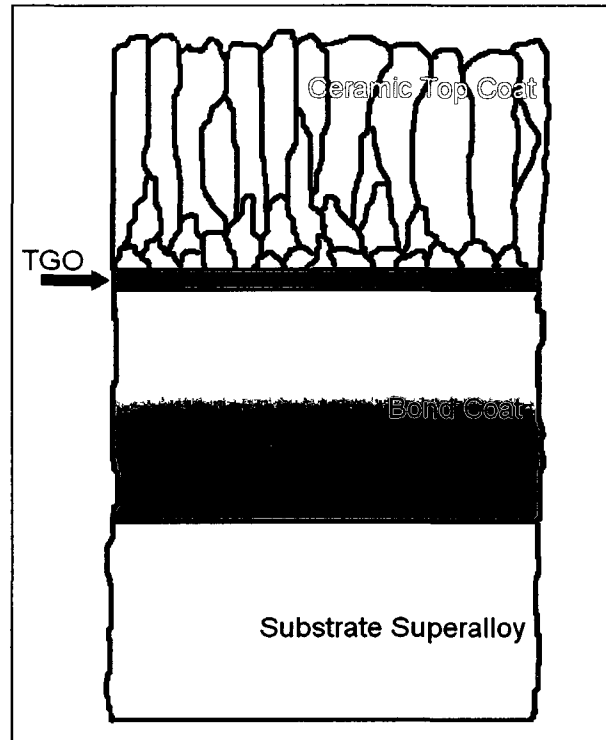


Figure 2.21: Typical TBC system structure

2.3.2.1 Ceramic Top Coat

The outermost layer of a TBC system consists of a high temperature resistant ceramic coating. Its primary role is to provide insulation from the high operating temperatures experienced at the surface of the turbine blades, and therefore maximize the temperature drop across its thickness (typically 150-250 μ m). Ceramics are known for their low thermal conductivity and therefore offer excellent insulating properties. Conventionally, this layer of the TBC is produced from zirconia or yttria-stabilized zirconia (YSZ), the latter being most currently employed [4]. YSZ offers good thermal protection by means of a low thermal conductivity (approximately 2.2 to 2.6 W/mK), which is made possible due to the intrinsic low thermal conductivity of zirconia as well as the phonon scattering defects introduced by the addition of yttria [64]. Typically, a concentration of 6 to 8 wt. % of yttria is added to the zirconia since this composition has been shown to optimize spallation life [65]. Also, when compared to

other ceramics, YSZ is characterized with a relatively high coefficient of thermal expansion (CTE) of $9.0 \times 10^{-6} \text{ K}^{-1}$ (at room temperature). The high CTE feature is important given that the top coat is applied directly onto the metallic bond coat (often a nickel based alloy). Since high operating temperatures are involved, a large CTE mismatch between the bond coat and top coat could lead to critical stresses at their interface and result in premature failure of the TBC system upon thermal cycling. In summary, the ceramic top coat must have the lowest possible thermal conductivity for insulation properties and a high CTE to minimize the mismatch with the CTE of the metallic bond coat. Figure 2.22 shows the ranges of thermal conductivity and CTE for various materials, thus demonstrating that YSZ exhibits properties that make it appropriate for use as top coat in TBC systems.

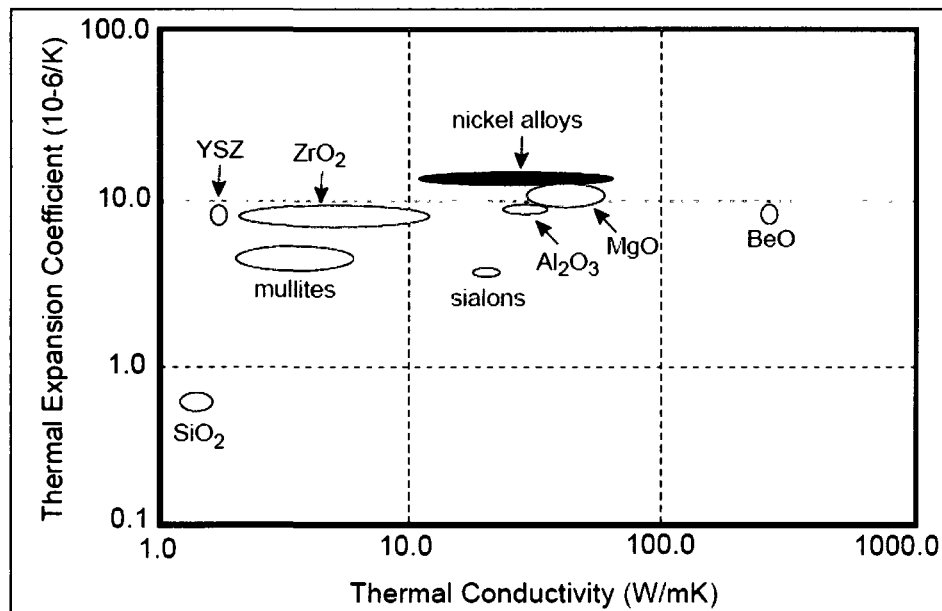


Figure 2.22: Thermal conductivity and coefficient of thermal expansion ranges of various materials [4]

2.3.2.2 Metallic Bond Coat and Thermally Grown Oxide

The bond coat is considered by some to be the most important component of a TBC system since it has many functions and has been associated with many TBC failure mechanisms, as discussed in a subsequent section. Bond coats consist of a thin metallic coating (typically 100-150 μm) applied directly onto the superalloy substrate in order to (1) promote bonding between the ceramic top coat and the underlying superalloy substrate, and (2) provide

protection against chemical attacks such as high-temperature oxidation and/or hot-corrosion. Suitably, stand-alone bond coats essentially serve the same purpose as bond coats found in TBC systems with the obvious exception of promoting adhesion of the ceramic top coat. Also, it is important to realize that the ceramic top coat does not provide any level of chemical protection due to its porous nature which allows oxygen to reach the bond coat surface with relative ease. As such, the levels of chemical protection offered by the bond coat are very similar with or without the presence of a ceramic top coat, provided that the effective bond coat surface temperatures remain equivalent. The concepts to be discussed in the following sections pertaining to bond coats used in TBCs therefore generally also apply to stand-alone bond coats used for chemical protection. Once again, for conciseness purposes, the remainder of these discussions will focus mainly on bond coats used in TBC systems.

Improved adhesion between the various layers of the TBC system is achieved by selecting a bond coat material with a CTE that is between that of the ceramic top coat and superalloy substrate. At room temperature, typical bond coats exhibit a CTE of approximately $13.5 \times 10^{-6} \text{ K}^{-1}$ [1]. Minimizing the CTE mismatch between the various TBC layers significantly reduces the interfacial stresses induced during thermal cycling and results in longer coating life [66].

Protection against oxidation is achieved by careful selection of the chemical composition of the bond coat in order to give it the ability to form a thin protective surface oxide scale known as the thermally grown oxide (TGO). The TGO scale is formed from the reaction of the metallic constituents of the bond coat with the oxygen penetrating through the porous top coat. It has been shown that a dense, uniform, continuous and slow growing alumina ($\alpha\text{-Al}_2\text{O}_3$) TGO scale is desirable [67] as it helps to restrict and prevent further oxidation of the bond coat (due to the low diffusivity of oxygen across the $\alpha\text{-Al}_2\text{O}_3$ layer) [68]. As such, bond coats are typically designed to be nickel based and aluminum rich in order to generate a protective alumina scale in preference to other oxides which can be detrimental to coating performance and longevity. Careful selection of the bond coat composition will thus ensure adequate formation of the TGO and play an important role in protecting the underlying superalloy turbine blades from oxidation and corrosion.

Bond coats are commonly found to be of two types. The first type is known as diffusion aluminide bond coats, which are typically manufactured by means of surface enrichment by diffusion techniques such as pack cementation. These coatings are based on the formation of the β -NiAl intermetallic compound (in some cases, the compound is modified with Pt), which remains stable at elevated temperatures, as seen in the Ni-Al phase diagram shown in Figure 2.23. The β -NiAl phase is rich in aluminum and therefore favours the formation of the alumina TGO scale upon exposure to oxygen. As such, diffusion aluminide coatings have been considered as bond coats in numerous studies [69-71]. The main drawback associated to diffusion aluminide bond coats is attributed to the strong tendency for interdiffusion of Al with the substrate. This favours the formation of γ' -Ni₃Al in the coating, which reduces its aluminum content and therefore limits its level of protection.

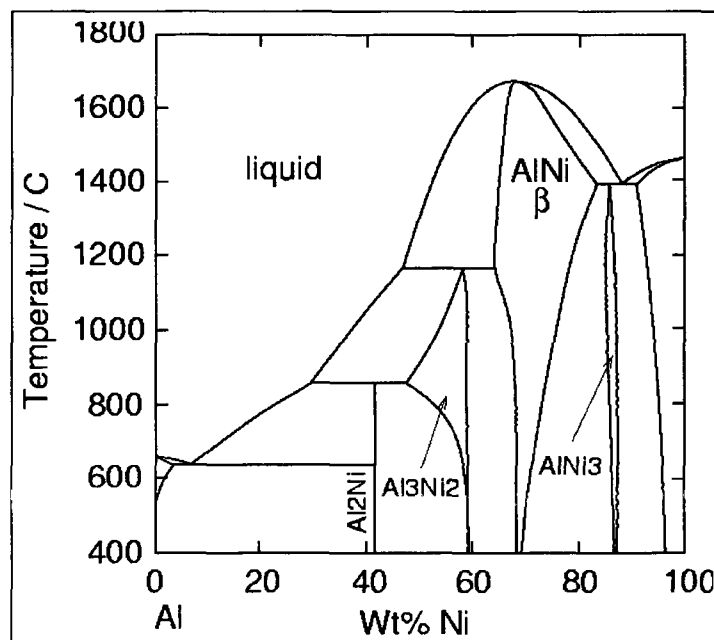


Figure 2.23: Ni-Al phase diagram showing the high temperature stability of β -NiAl [72]

The second type of bond coats consists of overlay coatings deposited by means of thermal spraying. Overlay coatings allow for much better control of the deposited materials properties, despite some expected material degradation during the thermal spraying process. Because of this, more complex alloys with improved properties have been developed for use as bond coats in TBCs. These alloys still contain important amounts of Ni and Al, however other alloying elements have been included such as Cr, Co, and Y (yttrium). These

compositions are often referred to as MCrAlY (where M may be Ni, Co or both) and are the type of bond coats predominantly found in modern TBCs. The addition of Cr has resulted in improved corrosion resistance [72], whereas the amount of aluminum is still sufficient to produce an alumina scale for proper oxidation resistance. The addition of Yttrium in the bond coat has been shown to promote adhesion of the TGO scale to the bond coat surface. This has been reported to be due to the influence of Yttrium on the formation of peg-like oxides that helped anchor the TGO scale to the coating surface [73]. Conversely, Smeggil [74] reported that the main role of Yttrium is to combine with sulphur and prevent its segregation to the oxide layer, which is otherwise detrimental to its adhesion.

The microstructure of MCrAlY coatings is typically characterized with two phases. The first is a face-centered-cubic (fcc) Ni/Co-base solid solution matrix often referred to as the γ -phase or γ -matrix. The second phase consists of fine precipitates of a body-centered-cubic (bcc) Ni-Al intermetallic known as the β -phase or β -NiAl [1]. A typical thermal spray MCrAlY coating microstructure is shown in Figure 2.24. The β -phase is the aluminum-rich phase from which aluminum is consumed in the oxidation reaction for the formation of the TGO scale, as discussed further in section 2.3.4.3.

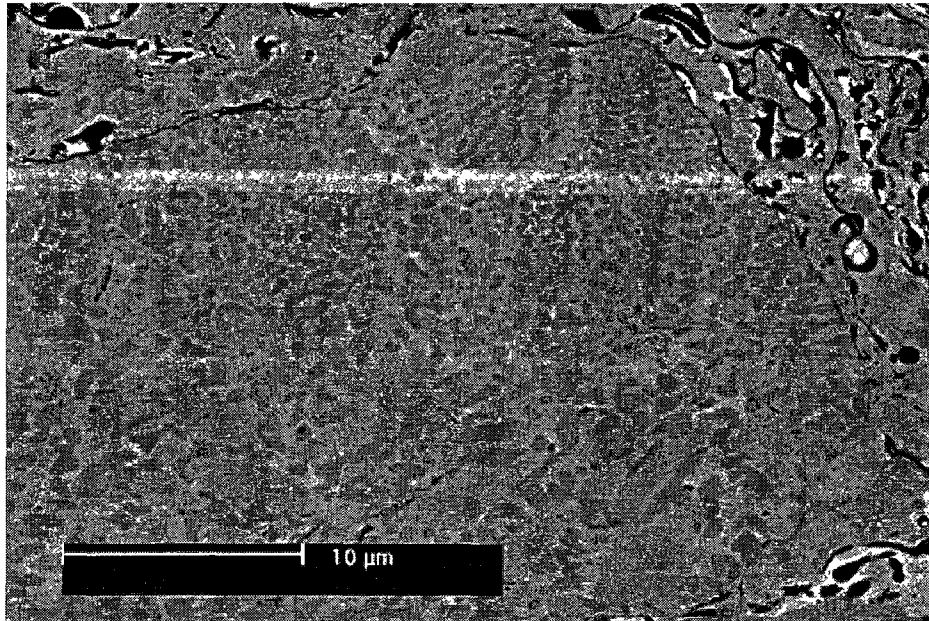


Figure 2.24: Typical two-phase microstructure of a thermal spray MCrAlY coating: the light grey and dark grey areas represent the γ -matrix and β -phase precipitates respectively (adapted from [76])

With the addition of various alloying elements to the original Ni-Al composition, MCrAlY coatings have given rise to new possibilities for improved performance of bond coats in TBC. Figure 2.25 summarizes the relative levels of protection of various bond coat materials such as diffusion aluminides and MCrAlY overlay coatings. As can be seen in this figure, MCrAlY overlay coatings offer better oxidation and corrosion resistance than diffusion aluminide coatings. As such, the remainder of the bond-coat related discussions presented in this report will focus on MCrAlY overlay coatings. In particular, CoNiCrAlY overlay coatings will be considered as they offer a combination of elevated levels of protection against both oxidation and hot-corrosion. In addition, this material can be used either as a bond coat material for TBC applications or as a stand-alone coating for improved high temperature oxidation/corrosion resistance. As such, CoNiCrAlY coatings are considered to be versatile coatings for high temperature application and have therefore been selected as the studied material in this work.

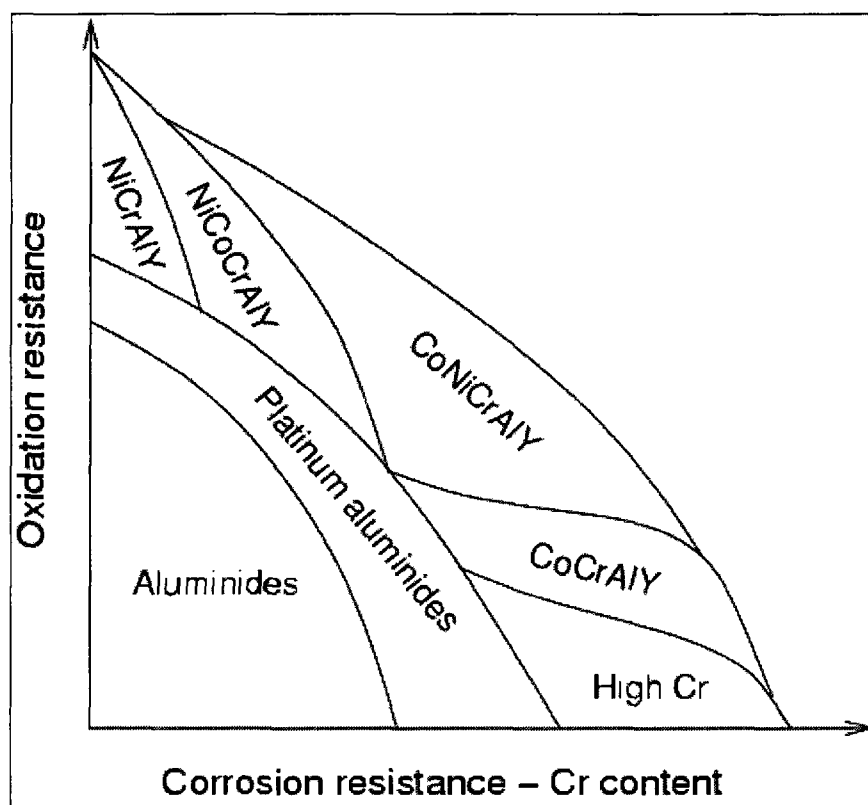


Figure 2.25: Relative levels of protection against oxidation and corrosion for the different bond coat materials [72]

2.3.3 Processing Methods and Typical Microstructural Features

This section of the report will discuss the TBC system processing techniques commonly used in the industry and identify some of the typical coating microstructural features observed. Although the current work concentrates on the bond coat and as a result no ceramic top coat was actually deposited or analyzed in this study, the manufacturing methods and resulting properties of both layers are of interest and have therefore both been included in the discussion. Given the fundamental differences in material properties between the top coat and bond coat, the processing techniques are also necessarily different and are therefore discussed in separate subsections.

2.3.3.1 Ceramic Top Coat

There are two popular deposition techniques currently used for the application of the ceramic top coat on the TBC structure. These two techniques are inherently different, and therefore important differences regarding coating morphology and performance are to be expected. The first popular deposition technique is plasma spraying [77-80]. Due to the nature of the deposition process, a plasma sprayed coating is formed by a series of material lamellar splats that are typically aligned parallel to the substrate, as seen in Figure 2.26a. The second method currently used for the deposition of the ceramic top coat is Electron Beam Physical Vapour Deposition (EB-PVD) [4, 77, 80]. EB-PVD uses electron beams as an energy source to vaporize the coating material which is then condensed onto the substrate. The process is performed under a vacuum environment to enable vaporization of the coating material at lower temperatures. The resulting coating typically has a columnar morphology, as seen in Figure 2.26b.

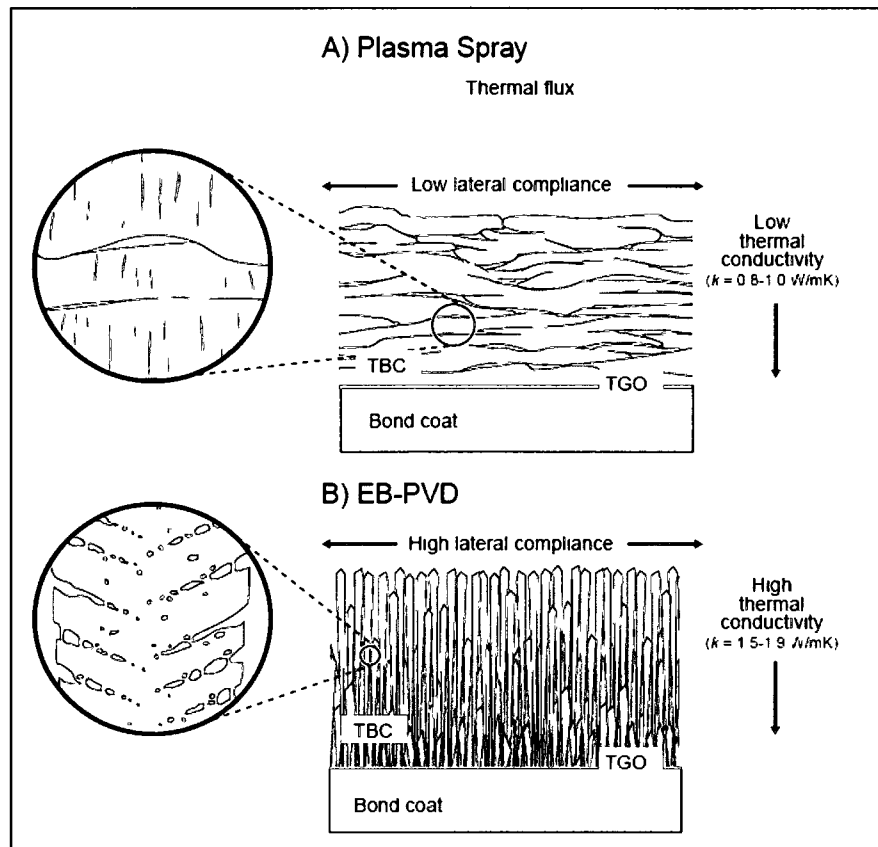


Figure 2.26: Different ceramic top coat morphologies for Plasma spraying and EB-PVD coating processes [4]

As seen in Figure 2.26, each deposition technique leads to different coating morphologies with specific properties. Coatings produced from plasma spraying have been shown to have lower thermal conductivities and overall better thermal insulation properties than coatings produced by EB-PVD. This is attributed to the pore morphology of plasma sprayed coatings (pores are parallel to the substrate) which has been shown to provide a higher impedance to heat flow and therefore reduce thermal conductivity [4]. Alternatively, plasma sprayed top coats are characterized as having low lateral compliance for thermal expansion due to the morphology of the ceramic splats and are therefore more susceptible to spallation failure than EB-PVD coatings. As such, stresses that develop at the bond coat and ceramic top coat interface during thermal cycling due to the CTE mismatch can be higher in plasma sprayed coatings, thus favouring earlier crack nucleation, propagation and failure of the coating. Conversely, EB-PVD coatings have displayed a better resistance to spallation due to their inter-columnar pore morphology. The elongated pore structure perpendicular to the substrate

increases the in-plane compliance of the coating (greater flexibility in the lateral direction than the lamellar splats resulting from the plasma process) and improves its spallation life [4, 80]. As such, EB-PVD top coats are viewed as more durable and generally superior to plasma sprayed top coats. Unfortunately, EB-PVD systems have a high capital cost in the range of \$20 million and, therefore, are reserved for market applications with high margin products [81]. For these various reasons, the use of plasma sprayed top coats is mostly limited to applications where thermal cycling is less severe such as land-based power generation gas turbines, whereas EB-PVD coatings are used in higher performance applications such as aircraft gas turbine engines.

Due to the high EB-PVD equipment cost, efforts have also been made to modify the basic plasma spraying process in order to produce coatings featuring vertical cracks to mimic the EB-PVD columnar structure [82, 83]. Theoretically, these coatings could have similar benefits to those achieved with EB-PVD and could therefore experience longer operating life. However, Madhwal *et al.* [83] reported that the thermal cycling life of the vertically cracked plasma sprayed coatings was somewhat lower than that of good “normal” plasma sprayed top coats. Further development and investigation of this technology thus appears to be required.

Finally, given that plasma spraying is a popular alternative for the top coat deposition, it is worth addressing the potential issues related to the use of this technique and its influence on the underlying bond coat properties. While much effort is given to manufacture the bond coat with minimal defects and specific microstructures, as is the case in the current work, one may expect the subsequent deposition of the ceramic top coat by means of a high temperature plasma spray process to cause thermally induced changes in the bond coat microstructure. Such changes would then be expected to reduce the effectiveness of the carefully deposited bond coat, thereby marginalizing previously carried out efforts. Fortunately, it is believed that such effects can be minimized for the following reasons. Firstly, extensive heating of the substrate in thermal spraying has been mostly resolved by the development of numerous substrate cooling techniques in order to allow deposition of coatings on temperature sensitive materials. Proper control of the spraying parameters and cooling conditions is thus expected to be achievable for the deposition of a ceramic top coat with minimal impact on the underlying bond coat microstructure. Secondly, bond coat surface pre-treatments are

regularly carried out in the form of controlled environment heat treatments prior to top coat deposition. These pre-treatments are designed to activate the oxidation dynamics of the bond coat in order to rapidly form a protective alumina oxide layer in preference to other oxides. As discussed later in this thesis, the oxidation behaviour of the bond coat is most critical in the early stages of oxidation. As such, should any microstructural changes occur due to deposition of the ceramic top coat, the major benefits attributed to careful deposition of the bond coat are likely to be preserved as a result of these surface pre-treatments.

2.3.3.2 CoNiCrAlY Bond Coat

MCrAlY bond coats are typically manufactured by thermal spraying techniques. The three most common bond coat deposition methods include air plasma spraying (APS), low pressure plasma spraying (LPPS) and high velocity oxy-fuel (HVOF). As discussed in previous sections, all of these methods involve significant heating of the coating material and cause melting and/or softening of the sprayed particles. Particle heating in plasma spraying is much more severe than in HVOF, however particle velocities are also much lower. The difference in process conditions between plasma and HVOF spraying has been shown to influence the morphology, microstructure and behaviour of the bond coat material.

Figure 2.27 shows optical microscope images of the morphology of CoNiCrAlY bond coat cross-sections as-deposited by LPPS, HVOF and APS. From these images, Shibata *et al.* [75] showed that the LPPS coating had a very dense microstructure consisting of well-flattened particles, which was considered to be an indication that most of the powder particles were molten during the deposition process. Conversely, the coating manufactured by APS was shown to have higher porosity, which was said to be due to the formation of particle surface oxides during the spraying process. Finally, the HVOF bond coat exhibited a relatively dense structure due to high particle velocities. The porosity observed in the HVOF coating was said to be attributed to the lack of deformation of un-molten particles.

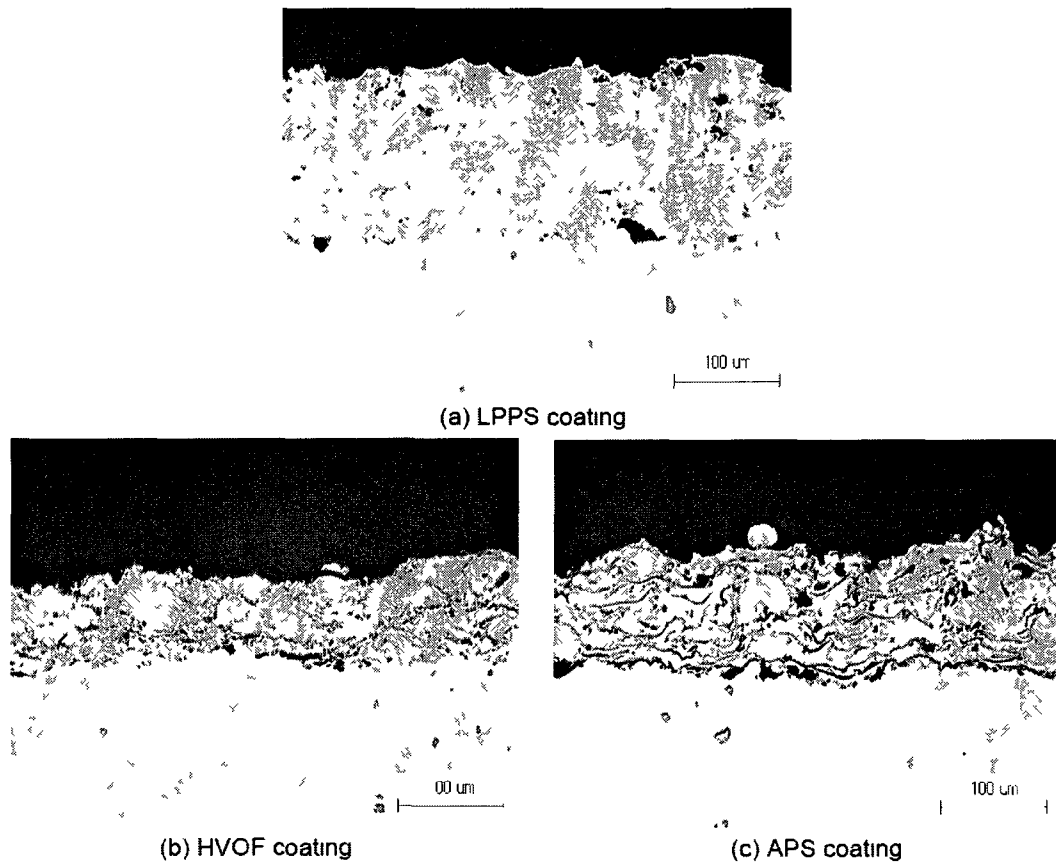


Figure 2.27: Optical microscope images showing typical CoNiCrAlY bond coat microstructures for (a) LPPS, (b) HVOF and (c) APS deposition techniques (adapted from [75])

Shibata *et al.* [75] also observed differences in coating microstructure for the three deposition techniques. Firstly, the oxygen content of the as-sprayed LPPS, HVOF and APS coatings was measured to be 0.16, 0.94 and 1.8 wt. % respectively. As expected, the APS coatings had the greatest oxide content due to the high process temperatures and spraying environment open to atmospheric air. A lower process temperature reduced the oxide content in the HVOF coating, whereas the controlled chamber environment used in LPPS proved most successful in limiting in-spray oxide formation. Finally, Shibata *et al.* [75] observed that the β -phase precipitates were only detectable in the HVOF coating. Although they do not provide an explanation for this observation, it is likely that particle melting and re-solidifying due to the high process temperatures involved in the LPPS and APS deposition techniques resulted in important microstructural transformations of the deposited material.

Higuera *et al.* [84] also investigated the influence of the deposition technique on the properties and microstructure on CoNiCrAlY bond coats. Figure 2.28 shows the cross-section of coatings obtained by APS and HVOF. Results obtained are similar to those reported by Shibata *et al.* [75]: when compared to HVOF coatings, APS coatings are characterized with higher porosity due to lower particle velocities and higher oxide content due to increased process temperature. Table 2.4 presents the porosity and oxide contents as well as additional coating properties such as microhardness and adhesion strength as reported by Higuera *et al.* [84]. The higher hardness of the HVOF coating was attributed to the lower process temperature and higher particle velocities causing greater particle plastic deformation and inducing work-hardening. Finally, both coatings exhibited high adhesion strengths: failure of the adhesive used in the adhesion testing procedure occurred before failure of the coating, and therefore actual values of bond strength are not available.

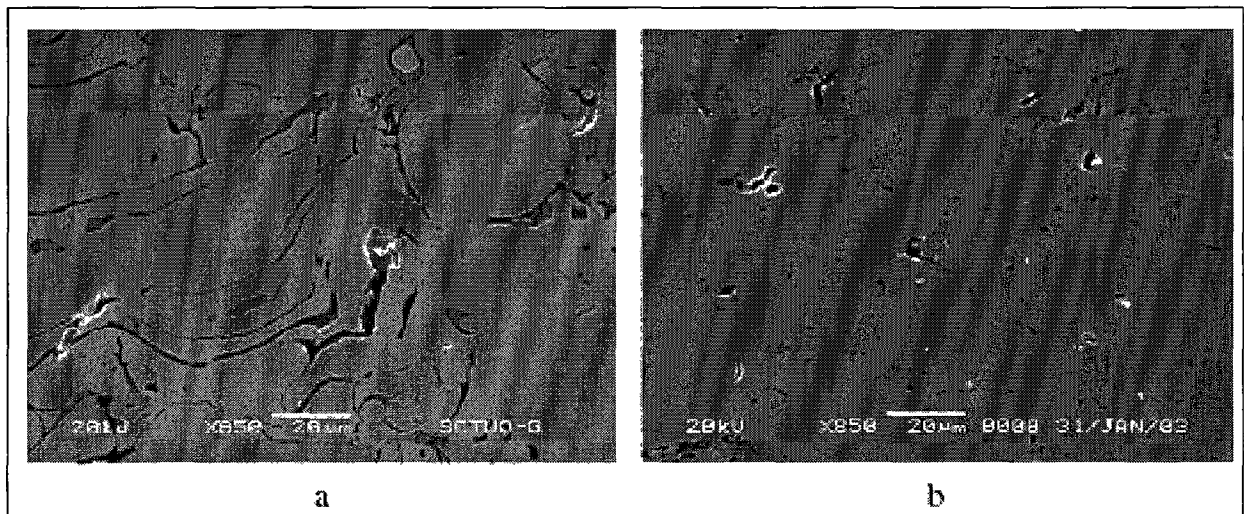


Figure 2.28: Scanning electron microscope images of CoNiCrAlY coating cross-sections obtained from different deposition techniques: (a) APS and (b) HVOF (adapted from [84])

Table 2.4: Various CoNiCrAlY bond coat properties for APS and HVOF deposition techniques [84]

Coating Property	APS	HVOF
Porosity (avg. vol. %)	5.1 ± 0.7	4.6 ± 1.5
Oxide Content (avg. vol. %)	5.8 ± 2.1	3.4 ± 0.8
Vicker's Microhardness (HV ₃₀₀)	155 ± 18	418 ± 31
Adhesion Strength (MPa)	>64	>64

2.3.4 TBC Failure Mechanisms

The present section of the report will define the major failure mechanisms that govern the operating life of TBC systems. Failure of a TBC system is generally associated with the delamination or spallation of the ceramic top coat (as shown in Figure 2.29) which occurs due to crack nucleation and propagation at the bond coat / TGO / top coat interfaces. Cracks typically form in areas of high stress concentration around the TGO due to the presence of high interfacial stresses induced during thermal cycling (caused by the differences of CTE of each coating layer). Investigation of the actual mechanisms by which failure occurs is now presented.



Figure 2.29: Example of a spalled TBC sample during thermal cycling [69]

2.3.4.1 Failure by Foreign Object Damage

This failure mechanism occurs when the coated component is subjected to particle impact and foreign object damage during engine operation [67]. The impact of foreign objects on the TBC system can cause chipping or local compression of the ceramic top coat, thereby creating a zone where thermal protection has been diminished. This can cause the formation of a “hot-spot” in the underlying bond coat which can cause thermal failure of the coating system, as seen in Figure 2.30. This type of failure cannot be avoided through means of coating improvements, and therefore will not be discussed further in this study.

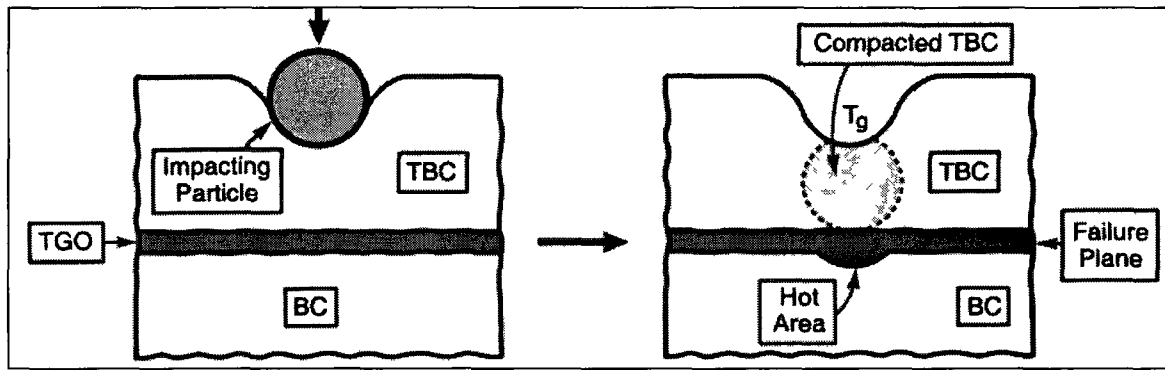


Figure 2.30: Foreign object damage failure mechanism (adapted from [67])

2.3.4.2 Thermo-mechanical Failure

Thermo-mechanical failures of TBC systems are associated with the continuous growth of the $\alpha\text{-Al}_2\text{O}_3$ TGO scale during thermal cycling. It has been shown that growth of the TGO is controlled by a diffusion mechanism and is essentially parabolic:

$$h^2 = 2bt \quad (\text{Eq. 2.13})$$

where h is the scale thickness, t is the time and b is the parabolic rate constant [67]. As mentioned previously, the formation of $\alpha\text{-Al}_2\text{O}_3$ is desirable because it has a low growth rate in comparison to other oxides.

In a first case, failure is caused by “undulating” or “rumpling” of the TGO scale. As the TGO scale continues to grow in time during thermal cycling, it becomes increasingly compressed between the bond coat and top coat, and therefore attempts to reduce stresses and strain

energy by lengthening. This is achieved by means of out-of-plane displacements which results in undulating or rumpling of the TGO scale [77]. Undulations within the TGO act as areas of increased stress concentration where crack nucleation typically occurs. With increasing thermal cycling and the resulting thermo-mechanical stresses, the cracks propagate until they coalesce and then become large enough to satisfy large scale buckling. This leads to spallation of the ceramic top coat and failure of the TBC system. Failure due to TGO rumpling has been observed in various studies [69, 85]. The sequence of thermo-mechanical failure due to TGO rumpling is illustrated in Figure 2.31.

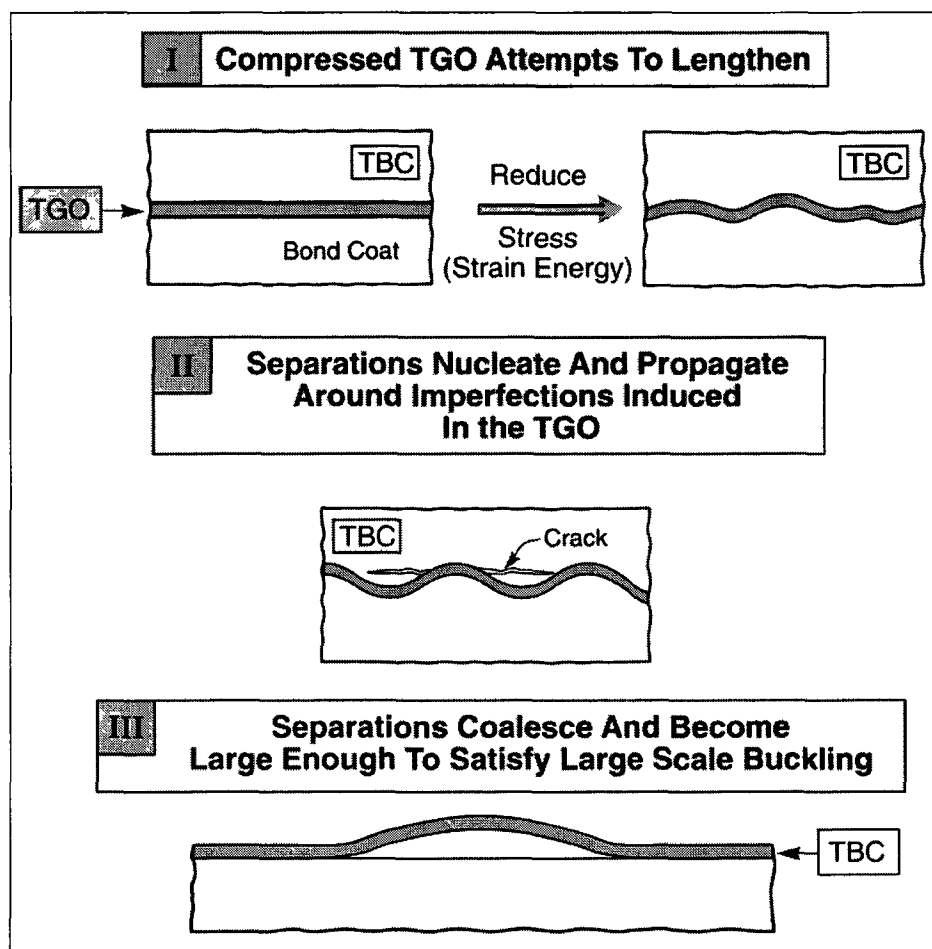


Figure 2.31: Sequence of thermo-mechanical failure due to TGO rumpling (adapted from [67])

In a second case, failure is caused by uneven growth of the TGO scale. During thermal cycling, the growth rate of the TGO can vary locally on the surface of the bond coat due to chemistry inhomogeneities or non-uniform top coat porosity. This can cause the TGO to

grow unevenly, leading to the formation of what is known as oxide imperfections [77]. These oxide imperfections represent stress concentration areas in the coating and are therefore more susceptible to crack nucleation. The repeated application of large normal stresses resulting from thermal cycling can eventually cause cracks to form and propagate, thus causing spallation failure of the TBC system. Failure by means of uneven TGO growth is schematically illustrated in Figure 2.32.

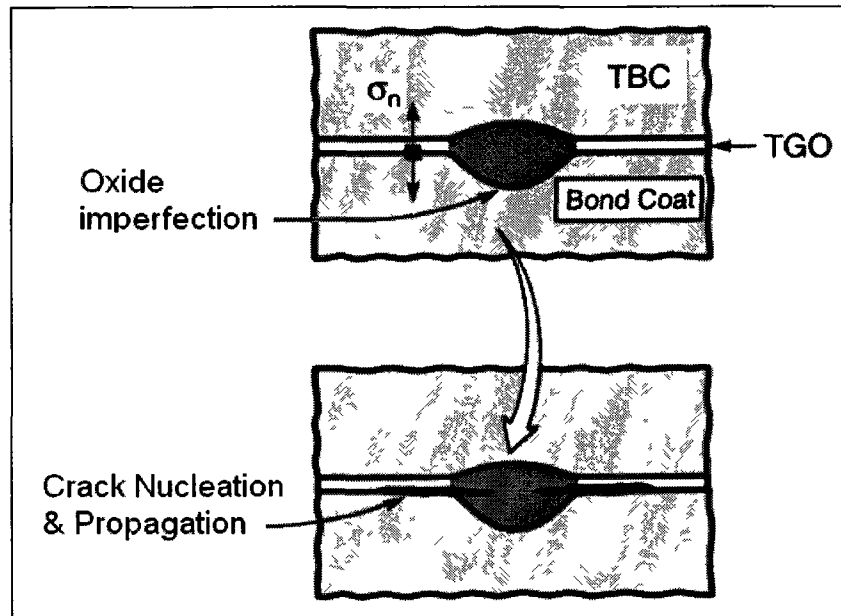


Figure 2.32: Schematic illustration of the failure of a TBC system due to uneven TGO growth and oxide imperfections (adapted from [67])

2.3.4.3 Chemical Failure: Bond Coat Oxidation

The present section is dedicated to investigating the bond coat oxidation mechanism and the resulting chemical failure of TBC systems. Oxidation of the bond coat is the result of oxygen seeping through the ceramic top coat and chemically reacting with the metallic elements in the bond coat. The evolution of the TGO scale growth resulting from prolonged oxidation of the bond coat is schematically represented in Figure 2.33. As discussed previously, a common MCrAlY bond coat is typically composed of two phases: a γ -phase matrix that is rich in Ni and/or Co as well as fine precipitates that form the β -NiAl phase. The β -NiAl precipitates are aluminum rich and therefore have a high affinity for oxygen. Upon exposure to high temperature gases, preferential oxidation of the aluminum contained within the β -

phase leads to the formation of $\alpha\text{-Al}_2\text{O}_3$. The diminishing concentration of aluminum in the bond coat causes dissolution of the $\beta\text{-NiAl}$ precipitates. For this reason, the β -phase precipitates are often described as an aluminum reservoir, and coating life is generally discussed in terms of the depletion of this phase [75]. Since TGO growth is governed by diffusion of aluminum to the surface of the bond coat, β -phase precipitates closest to the surface are the first to dissolve. Progressive consumption of Al for TGO scale growth and dissolution of $\beta\text{-NiAl}$ precipitates result in the formation of a region in the bond coat where β -phase precipitates have disappeared. This region is known as the depletion zone and has been shown to grow in thickness with increasing oxidation time [75, 86]. Eventually, diffusion of Al through the increasingly thick depletion zone becomes unfavourable, and the oxygen then reacts with the other metallic constituents in the γ -matrix. Given that α -alumina is characterized with a low diffusivity of oxygen, the metallic constituents from the γ -matrix diffuse outward across the alumina layer and form complex mixed oxides on the surface of the α -alumina scale. For example, while performing prolonged isothermal oxidation experiments of thermal spray CoNiCrAlY coatings at elevated temperatures, Shibata *et al.* [75] observed the formation of spinel (NiO) and NiCo_2O_4 on top of the α -alumina TGO scale. Tang *et al.* [87] also performed oxidation experiments on thermal spray CoNiCrAlY coatings and observed the appearance of $(\text{Co, Ni})\text{Cr}_2\text{O}_4$ and $(\text{Co, Ni})\text{Al}_2\text{O}_4$ mixed oxides on the α -alumina TGO scale. Mixed oxides and spinel are characterised as fast growing oxides and are therefore considered detrimental to TBC system integrity as they accelerate thermo-mechanical induced failures.

The event by which the preferential formation of α -alumina as the dominant oxide in the TGO scale comes to an end represents the onset of what is known as chemical failure of a TBC system. The subsequent formation of fast growing mixed oxides accelerates the overall TGO growth rate and protrusion of these oxides can initiate the thermo-mechanical failure mechanisms.

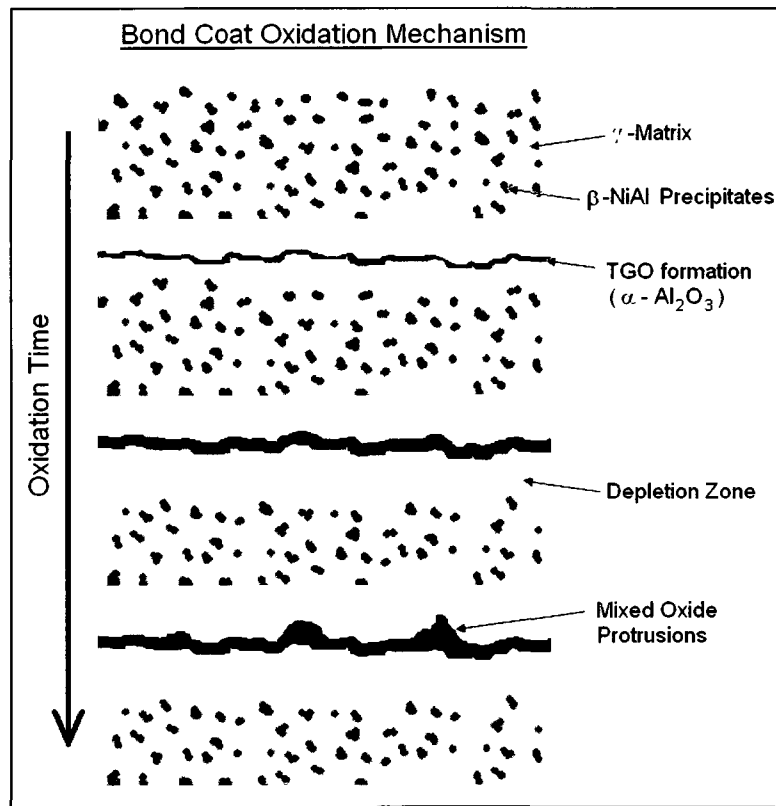


Figure 2.33: Evolution of TGO growth with increasing oxidation time

2.3.4.4 Failure Mechanisms: Summary

In summary, it has been demonstrated that the dominant failure mechanisms of TBC systems are directly associated with the growth dynamics of the TGO scale and therefore more specifically with the oxidation behaviour of the bond coat during thermal cycling. Thermo-mechanical failure mechanisms can first be mitigated by minimizing the growth rate of the TGO. As such, it has been demonstrated [67, 68] that the formation of a dense α -alumina TGO scale in preference to other oxides is desirable due to its slow growth rate and low diffusivity of oxygen across its thickness. Also, a continuous and uniform TGO scale is desirable in order to prevent the formation of oxide imperfections [67, 77]. Finally, depletion of the aluminium rich β -phase is undesirable as this causes the onset of fast growing mixed oxides which are detrimental to TBC system longevity. Better control of the TGO growth dynamics could therefore lead to significant improvements of TBC system performance.

2.3.5 Improving TBC Performance

There have been numerous studies performed specifically on bond coat features with the common objective of improving the durability and performance of TBC systems. These studies have investigated various facets of the bond coat from microstructure to manufacturing in an attempt to improve its oxidation behaviour. The present section summarizes some of the work previously carried out for TBC system performance improvement.

Firstly, research work has been performed to investigate the influence of manufacturing the bond coat using various deposition techniques [75, 84, 88]. Shibata *et al.* [75] compared the LPPS, APS and HVOF techniques and showed that the oxidation rate was highest for the APS bond coat when subjected to isothermal high temperature oxidation experiments. This was attributed to the high porosity of the APS coatings, which allowed oxygen to penetrate in the bond coat and form oxides from within the coating. As such, the higher density of the as-deposited LPPS and HVOF coatings contributed to a lower oxide growth rate during the oxidation tests. Results also showed that higher levels of formation of spinel and undesirable mixed oxides were observed for increasing oxide content within the as-deposited coatings (due to in-spray oxidation of the particles). Tang *et al.* [87] further investigated the effect of in-spray surface oxidation of CoNiCrAlY particles deposited by HVOF. Their work demonstrated that oxides formed during the HVOF thermal spray process promoted the formation of undesirable spinel-type oxides during the primary stage of bond coat oxidation. It was therefore concluded that in-spray particle oxidation should be minimized to reduce the formation of detrimental, fast growing non-alumina oxides.

Another approach for the improvement of TBC systems has been to manufacture bond coats with a nanocrystalline microstructure. Nanocrystalline materials are characterized with grain sizes ranging from 1 to 100 nm [89] and have been shown to exhibit increased diffusion rates and mechanical properties due to the increased amount of atoms associated to grain boundary area [89-91]. Ajdelsztajn *et al.* [86] and Tang *et al.* [92] both demonstrated that a bond coat with nanocrystalline microstructure favoured the formation of the α -alumina scale due to enhanced diffusion of aluminium at the grain boundaries. Wang [93] had observed similar

results upon close examination of the formation mechanisms of Al_2O_3 on the surface of nanocrystalline materials. His results showed that nanocrystallization provides two beneficial effects on the oxidation mechanism due to the increased amount of grain boundaries. Firstly, grain boundaries act as nucleation sites for scale formation and therefore a scale with a more uniform thickness is observed. Secondly, diffusion of aluminium is increased at grain boundaries, thus favouring the selective oxidation of aluminum and the formation of a continuous Al_2O_3 scale. The method by which the nanocrystalline bond coat materials are synthesized has also been shown to have an effect on its oxidation behaviour. Ajdelsztajn *et al.* [76] produced nanocrystalline NiCrAlY powders by cryomilling, a process where powders are mechanically milled in a liquid-nitrogen environment for numerous hours in order to introduce large amounts of dislocations and ultimately refine the material's grain structure down to the nanometer scale. The cryomilling process was shown to introduce nitride dispersoids within the deposited powder which was believed to act as nucleation sites for the formation of $\alpha\text{-Al}_2\text{O}_3$, thus further improving the oxidation behaviour.

Many studies have also been performed to investigate the effect of various bond coating surface treatments for TBC performance improvement. The influence of the bond coat surface roughness has been the focus of many studies [94-97]. Generally, it appears that for TBCs with top coats manufactured by plasma spraying, a bond coat with a rough surface (roughness amplitude of $\sim 20\mu\text{m}$) is desirable, whereas TBCs with ceramic top coats deposited by EB-PVD perform better when applied on a bond coat with a smooth surface finish. Studies have also investigated the effect of performing pre-oxidation of the bond coat in a controlled environment before the application of the ceramic top coat [95, 97-99]. The findings reported in these studies all agree that performing pre-oxidation treatments on the bond coat using an environment with controlled temperature and oxygen content can favour the formation of the desirable $\alpha\text{-Al}_2\text{O}_3$ scale and thus improve the oxidation behaviour of the bond coat.

In summary, it is generally accepted that the microstructure of an MCrAlY alloy coating is sensitive to its manufacturing method, and therefore selecting a deposition technique with a lower process temperature that minimizes chemical and microstructural transformations is beneficial. Also, bond coats should be manufactured with a minimal level of porosity to

prevent oxides to form within the bond coat. It has also been suggested that improved TBC performance could be achieved by manufacturing bond coats with a nanocrystalline microstructure. Nanocrystalline bond coats produce a more uniform α -Al₂O₃ scale that remains stable for longer oxidation times due to their fine grain structure. It should be noted that the studies mentioned previously have investigated the effect of nanocrystalline bond coats using HVOF as the deposition technique, and therefore the full benefits of the nanocrystalline microstructure may not have been realized due to in-spray oxidation and thermally induced microstructural transformations. As such, nanocrystalline bond coats manufactured by CGDS may yield further improvements to TBC system performance. Surprisingly, few studies on bond coats deposited by CGDS have been performed. Zhang *et al.* [94] performed preliminary oxidation testing on nanocrystalline NiCrAlY bond coats manufactured by CGDS, however the as-deposited coatings were found to be porous, and the study thus focused on the influence of surface shot-peening on the oxidation behaviour. Although bond coat surface treatments have been shown to mitigate some of the issues associated with the bond coat oxidation behaviour, it appears that the most significant benefits can be drawn from modifications of the bond coat microstructure itself. Once the fundamental oxidation behaviour is optimized, further improvements may be achieved by means of additional bond coat surface treatments. As such, the focus of this report will now turn to investigate the oxidation behaviour of nanocrystalline bond coats by means of the CGDS deposition technique.

Chapter 3 - Research Objectives

3.1 General Objectives

The general purpose of this study is to further advance current TBC technology and ultimately move closer to the development of a “prime-reliant” TBC system for improved gas turbine engine durability, performance and efficiency. Investigation of the relevant literature has suggested that improvements to TBC systems and mitigation of the common failure mechanisms can be achieved by improving predictability of the bond coat microstructure and, more specifically, enhancing control of its oxidation behaviour. Control of the bond coat oxidation behaviour is currently limited due to undesirable microstructural changes encountered within the material throughout coating manufacturing, thereby reducing the effectiveness of the coating properties in comparison to those of the carefully designed original feedstock powders. These changes have been attributed to the high processing temperatures of the traditional thermal spray deposition techniques typically used for bond coat manufacturing. To address these issues, this research work proposes to deposit bond coats using CGDS, a coating technology characterized with low processing temperatures and a reported ability to preserve a material’s microstructure throughout the deposition process. The aim of this research project is thus to demonstrate that CGDS is an alternative solution for the manufacturing of bond coats and that its inherent features can lead to improved bond coat oxidation behaviour.

3.2 Feasibility of CoNiCrAlY CGDS Coatings

The first specific objective for this research work is to verify the feasibility of manufacturing bond coatings using the CGDS deposition technique. CoNiCrAlY is a bond coat material commonly used in the industry that provides a good combination of oxidation and corrosion protection at elevated temperatures. It is commercially available in the form of powder particles of various size ranges which makes it suitable for processing using the CGDS technique. As such, a specific CoNiCrAlY alloy was previously selected and considered for all experimental trials presented in this work.

3.2.1 Conventional Coatings

As discussed in Chapter 2, it has been demonstrated that deposition of a material using traditional thermal spraying techniques such as plasma spraying and HVOF typically results in a coating with high oxide content and microstructural changes. These coating features have been shown to be detrimental to TBC performance and it has thus been proposed to deposit the bond coat using the CGDS deposition technique. Therefore, as a first objective, this study aims at demonstrating the feasibility of manufacturing conventional CoNiCrAlY coatings (micron-scale grain size microstructure) from a conventional CoNiCrAlY feedstock powder using the CGDS deposition technique. Similarly to Ni-based superalloys, CoNiCrAlY alloys have high strength at elevated temperatures and are therefore characterized as having a relatively high critical velocity for CGDS deposition. In order to form a CGDS CoNiCrAlY coating, it must be verified that sufficient plastic deformation of the particles is achieved upon impact. As such, assessing the feasibility of conventional CoNiCrAlY coatings by CGDS is important.

3.2.2 Nanocrystalline Coatings

Upon investigation of the relevant literature, it has also been suggested that the use of a bond coat with a nanocrystalline microstructure could be beneficial for the durability of a TBC system. Additionally, it has been demonstrated that CGDS has been successful in manufacturing various types of coatings with a nanocrystalline microstructure. This research work thus proposes to develop nanocrystalline CoNiCrAlY bond coats from nanocrystalline feedstock powder particles using the CGDS deposition technique. In addition to the inherent high strength of the CoNiCrAlY alloy, the increased mechanical properties resulting from the proposed nanocrystalline microstructure will further increase its critical velocity, thus making it more difficult to deposit using the CGDS technique. As such, the feasibility of nanocrystalline CoNiCrAlY coatings manufactured by CGDS must be verified.

3.3 Optimization of CGDS Parameters

Once the feasibility of manufacturing conventional and nanocrystalline CoNiCrAlY coatings by CGDS has been demonstrated, the present work will aim at optimizing the spraying parameters in order to achieve coatings of the highest possible quality. It has been discussed in chapter 2 that bond coats characterized with high levels of porosity are undesirable as extensive oxidation within the coating (occurring at the voids) causes rapid depletion of the β -phase and therefore limits the coating's protective capability. Reducing the void content within the bond coat is therefore important to achieve an improved oxidation behaviour. As such, this work also seeks to optimize the CGDS parameters for both the conventional and nanocrystalline CoNiCrAlY powder feedstocks in order to obtain coatings with minimal levels of porosity.

3.4 Investigation of Microstructural Changes Induced by CGDS

It has been previously demonstrated that microstructural changes such as grain growth and oxide inclusions in thermal spray bond coats are detrimental to their oxidation behaviour and therefore limit their effectiveness. Part of the incentive to manufacture bond coats using the CGDS deposition technique is attributed to its reported ability to maintain a material's microstructure throughout the spraying process due to its relatively low processing temperatures. Because of this key feature, the properties of CGDS coatings have been shown to be very similar to those of the original feedstock particles, and therefore this deposition technique is said to offer better control of a material's microstructure during the spraying process. It is therefore expected that improved control of the bond coat microstructure will be achieved if it is deposited using the CGDS technique. To verify this presumption, this research work will perform a detailed investigation of the microstructure of CGDS CoNiCrAlY coatings and compare it to that of the original feedstock powder in order to assess whether any microstructural changes have occurred during the deposition process. More specifically, the grain structure and phase composition of the CoNiCrAlY powder and resulting CGDS coatings are to be examined.

3.5 Investigation of Bond Coat Oxidation Behaviour

As discussed previously, most TBC failure mechanisms have been associated with the oxidation behaviour of the bond coat when exposed to gases at elevated temperatures. It has been shown that the formation of a dense uniform α -alumina scale is desirable in preference to other oxides on the surface of the bond coat as it has a slow growth rate and enhances the durability of TBC systems. It has also been demonstrated that the microstructural changes in the bond coat resulting from thermal spraying are detrimental to its oxidation behaviour and performance. As such, this work aims at comparing the performance of conventional and nanocrystalline bond coats manufactured by CGDS to those of thermal spray bond coats by investigating their oxidation behaviour. Once again, given the complexity of TBC systems due to the various interactions between the numerous coating layers, it was decided that this work should concentrate solely on the investigation of the oxidation behaviour of free-standing bond coatings without the presence of the superalloy substrate or ceramic top coat. Therefore, this approach allows proper identification of the influence of the deposition technique and resulting coating microstructures on the bond coat oxidation behaviour. For this part of the study, plasma and HVOF sprayed CoNiCrAlY coatings will be manufactured in addition to the conventional and nanocrystalline CGDS coatings. Isothermal oxidation experiments will be carried out on all samples to assess their oxidation behaviour. More specifically, investigation of the oxide scale morphology, growth rate and phase composition is to be performed. Finally, this study seeks to correlate the results of these oxidation experiments to the different coating microstructures resulting from the various deposition techniques.

Chapter 4 - Experimental Research Approach

The present chapter will discuss the experimental research approach used to achieve the previously outlined study objectives. More specifically, this chapter will define the feedstock materials considered in this study, the experimental apparatus used for the deposition of bond coatings, and finally the various analysis techniques required for full characterization of the bond coat powders and coatings.

4.1 Feedstock Materials

The current section of this report will describe the feedstock materials considered for this study. As mentioned in a previous chapter, CoNiCrAlY alloys are commonly used as bond coat materials in a variety of TBC or stand-alone high temperature applications given that they offer a good combination of high temperature oxidation and hot-corrosion resistance. In addition, these materials are manufactured in the form of powder and are available in various compositions and size ranges, thus making them suitable for CGDS and other thermal spray processes. For these reasons, CoNiCrAlY has been selected as the bond coat material to be considered in all experimental trials reported in this study. As described in the research objectives, it is desired to study the performance of both conventional and nanocrystalline CoNiCrAlY bond coats. As such, feedstock materials with these microstructures have been selected and are described below.

4.1.1 Conventional CoNiCrAlY Powder

The conventional feedstock powders considered in this study are commercially available CoNiCrAlY alloys from Sulzer Metco and are known as AMDRY 9951 and AMDRY 9954. Both powders have an identical chemical composition and exhibit a spherical particle morphology resulting from their synthesis by spray atomization. The only difference between the two powders is their particle size range: the AMDRY 9951 powder is finer with particle sizes ranging from 5 μ m to 37 μ m, whereas the AMDRY 9954 powder is coarser with particles

ranging from 11 μ m to 62 μ m in size. The chemical composition of these powders as reported by the manufacturer is presented in Table 4.1.

Table 4.1: Chemical composition of the AMDRY 9951 / 9954 CoNiCrAlY powders

Element	Co	Ni	Cr	Al	Y
Weight %	37.97	32.01	21.22	8.04	0.50

The selection of this specific CoNiCrAlY alloy was motivated simply by the fact that it was readily available and currently used by various gas turbine manufacturers including GE and Rolls Royce. It is believed that the selection of this specific MCrAlY composition for the present work, as opposed to another MCrAlY material, will not influence the research objectives outlined previously. Although each MCrAlY alloy is expected to exhibit its own specific oxidation behaviour and therefore offer varying levels of protection, the trends in oxidation behaviour resulting from the different deposition techniques that will be observed in this work are expected to carry over to all MCrAlY compositions since they all share similar oxidation dynamics.

4.1.2 Nanocrystalline CoNiCrAlY Powder

CoNiCrAlY powders with nanocrystalline microstructures are not commercially available and therefore need to be synthesized by additional material processing routes. In order to obtain nanocrystalline CoNiCrAlY powder, the AMDRY 9954 powder was subjected to cryomilling, a mechanical milling technique that has been shown to be one of many successful processes used to produce materials with nanocrystalline microstructures [100]. In cryomilling, a powder is mechanically milled for several hours under a constant supply of liquid nitrogen in an attritor mill. Stainless steel balls (typically 4mm to 7mm in diameter) are used as the grinding media. Typical cryomilling equipment is shown in Figure 4.1.

The formation of a nanocrystalline microstructure is achieved as powder particles get trapped between the larger stainless steel balls upon mixing and undergo extensive plastic deformation resulting from their crushing, fracturing and re-welding. This process introduces shear bands containing large amounts of dislocations which increase the atomic level strain within the material. When the dislocation density becomes sufficiently large, the crystal

breaks down into finer subgrains with low-angle grain boundaries. As milling continues, previously unstrained regions in the material are deformed, and therefore the grain size decreases steadily. The small angle grain boundaries are replaced by higher angle grain boundaries, thus implying grain rotation, and ultimately dislocation-free nanocrystalline grains are formed [100]. The use of liquid nitrogen as milling environment prevents grain growth of the milled material which could result from the exothermal severe plastic deformation process. Additionally, milling under a supply of liquid nitrogen has been shown to introduce fine nitride dispersoids within the milled material which have been shown to act as strengthening mechanisms [101] as well as nucleation sites for the formation of α -Al₂O₃ in CoNiCrAlY alloys [76]. Cryomilling of the AMDRY 9954 CoNiCrAlY powder for this study is to be performed in Professor Mathieu Brochu's laboratory at the Mining and Materials Engineering Department at McGill University.

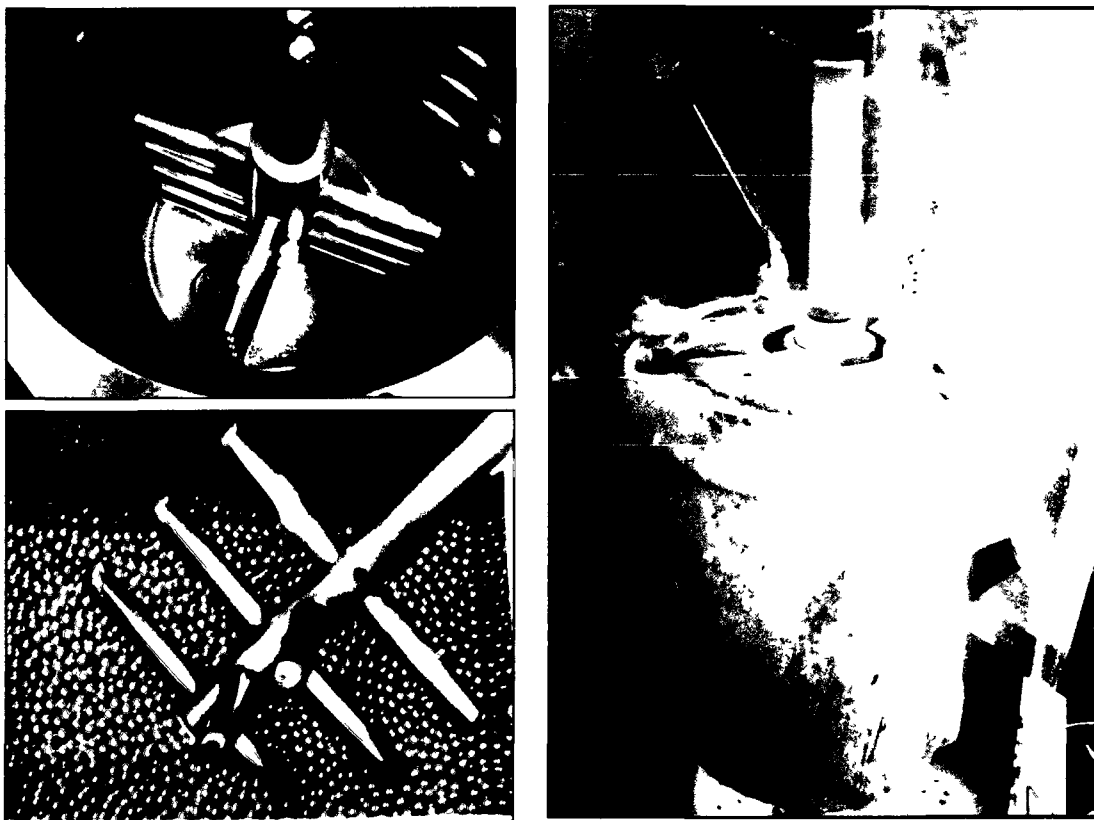


Figure 4.1: Typical cryomilling equipment: (top left) the cryomilling tank, (bottom left) the impeller and stainless steel balls used as grinding media, and (right) the milling process where mixing of the stainless steel balls and powder particles is carried out for several hours under a liquid nitrogen environment

4.2 *Experimental Equipment for Bond Coat Deposition*

The present section of the report will provide a detailed description of the equipment used in this study to manufacture the CoNiCrAlY bond coats. The discussion will focus primarily on the CGDS equipment developed at the University of Ottawa Cold Spray Laboratory given that most trials will be performed using this system. A brief description of the plasma and HVOF systems used in this study to manufacture thermal spray bond coats for comparison purposes is also provided.

4.2.1 University of Ottawa Cold Spray Laboratory Facility

The following subsections outline the various features of the CGDS facility developed at the University of Ottawa Cold Spray Laboratory.

4.2.1.1 *Driving and Carrier Gas Supplies*

For all trials performed in this study, helium was used as both the driving and carrier gases. CoNiCrAlY is a hard material with a high critical velocity, and therefore elevated gas velocities are required to accelerate the powder particles sufficiently. As described in Chapter 2, helium has a high speed of sound when compared to air or nitrogen due to its high specific heat ratio and gas constant. As such, for a given nozzle geometry (and consequently fixed nozzle exit Mach number), the gas velocity of helium will be considerably higher. In addition, helium is an inert gas and will not cause chemical reactions such as oxidation with the sprayed material.

For the main driving gas, six industrial grade high pressure helium cylinders are connected to a gas manifold followed by a pressure regulator to control the nozzle inlet pressure. The simultaneous use of six helium cylinders is necessary to prevent experimental errors caused by noticeable pressure fluctuations in the cylinder due to the high helium volume flow rate.

Six high pressure nitrogen cylinders are also connected to a manifold and pressure regulator and are used to preheat the CGDS system when the gas heater is activated. The gas heater introduces a large thermal lag, and therefore it is preferable to preheat the system using an inexpensive gas such as nitrogen. When the system reaches the desired temperature, the gas

supply input is changed from nitrogen to helium by means of a three-port ball valve located upstream of the gas heater.

The carrier gas supply (also helium) is used to create a positive pressure difference between the powder canister and nozzle inlet. The pressure difference induces a flow which entrains the powder particles into the nozzle. A single high pressure helium cylinder equipped with a pressure regulator is used for this purpose.

4.2.1.2 *Spraying Chamber*

At the onset of this research project, the existing CGDS facility consisted of a spraying chamber with limited access and insufficient process variable monitoring capabilities. A new spraying chamber was built in order to address these issues. This new spraying chamber is mounted on the surface of a rigid tabletop and was designed with clear acrylic door panels on all sides for improved visibility and accessibility. The new spray chamber, shown in Figure 4.2, is also equipped with a ventilation system consisting of a 1.5hp fan and a 0.4 μ m particulate filtering device. The enclosure is sealed to ensure that any powder particles that did not adhere to the substrate during spraying either remain inside the chamber or are collected in the filtered ventilation system. The main driving gas line and the powder flow line are connected to the spraying chamber by port connectors located on its upper panel.

The nozzle is positioned vertically in the spraying chamber on a linear stage and aims at the substrate holder which is mounted on a computer controlled two-axis traversing system. This is shown in Figure 4.3. The linear stage is equipped with a micrometer which allows careful adjustment of the spraying stand-off distance (SOD). The traversing system consists of two perpendicular lead screw tracks (providing two-axis displacement capability, referred to as the X-axis and Y-axis) activated by electronic stepper motors. A custom computer program (also known as a Virtual Instrument) was developed using the LabView software to control the motor rotational speed and direction, as well as the required number of steps in order to achieve the desired traverse speed and displacement with a resolution of ± 0.1 mm/s and 0.0064mm respectively. Features such as automatic X-Y displacement and multiple coating pass capabilities have been implemented into the software for easier system use when coating larger surfaces.

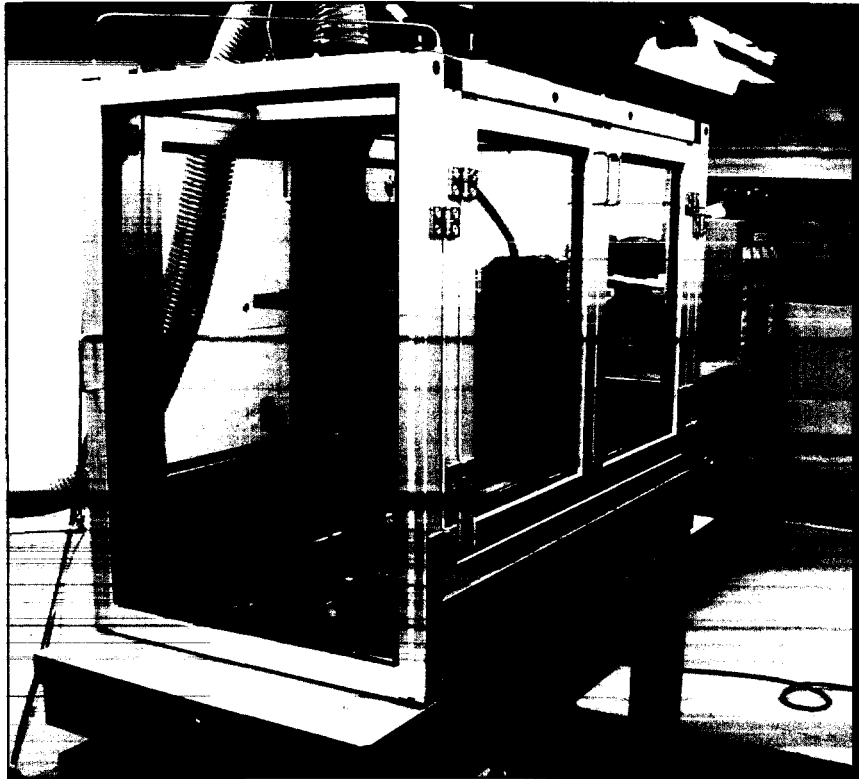


Figure 4.2: Spraying chamber at the University of Ottawa Cold Spray Laboratory

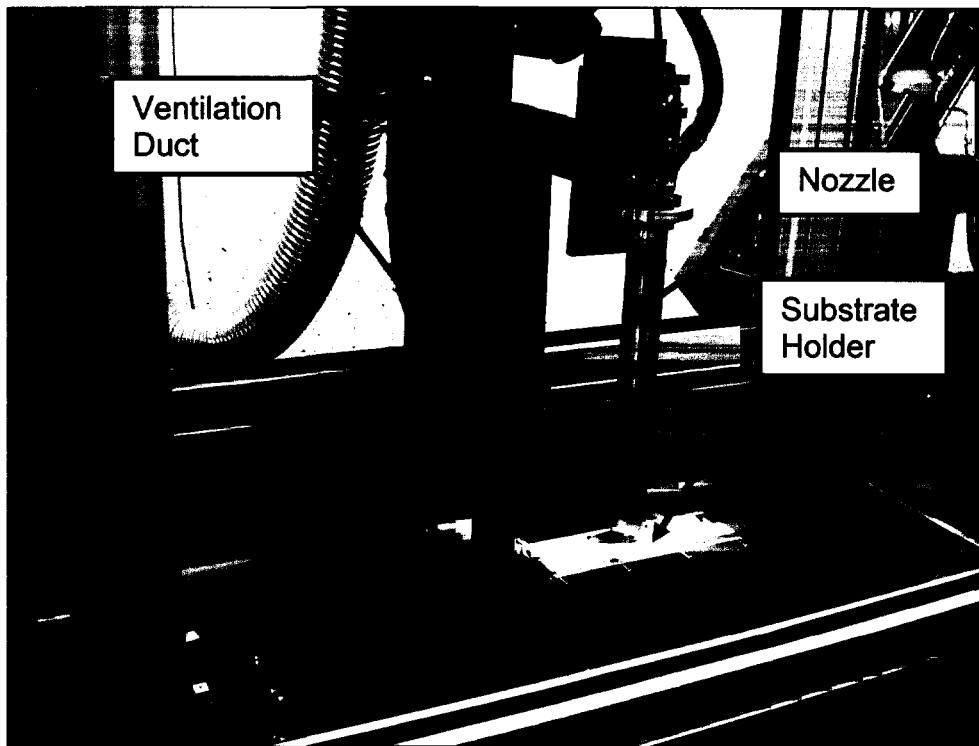


Figure 4.3: View of the new spray chamber interior and the two-axis traversing system

In order to improve the system's process variable monitoring capabilities, the new spray chamber was also equipped with numerous measurement probes. Pressure transducers and thermocouple probes were positioned at various locations along the main driving gas line, and most importantly near the inlet of the nozzle. The nozzle inlet conditions, although different to the gas stagnation properties defined in section 2.2.4.4, are used in this study as reference conditions for repeatability purposes. The signals received from the pressure and temperature sensors are collected and analyzed by means of another LabView data acquisition Virtual Instrument. Raw data is collected in a continuous loop at a rate of nearly 10 samples per second and is then processed and converted into meaningful units. The processed data is then displayed on-screen in near real-time, thus enabling the user to carefully monitor the pressure and temperature profiles throughout the spraying process. The software also monitors the amount of gas remaining in the high-pressure cylinders and warns the user when replacement of the cylinders is required. Finally, the virtual instrument also enables the user to save the data to a file for future reference. Figure 4.4 shows a screenshot of the LabView virtual instrument displaying a typical temperature and pressure profile during a CGDS trial.

The modifications made to the CGDS apparatus have significantly increased the level of precision and repeatability that can be achieved between different experimental trials. In addition, the new spray chamber offers added flexibility and accessibility for easier and more efficient use.

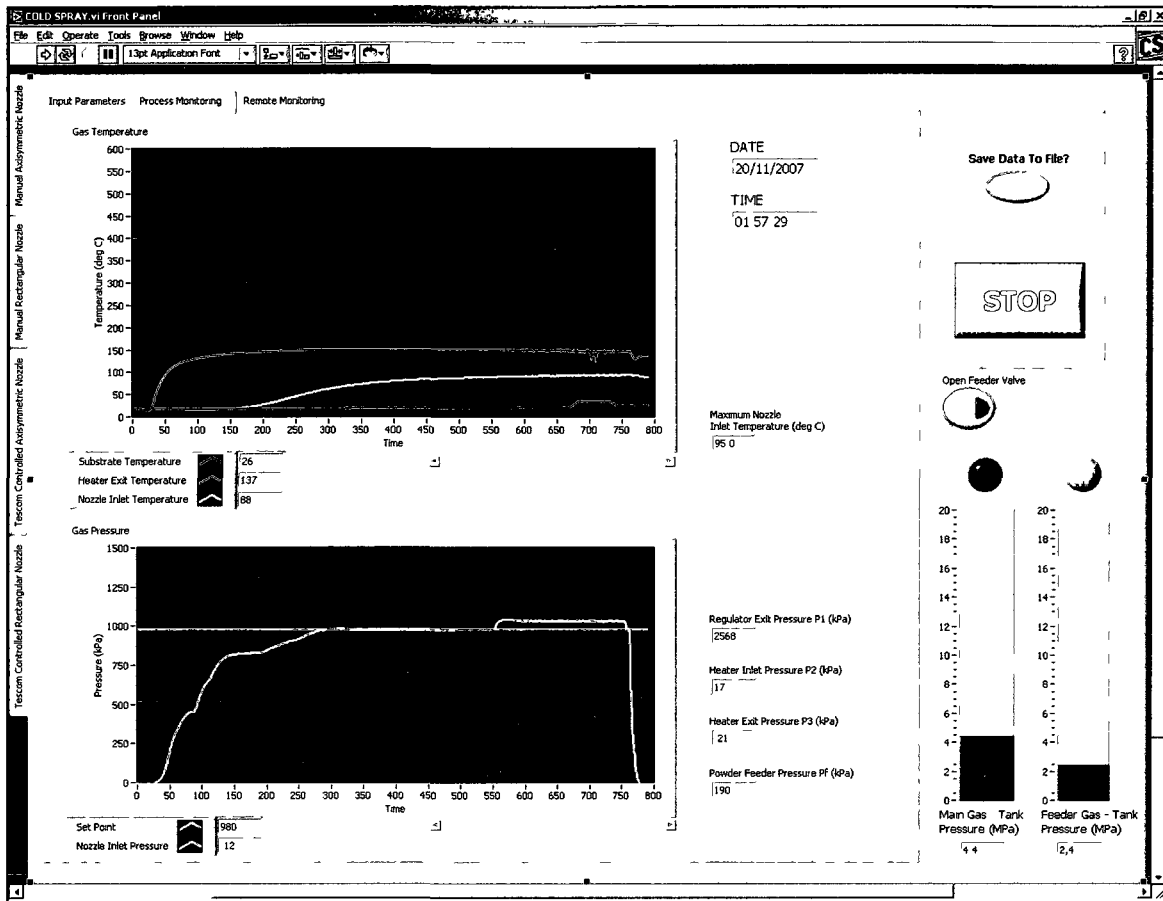


Figure 4.4: Screenshot of the LabView Virtual Instrument used for data acquisition and process monitoring

4.2.1.3 CGDS Supersonic Nozzle

The design of the nozzle to be used for the deposition of CoNiCrAlY coatings was based on the findings reported by a previous researcher from the Cold Spray Laboratory Group at the University of Ottawa [102]. This researcher performed several numerical simulations on an axisymmetric converging-diverging nozzle with various dimensions for the throat area, nozzle exit area and nozzle length. The modeling work had been originally performed to find a nozzle geometry capable of accelerating aluminum powder particles (20 μ m in size) above a velocity of 900m/s. Based on these simulations, it was determined that a converging-diverging nozzle with a 2mm diameter throat, 250mm diverging section length and 7.3mm exit diameter would achieve the desired result. Both the converging and diverging sections of this nozzle were designed to feature linear profiles as a result of limited manufacturing resources for complex internal nozzle geometries. Numerous nozzles with these dimensions

and profile have thus been manufactured and used to produce coatings from many different powder materials [15, 32, 47, 56] including nanocrystalline nickel [53] with minimal porosity and defects. It is thus proposed to use a nozzle with the aforementioned geometry for the manufacturing of CoNiCrAlY coatings. As seen in Figure 4.5, the nozzle is equipped with a manifold containing two inlet ports: one for the driving gas flow and the other for the powder injection line. The manifold acts as a mixing chamber at the inlet of the nozzle for the driving gas and powder particles.

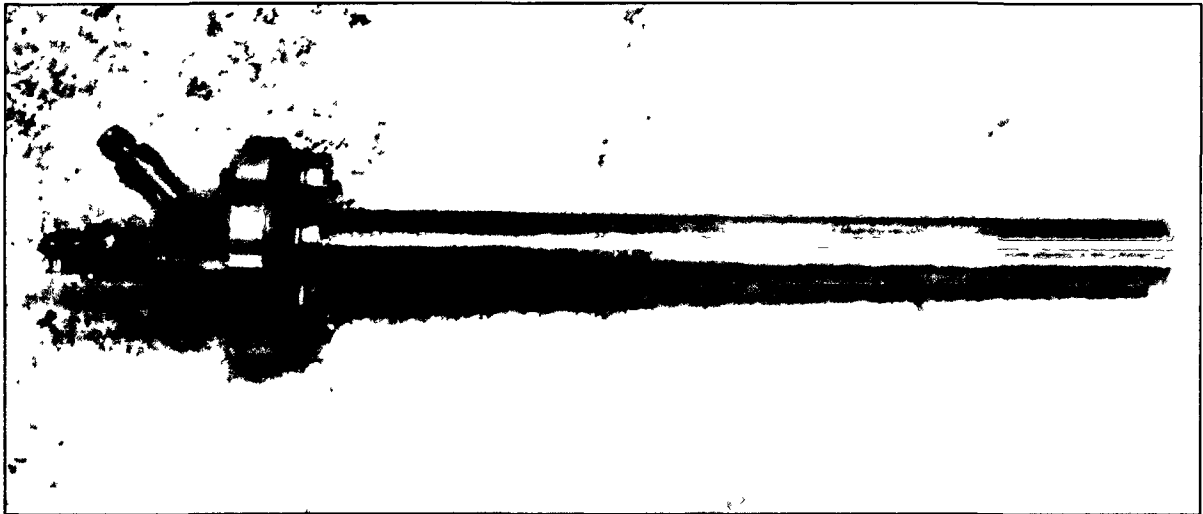


Figure 4.5: Axisymmetric converging-diverging cold spray nozzle

4.2.1.4 Gas Heater

The CGDS experimental apparatus is equipped with an electric gas heater capable of producing gas temperatures of up to 650°C at the nozzle inlet. The gas heater consists of a 4m long stainless steel pipe with an outer diameter of 5/8". The pipe is formed into the shape of a coil and is connected to a 30kW power supply. When electrical power is applied, the pipe is used as an electrical resistance and power is dissipated in the form of heat. As the driving gas flows through the heated pipe, it collects thermal energy by convective heat transfer, thereby increasing its temperature. The power supply voltage can be adjusted by means of a variac control, thus allowing the operators to vary the heater power and consequently the gas temperature. The heater coil is insulated using ceramic wool to prevent excessive losses to the environment.

4.2.1.5 Powder Feeder

The supply of powder to the cold spray nozzle is controlled by means of a commercially available powder feeder (Praxair, model 1264, Praxair Surface Technologies). The powder feeder consists of a canister in which the feedstock powder is placed prior to the spray trials. As mentioned previously, a carrier flow is used to pressurize the canister in order to create a positive pressure difference between the canister pressure and the nozzle inlet, thus creating a flow and pushing the powder particles towards the nozzle inlet. A perforated wheel is located at the base of the canister and mounted on a drive shaft controlled by a variable velocity servomotor. Small packets of powder particles fill each hole of the wheel as it turns, and when these holes line up with the feeder outlet port, the powder packet is pushed by the carrier flow into the feeding line towards the nozzle. Increasing the wheel rotation speed increases the number of powder packets supplied to the feeding line per unit time, thus resulting in higher powder feed rates. The powder feeder is also equipped with a hammer assembly that taps the wheel as it rotates to dislodge any particles that may have a tendency to clog. The powder feeder used in this study is shown in Figure 4.6.



Figure 4.6: Powder feeder at the University of Ottawa Cold Spray Laboratory

4.2.1.6 Substrate Material

All CoNiCrAlY coatings manufactured throughout this work were deposited on aluminium T-6061 alloy substrates prepared from extruded flat bar stock. Prior to the coating process, the substrates were cleaned with acetone in order to remove any surface contaminants and grease. The selection of aluminium as a substrate material was motivated mainly by its wide availability and low cost. While it is recognized that the bond coat is typically applied on a nickel-based superalloy substrate, the nature of the substrate material for this specific work was not particularly important for various reasons. As will be discussed further in a later section, the coating samples used for the oxidation experiments will be sectioned from the substrate in order to obtain free-standing coating samples for the specific purpose of eliminating the influence of the substrate on the bond coat oxidation behaviour. As such, the type of substrate material is somewhat irrelevant for the oxidation test coating samples as long as the coatings can be successfully deposited with minimal defects. With this in mind the objectives pertaining to the feasibility and optimization of CGDS CoNiCrAlY coatings could just as easily have been carried out using a different substrate material. However, in addition to its availability and low cost, the good machinability of aluminium also allows for easier removal of the coating sample from the substrate, thereby making it the substrate material of choice for this work.

4.2.1.7 In-flight Particle Velocity Measurement Tool: Cold Spray Meter

In order to improve the CGDS deposition process for the CoNiCrAlY feedstock powders, particle velocities at the spray nozzle exit were measured. Particle velocity measurements were carried out using a laser in-flight diagnostic system known as the Cold Spray Meter (Tecnar Automation Ltd., St-Bruno, Québec, Canada). While a continuous laser illuminates a measurement volume, a dual-slit photomask captures the signal generated by individual particles passing in front of the sensor. The signal from the photo sensor is amplified, filtered and analyzed. In-flight diagnostic of each individual particle that crosses the measurement volume is performed by determining the time between the two peaks of the particle signal. Particle velocities are then obtained by dividing the known distance between the two-slits by their time of flight [103]. Originally, these particle velocity measurements were to be used to maximize the particle impact speed during CGDS and therefore optimize the spraying

parameters in order to improve coating properties. Unfortunately, the Cold Spray Meter was only available near the early onset of this research work, and as a result only a few particle velocity measurements were obtained from this diagnostic tool during the initial coating optimization trials. Nevertheless, these results have been included in this work given that they provide some insight with respect to powder acceleration in the CGDS deposition process and therefore provide an interesting contribution to the discussion.

4.2.2 Thermal Spray Equipment

In order to compare the oxidation behaviour of the CoNiCrAlY CGDS coatings with that of thermal spray bond coats, additional coating samples were manufactured using the APS and HVOF spraying techniques. These thermal spray coatings were produced using the same conventional feedstock material as those prepared using CGDS: more specifically, the AMDRY 9954 feedstock powder was used based on the powder manufacturer's recommendations. The thermal spray coatings were then subjected to identical sample preparation procedures and oxidation testing routines as the CGDS coatings. This allowed for direct comparison of the oxidation behaviour of bond coats produced with different spraying techniques. Thermal spraying equipment is not available at the University of Ottawa, and as such deposition of CoNiCrAlY coatings by APS and HVOF spraying was outsourced to the Quebec Coating Division of Vac Aero International Inc. The APS coatings were produced using a SG100 plasma torch from Praxair with Ar and He as the primary and secondary plasma gases respectively. The HVOF coatings were manufactured using a DJ2600 HVOF torch from Sulzer Metco with H₂ and O₂ as combustion gases. The specific deposition parameters for both the HVOF and APS coatings are presented in Table 4.2.

Table 4.2: Deposition parameters for the thermal sprayed CoNiCrAlY coatings

HVOF		APS	
Spray gun	DJ-2600	Spray Gun	SG-100
Oxygen pressure (psi)	170	Current (A) / Voltage (V)	800 / 39
Hydrogen pressure (psi)	142	Primary gas Ar pressure (psi)	50
Air pressure (psi)	100	Secondary gas He pressure (psi)	110
Stand-off distance (in)	11	Stand-off distance (in)	5
Powder feedrate (lbs/h)	7.0	Powder feedrate (lbs/h)	3.0

4.3 Material Characterization and Investigation

The present section of this thesis will outline the investigative approach that was followed for the characterization of the various bond coat materials in order to realize the previously defined objectives of this research project. More specifically, this section presents the various methods of analysis of the bond coat material samples for the CGDS process optimization, the investigation of microstructural changes induced by the CGDS process and the investigation of the bond coat oxidation behaviour.

4.3.1 Coating Characterization for CGDS Optimization

The conventional and nanocrystalline CoNiCrAlY coating samples prepared in this study were investigated both qualitatively and quantitatively in order to assess their properties. The feasibility of the deposition of these coatings by CGDS was verified by observing the formation of any coating build-up during the spraying process, regardless of the resulting coating properties. Conversely, optimization of the CGDS deposition process for the CoNiCrAlY powders required further characterization of the coatings. This was achieved by examining the coating cross-sections using optical microscopy (OM) and scanning electron microscopy (SEM) (Zeiss, model Evo10) equipped with SE, BSE, EDS, EBSD and CT scan detectors. Prior to microscope investigation, the coating samples were prepared according to standard metallographic techniques: samples were sectioned in a cut-off saw (Struers Secotom-10), mounted in a thermosetting epoxy resin (Struers LaboPress-3) and polished to a 1 μ m surface roughness finish (Struers TegraPol, TegraForce-5 and TegraDoser-5). The various apparatus used for coating analysis are shown in Figure 4.7 and Figure 4.8. Optical microscope images were used to qualitatively evaluate the coating structure for the presence of visible defects such as cracks and undeformed particles. The images were also analyzed using the Clemex Vision Lite image analysis software in order to evaluate the coating porosity levels and thickness. The coating process is to be considered optimized when the CGDS coatings exhibit no crack content, sufficient build-up (minimum coating thickness of 150 μ m) and limited porosity (maximum percentage area porosity of 3.0%).

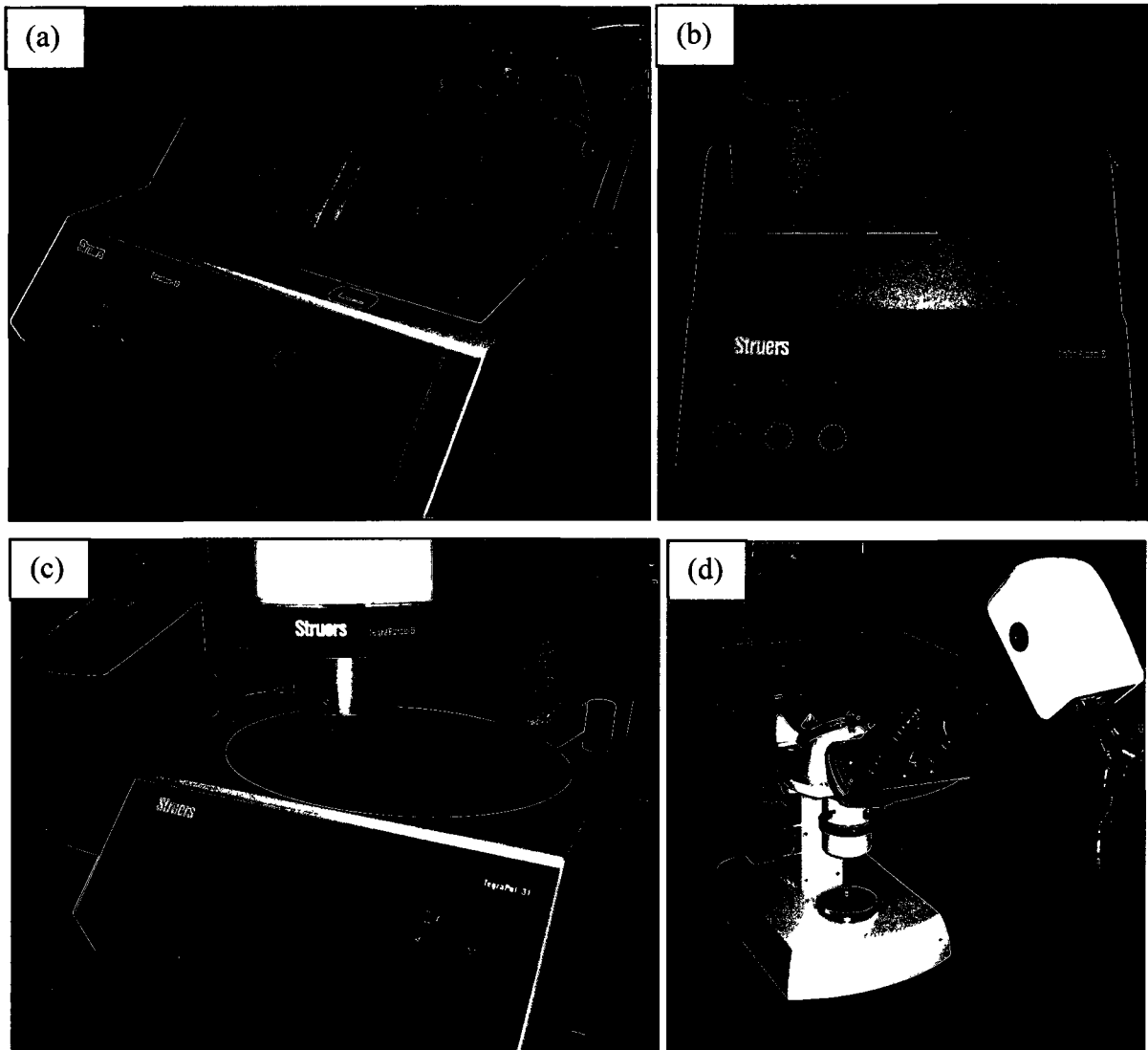


Figure 4.7: Sample preparation equipment and analytical instruments used for sample investigation: (a) Cut-off saw with aluminum oxide blade (Struers Secotom-10); (b) Thermosetting resin mounting chamber (Struers LaboPress-3); (c) Sample polisher (Struers TegraPol, TegraForce-5 and TegraDoser-5); (d) Optical microscope equipped with digital camera for image analysis (XJP-3A metallurgical microscope and Clemex Vision Lite Software)

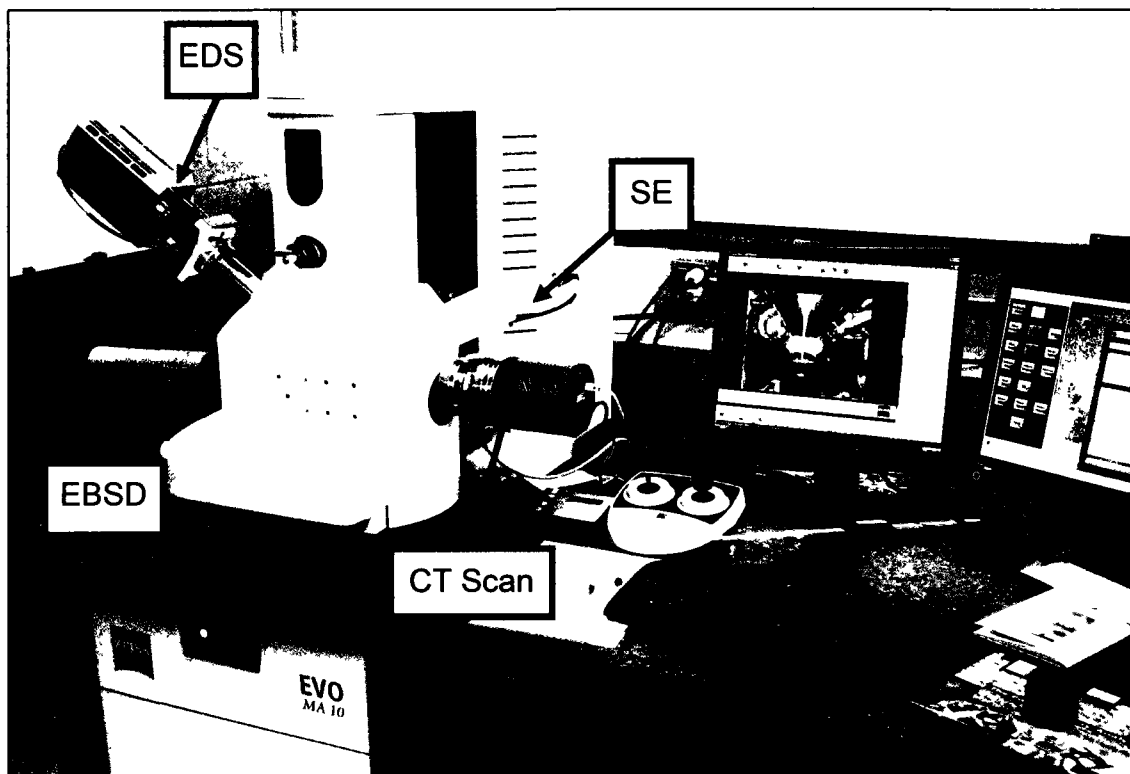


Figure 4.8: Scanning Electron Microscope (Zeiss Evo10) with SE, BSE, EDS, EBSD and CT Scan detectors

4.3.2 Investigation of Microstructural Changes Induced by CGDS

In order to determine whether microstructural changes occur throughout the CGDS deposition process, full characterization of both the original feedstock powders and resulting coating microstructures needed to be obtained and compared. The phase compositions of the powders and coatings was therefore obtained by performing X-ray diffraction analyses (XRD) using a Philips X-Pert model PW 1830 generator diffractometer (shown in Figure 4.9) with CuK α radiation. During an XRD scan, the sample is bombarded by X-rays with incident radiation angles varying within a predefined range. Every individual crystalline material phase is characterized with a specific crystal lattice size and atomic plane spacing. The incident X-rays are reflected by the sample's atomic planes and a detector measures the amount of X-rays (counts) to have been reflected for a given angle of incidence. Results of the analysis show a pattern of peaks (high number of counts) of collected x-rays for specific incidence angles, which can then be looked up and cross-referenced in a material database to identify the phase composition. Investigation of the phase composition of the original powders and CGDS

coatings is important to verify whether any changes in composition have occurred during the deposition process.

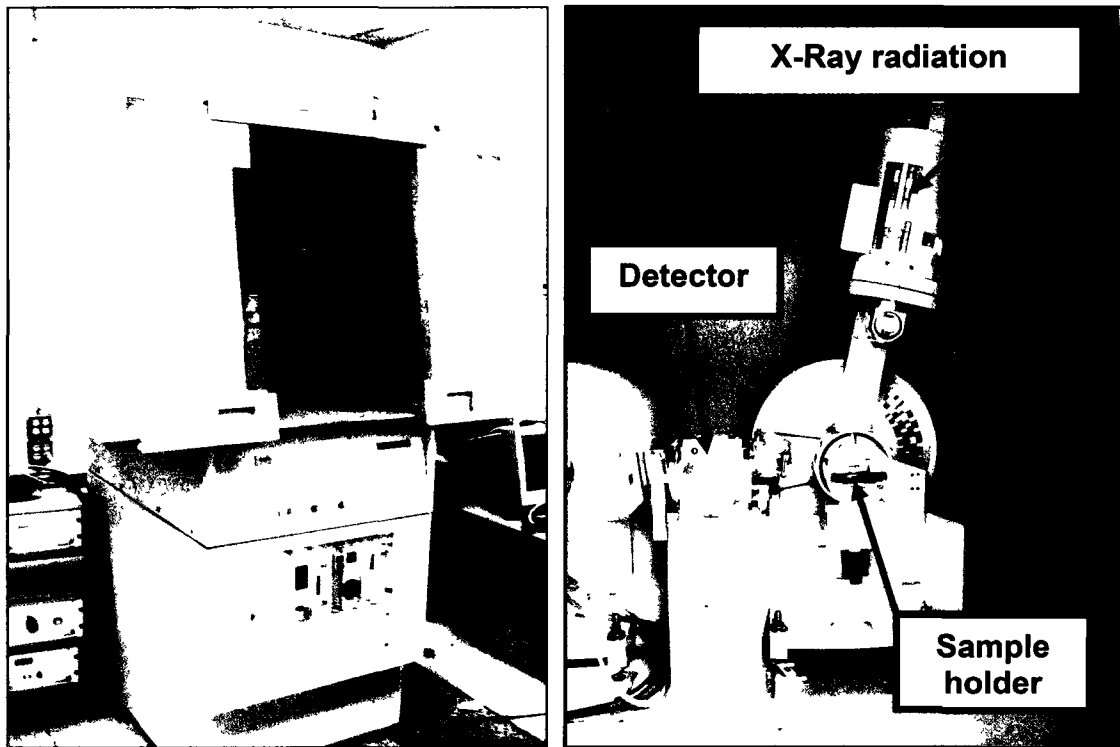


Figure 4.9: XRD equipment required for phase identification of the powders and CGDS coatings

Further investigation of the powders and coatings microstructures was achieved by means of transmission electron microscopy (TEM) using a FEI Tecnai-G2 F20 microscope (shown in Figure 4.10). Prior to TEM observation the powder samples were cold mounted in epoxy followed by grinding, polishing, and ion milling. The coating samples were prepared by removing the substrate by sanding, followed by dimpling and ion-milling. TEM equipment is not available at the University of Ottawa, and as such the TEM work was performed through a collaboration with Professor Alejandro Zúñiga's research group at the Department of Mechanical Engineering at the University of Chile in Santiago, Chile. The TEM work consisted of performing selected area electron diffractions (SAED) in order to once again identify the phases and general structure within the materials. These results were then used to validate the findings from the XRD analyses and as such confirm which phases are present in the materials. Additionally, the TEM analyses were used to obtain various bright field (BF)

and dark field (DF) TEM images in order to investigate the grain structure, namely the grain morphology and average grain size of the materials considered. When combined with the findings from the XRD scans, the results of the TEM analysis will provide a complete picture of the original powders and resulting CGDS coatings microstructures. It will then be possible to demonstrate whether any microstructural changes have occurred during the CGDS deposition process.

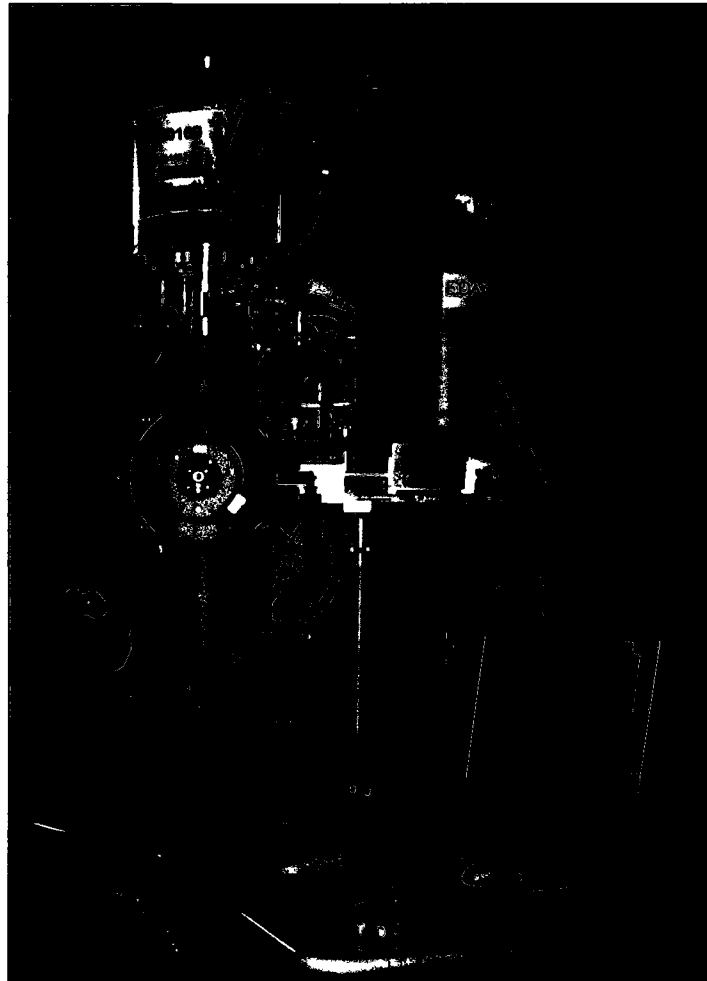


Figure 4.10: Transmission Electron Microscope to be used for microstructural analysis of the powder and coating samples

4.3.3 Investigation of Bond Coat Oxidation Behaviour

The assessment of the oxidation behaviour of the conventional and nanocrystalline CGDS coatings was achieved by performing high-temperature isothermal oxidation experiments. For comparison purposes, the thermal sprayed coating samples (APS and HVOF) also

underwent identical isothermal oxidation testing. All coatings in the as-sprayed condition were cut into 15mm x 15mm samples and sectioned from the substrate surface. The sectioned surface was then polished in order to remove any remaining substrate material on the coating sample, thus resulting in free-standing CoNiCrAlY coating samples. The samples were then subjected to isothermal heat treatments in a furnace at 1000°C in static atmospheric air. The samples were positioned in the furnace once the set point temperature was reached and were then allowed to soak for durations of 5, 25, 50 and 100 hours respectively. Following the heat treatments, the samples were removed from the furnace and allowed to cool to room temperature. Each sample was weighed before and after the oxidation experiments using a digital weighing scale with 100µg resolution (Sartorius Extend - model ED124S). These measurements were carried out in order to determine the mass gain of the samples due to the formation of oxides during the heat treatments, thus providing valuable information regarding the oxide growth rate of each sample.

Following each respective heat-treatment, the samples were subjected to an XRD analysis in order to identify the oxides that have formed on the surface of the sample. The XRD analysis also provided insight with respect to the relative importance of the various oxides by comparing their different peak intensities. Additionally, comparing XRD scans performed after various oxidation times illustrated the growth dynamics of the various oxides with respect to time. It was then possible to determine whether α -alumina forms in preference to other mixed oxides and to identify the approximate time for the onset of these mixed oxides.

Finally, the oxidation test samples were observed by means of SEM microscopy. Images of the coating sample surface were taken to examine the morphology of the various oxides qualitatively. Backscattered SEM images of the coating samples cross-section were also taken in order to investigate the oxide scale thickness. These cross-section images also provided evidence of the formation of a β -phase depletion zone near the surface of the coating resulting from the consumption of the aluminum in β -phase during the oxidation process. Once again, comparing SEM images taken after various oxidation times illustrated the growth dynamics of the various oxides and depletion zone with respect to time.

Chapter 5 - Synthesis and Characterization of Feedstock Powders

Prior to coating manufacturing, it is appropriate and necessary to investigate the powder materials to be considered in this study. One of the main objectives of this work is to manufacture bond coats with the CGDS deposition technique from both conventional and nanocrystalline CoNiCrAlY powders. As such, the objective of the present chapter is to fully characterize the microstructures of both the as-received and as-cryomilled powders in order to demonstrate their conventional and nanocrystalline structures respectively. This is achieved by means of SEM, XRD and TEM analyses. It should also be recalled that although the conventional CoNiCrAlY powders were commercially available, the nanocrystalline CoNiCrAlY powder required to be synthesized by means of cryomilling. A brief description of the cryomilling parameters used for the synthesis of the nanocrystalline powder is thus also presented.

5.1 As-received (conventional) powders

As defined in section 4.1.1, a conventional CoNiCrAlY alloy with a nominal composition of Co-32Ni-21Cr-8Al-0.5Y (wt. %) was selected for this study. This alloy is manufactured in the form of spherical powder particles by means of spray atomization and is commercially available in two different particle size ranges (Sulzer Metco): AMDRY 9951 (5-37 μ m) and AMDRY 9954 (11-62 μ m). Figure 5.1 confirms the spherical morphology of the AMDRY 9951 and AMDRY 9954 powders and also demonstrates the coarser particle sizes of the AMDRY 9954 feedstock. Furthermore, the size of the particles appears to fall within the specified ranges advertised by the manufacturer.

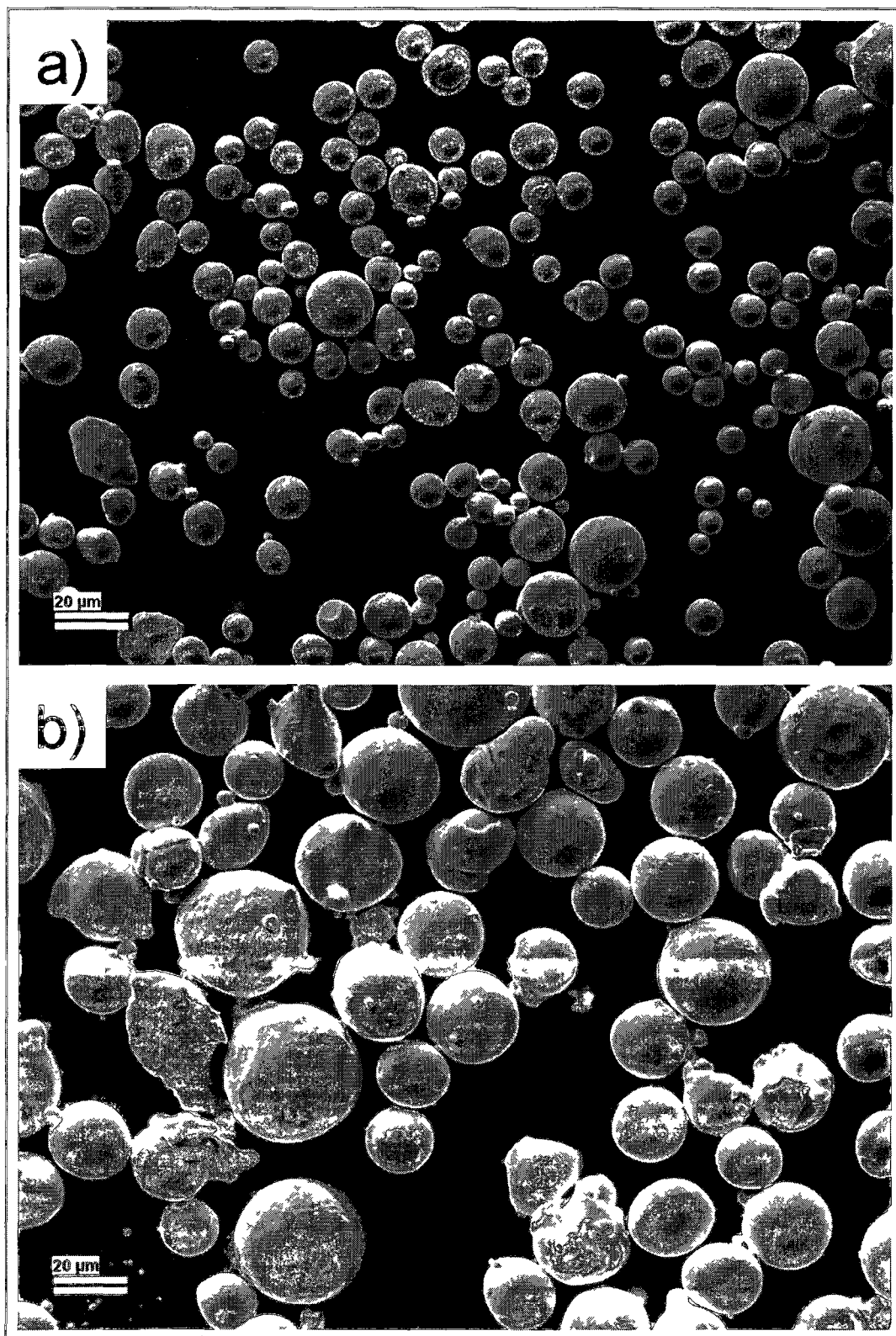


Figure 5.1: SEM images showing the morphology of the as-received CoNiCrAlY powders: (a) AMDRY 9951, (b) AMDRY 9954

Examination of the cross-section of a typical particle from the AMDRY 9951 powder, as seen in Figure 5.2, reveals the expected two-phase γ/β microstructure commonly observed in MCrAlY materials. The light gray area is expected to correspond to the γ -matrix phase while the darker gray precipitates would correspond to the β -NiAl phase. EDS analysis was also carried out on these powders which revealed an average oxide content of 0.03 ± 0.03 (wt. %).

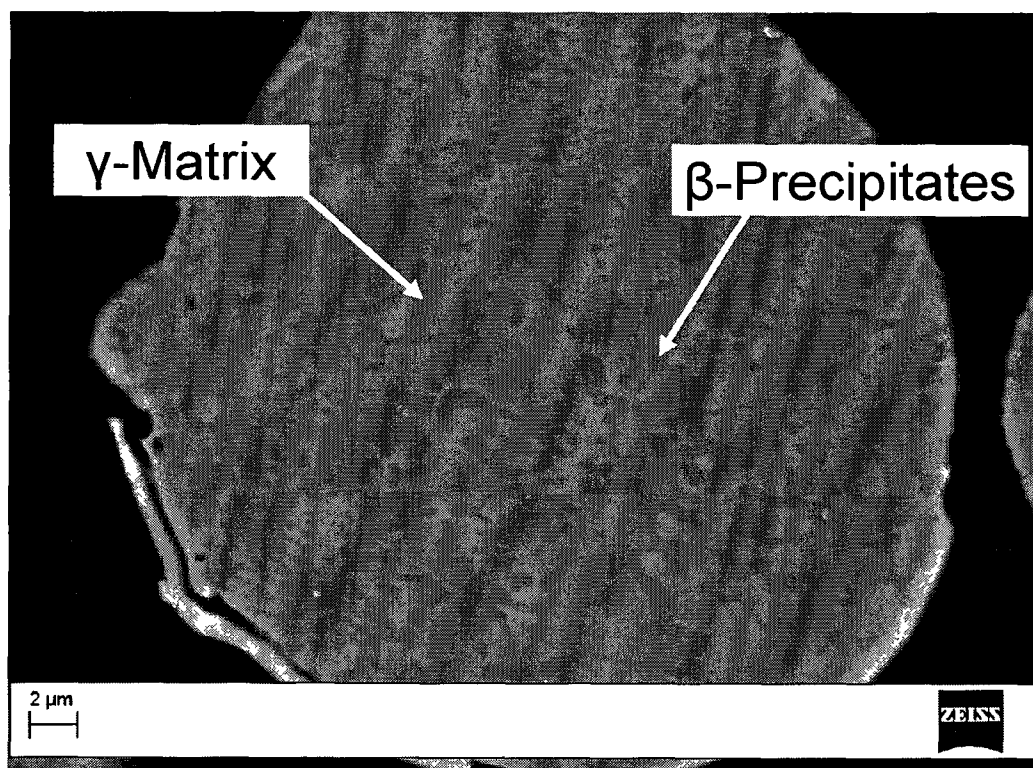


Figure 5.2: Single particle cross-section showing the presence of two visible phases in the as-received CoNiCrAlY powder

In order to correctly identify both phase compositions, an XRD analysis was carried out on both the AMDRY 9951 and AMDRY 9954 powders. The XRD analyses were carried out with a Philips X-Pert model PW 1830 generator diffractometer with $\text{CuK}\alpha$ ($\lambda=0.15406$ nm) radiation. Detailed scans with step size of 0.01° and step time of 2 seconds were conducted with 2θ values ranging from 20° to 85° . It should be noted that these scan settings were used for all XRD analyses performed throughout this work (all powders and coatings) in order to allow for proper comparison between the various materials. Results from the XRD analysis of the two conventional powders are shown in Figure 5.3. For both powders, phase identification reveals the presence of a dominant phase represented by three strong peaks

associated to the (1 1 1), (2 0 0) and (2 2 0) atomic planes. This phase corresponds to an fcc γ -matrix consisting of a Co-Ni-Cr solid solution. The presence of a second phase characterized with weaker peaks can also be observed and is identified as a NiAl bcc β -phase. The presence of a small “hump” underneath the largest β -phase peak of the AMDRY 9951 feedstock can also be observed. The XRD spectra of the AMDRY 9954 powder however does not reveal the presence of such a hump, thereby suggesting that the hump is in fact exclusively related to the very fine particles (those ranging from 5-11 μ m) in the AMDRY 9951 powder lot. It is believed that the small hump is attributed to the presence of some amorphous phase content in the as-received AMDRY 9951 feedstock powder. Given that this powder was produced by spray atomization, a process known to lead to fast particle solidification and high cooling rates [104], it is rationalized that solidification likely occurs too rapidly in the case of very fine particles for crystallization to take place, thereby leading to the presence of amorphous microstructures. This could explain why the XRD spectrum of the finer AMDRY 9951 powder exhibits some amorphous microstructure content whereas that of the coarser AMDRY 9954 powder does not.

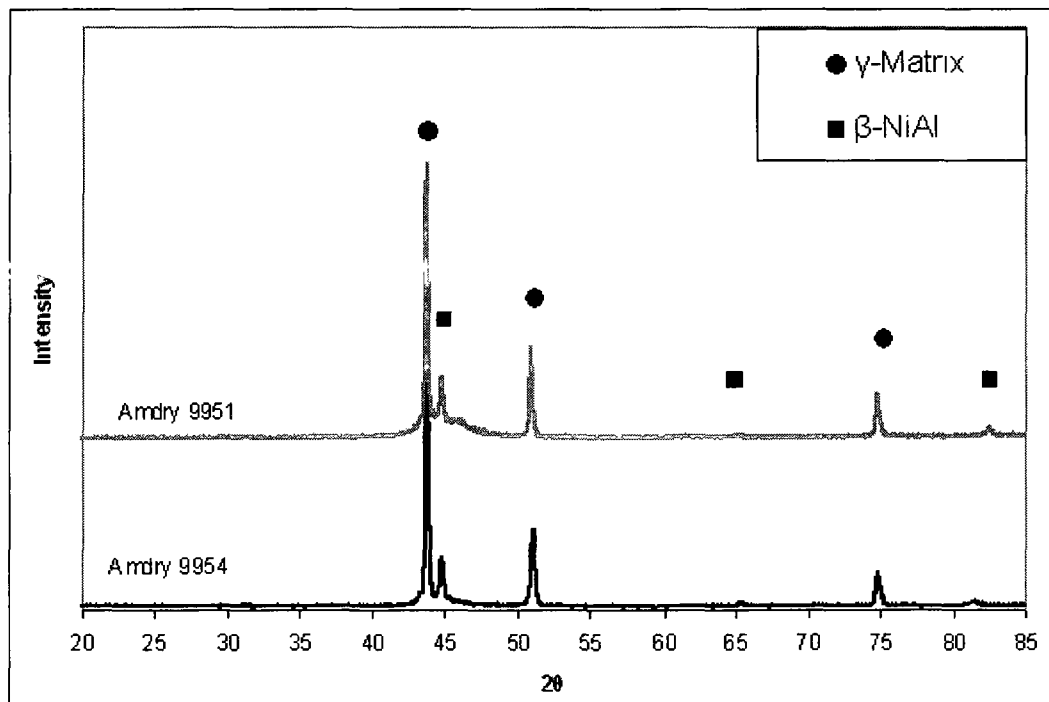


Figure 5.3: XRD spectra of as-received AMDRY 9951 and AMDRY 9954 CoNiCrAlY powders

TEM investigation of the as-received powder was also carried out using a FEI Tecnai-G2 F20 microscope operated at 200 kV in order to assess the material's grain structure and to confirm the phase composition identified by the XRD analysis. Figure 5.4 shows the SAED pattern for the as-received AMDRY 9951 powder and reveals strong diffraction spots that were identified to correspond to the (2 0 0) and (4 0 0) γ -phase. This suggests that this powder is likely polycrystalline and composed of micro-sized γ -phase grains, thereby demonstrating the conventional nature of this material. Ring-shaped diffraction patterns are also observed and confirm the presence of the β -phase. These rings are identified to be (2 0 0), (2 1 1) and (2 2 0) β -NiAl. The ring-like shape of this diffraction pattern indicates a fine grain size, therefore suggesting the presence of fine β -NiAl precipitates within the γ -matrix. The presence of both the γ and β phases in the diffraction pattern confirms the results obtained from the XRD analysis. Conversely, the diffraction pattern of Figure 5.4 does not suggest the presence of amorphous microstructure content in the powder. This is likely attributed to the high intensity of diffractions associated to the crystalline structures, thereby hindering the observation of the amorphous halo in the diffraction pattern.

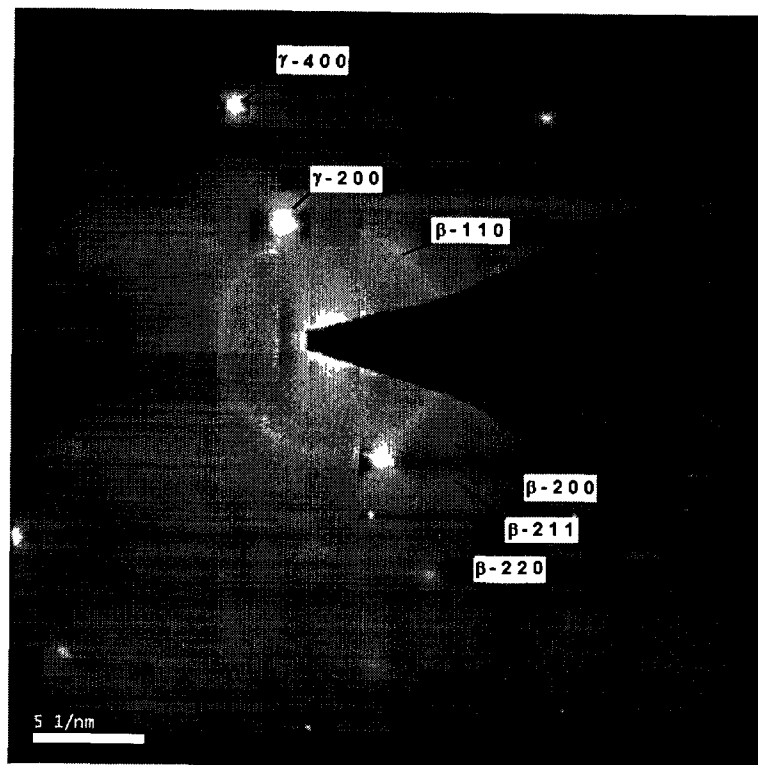


Figure 5.4: TEM image showing the SAED of the as-received conventional CoNiCrAlY powder

Figure 5.5 shows (a) a BF TEM image of the as-received CoNiCrAlY powder and (b) the DF image corresponding to the β -phase diffractions. The images confirm the presence of very fine grained precipitates (β -NiAl) embedded in the γ -matrix. These β -phase precipitates were determined to have an equiaxed morphology and grain sizes of approximately 5 nm. It is important to note that although the β -precipitates can be considered as nanocrystalline in size, the bulk of the material is composed of the γ -matrix which was previously shown to exhibit a microstructure with relatively coarse grain sizes, and as such this powder material can be considered as conventional.

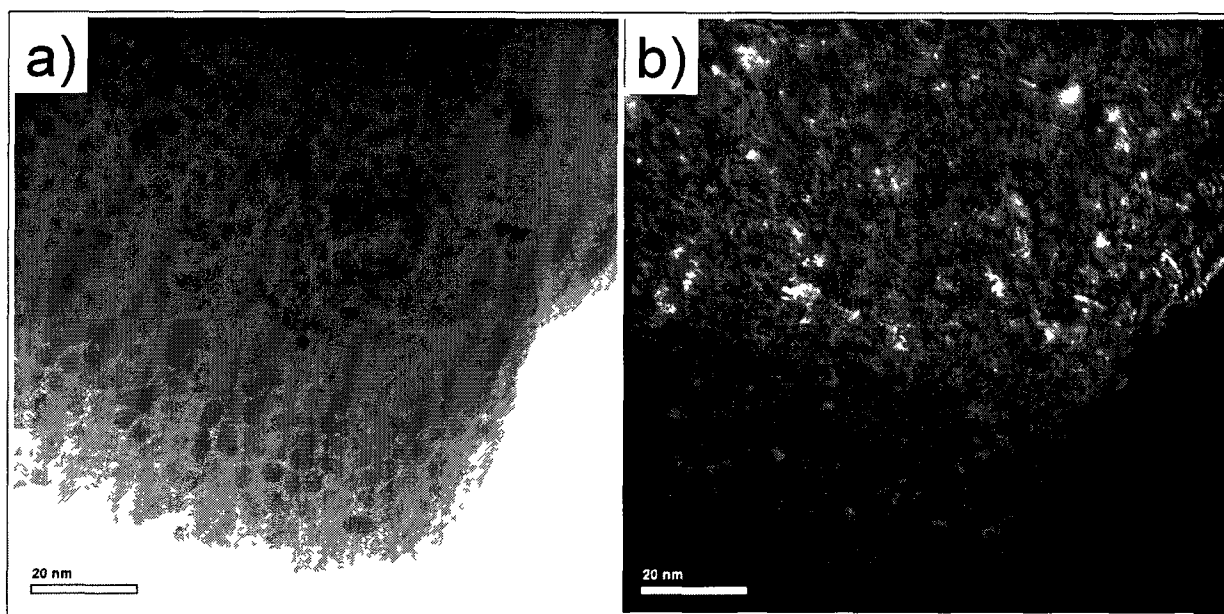


Figure 5.5: (a) BF and (b) DF TEM images showing the presence of fine β -precipitates embedded in the γ -matrix

5.2 *As-cryomilled (nanocrystalline) powder*

5.2.1 Powder synthesis

As detailed in section 4.1.2, CoNiCrAlY powders with nanocrystalline microstructures are not commercially available and therefore require to be synthesized. Cryomilling was selected as a mechanical milling technique for this study given that it has been shown to be one of many successful processes used to produce materials with nanocrystalline microstructures [100]. The AMDRY 9954 conventional feedstock powder was thus mechanically milled for 8 hours

at 200 rpm under a constant supply of liquid nitrogen in an Attritor Union Process 01-HD Szegvari mill. Stainless steel 440 balls (4.8 mm in diameter) were used as the grinding media with a ball-to-powder weight ratio of 24:1.

5.2.2 Powder characterization

The morphology of the as-cryomilled (nanocrystalline) CoNiCrAlY powder is shown in Figure 5.6. As can be seen from this figure, the as-cryomilled CoNiCrAlY powder no longer has the spherical morphology observed in the as-received powder, but rather has an irregular flake-like morphology resulting from the severe plastic deformation, crushing and welding of the particles throughout the milling process.

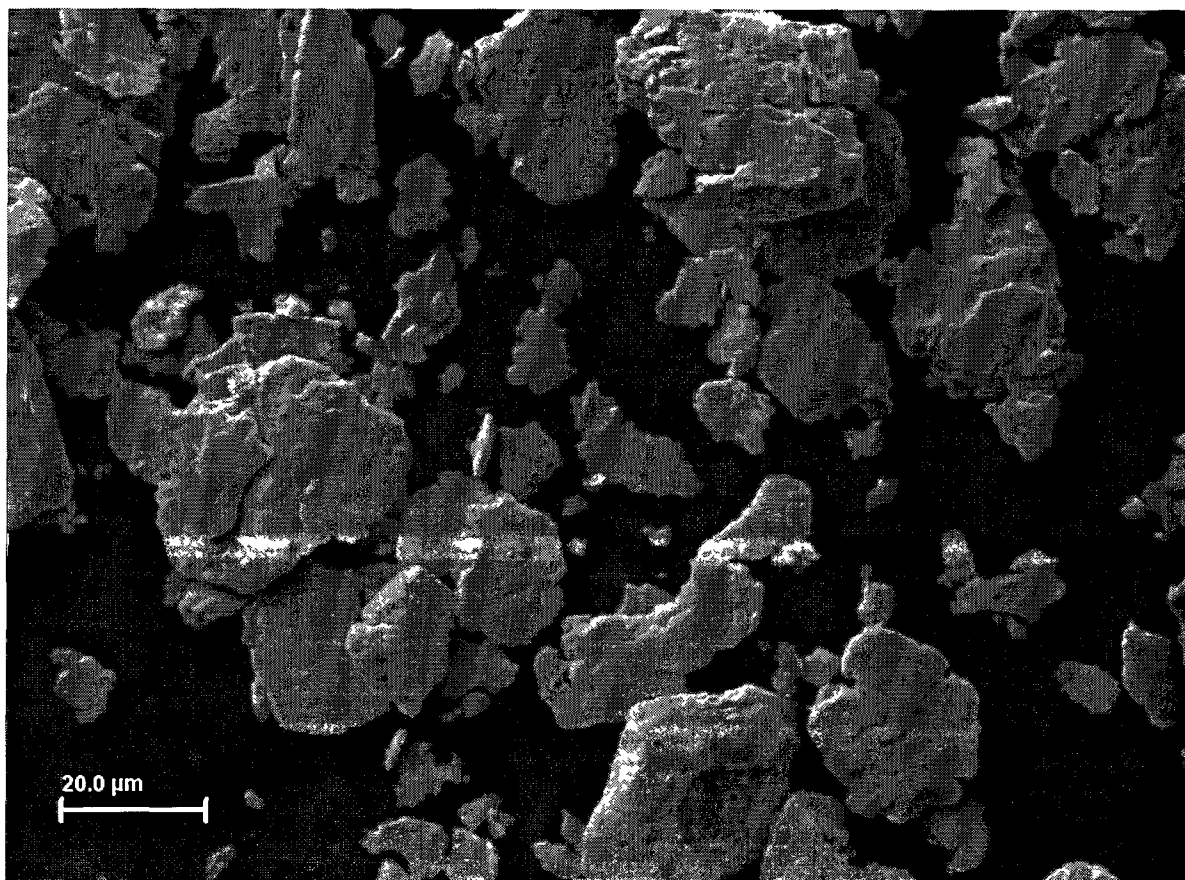


Figure 5.6: SEM image showing the morphology of the as-cryomilled CoNiCrAlY powder

The as-cryomilled powder size distribution was evaluated by means of powder granulometry performed with a Mastersizer 2000 from Malvern Instruments Ltd. (Malvern, UK). Results of this analysis revealed a particle size distribution ranging from 1 to 70 μm with an average equivalent particle diameter of 20 μm . The complete powder size distribution is shown in Figure 5.7.

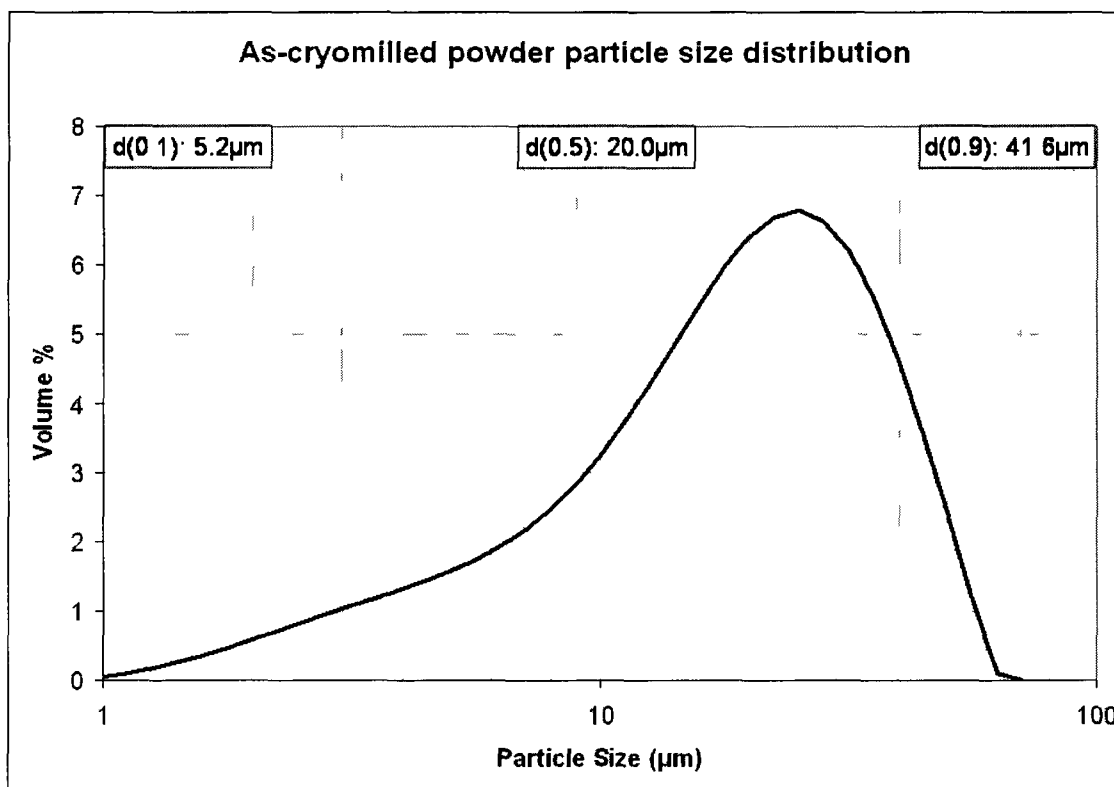


Figure 5.7: Particle size distribution of the as-cryomilled CoNiCrAlY powder

Examination of the cross-section of a typical as-cryomilled particle, as shown in Figure 5.8 also reveals interesting characteristics. Firstly, the shape of the particle cross-section shows further evidence of the extensive plastic deformation undergone by the initially spherical powder particle during the cryomilling process. Also, contrarily to the as-received powder, the as-cryomilled powder does not feature the expected two-phase γ/β microstructure. This is further evidenced in Figure 5.9, which compares the XRD spectra of both the as-received and as-cryomilled CoNiCrAlY powders, as peaks associated to the β -phase appear to be absent in the as-cryomilled powder. The apparent disappearance of a material's precipitate phase during mechanical milling has been observed elsewhere and has been attributed to a

dissolution mechanism resulting from the severe plastic deformation inherent to the milling process [101]. Extensive plastic deformation of the powder particles during mechanical milling produces a high density of point and line defects in the material which extends the solubility of Al of the γ -matrix phase, thereby causing dissolution of the Al-rich β -precipitate phase. Such a dissolution mechanism appears to have taken place during cryomilling of the CoNiCrAlY powder considered in this study.

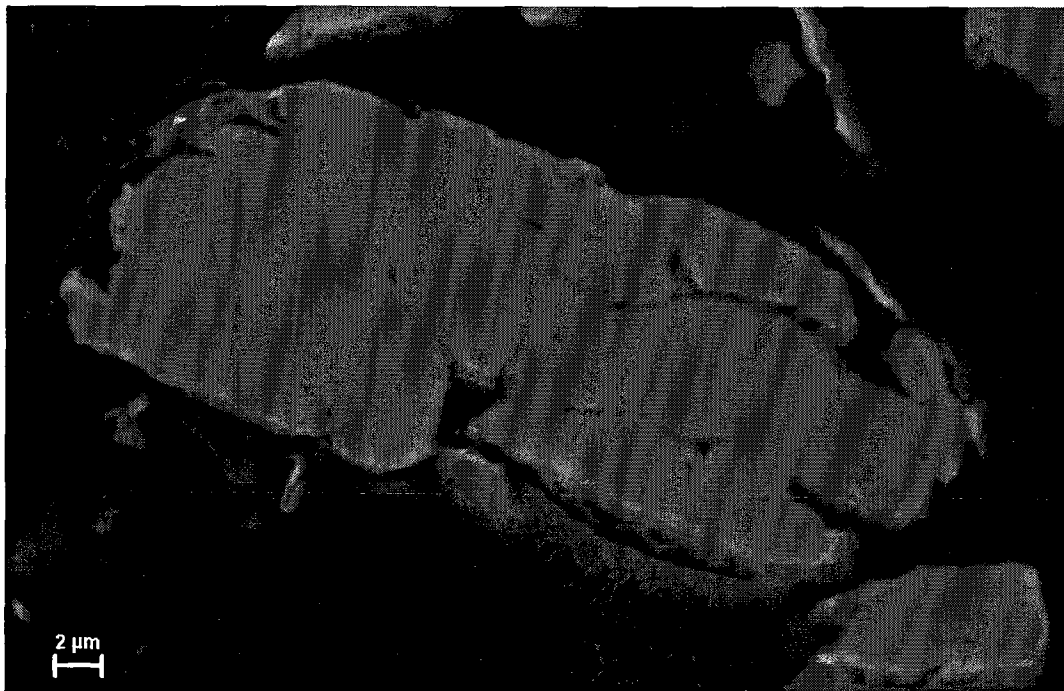


Figure 5.8: Cross-section view of a typical as-cryomilled powder particle

Further analysis of the XRD spectra also reveals broadening of the γ -phase peaks, thus suggesting a refinement of the material's grain structure. The grain size of a material can typically be estimated from an XRD spectrum by means of techniques involving peak width measurements, however due to the occurrence of some overlapping of the main β and γ phase peaks, determining the average grain size of these powders is not sufficiently accurate with the XRD technique. Also, peak broadening can be the result of strain effects within the crystal lattice, which would not be unexpected in this case given the severe plastic deformation inherent to the powder synthesis process. Evaluating the material's grain size by means of XRD techniques could thus introduce additional errors, and as such another investigation technique such as TEM is preferable.

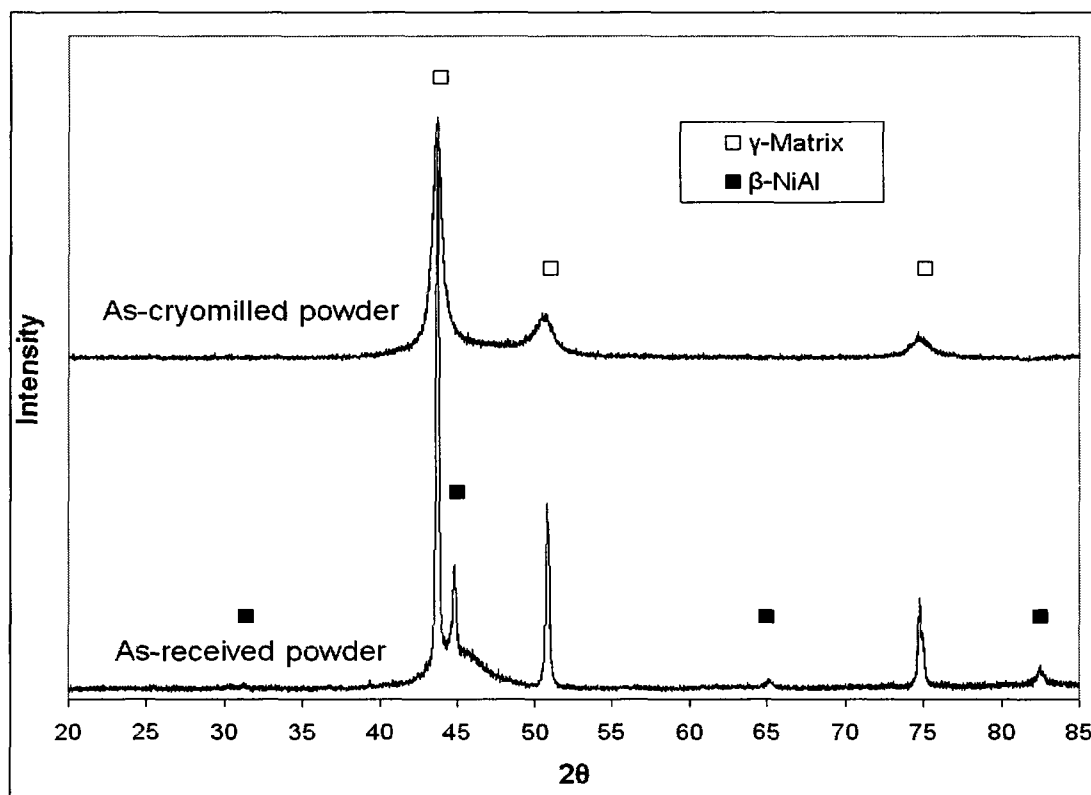


Figure 5.9: Comparison of the XRD spectra of the as-received and as-cryomilled CoNiCrAlY powders

In order to fully characterize the microstructure of the as-cryomilled powder and compare it to that of the as-received powder, TEM investigation was also carried out. Figure 5.10 shows the SAED pattern of the as-cryomilled powder and is observed to be significantly different to that of the as-received powder (Figure 5.4) as it clearly reveals multiple diffraction rings associated to the γ -phase Co-Ni-Cr solid solution. The presence of these diffraction rings as opposed to diffraction spots, as was observed in the as-received powder, demonstrates that the grains in the γ -matrix have undergone considerable refinement. This also confirms that the γ -phase peak broadening observed in the XRD analysis is in fact attributed to a refinement in the material's grain size. As described in section 4.1.2 of this report, grain size reduction in cryomilling is a well known phenomenon which is achieved as powder particles undergo extensive plastic deformation resulting from their crushing, fracturing and re-welding. The process introduces shear bands containing large amounts of dislocations which increase the atomic level strain within the material. When the dislocation density becomes sufficiently large, the crystal breaks down into finer subgrains with low-angle grain boundaries. As

milling continues, previously unstrained regions in the material are deformed, and therefore the grain size decreases steadily until dislocation-free nanocrystalline grains are formed [101]. Furthermore, the SAED pattern shows that diffractions associated to the β -phase appear as very faint ring fragments, thus suggesting a much lower β -phase content. Once again, these findings are in accordance with the XRD results and support the concept of the deformation driven dissolution mechanism of the β -phase precipitates.

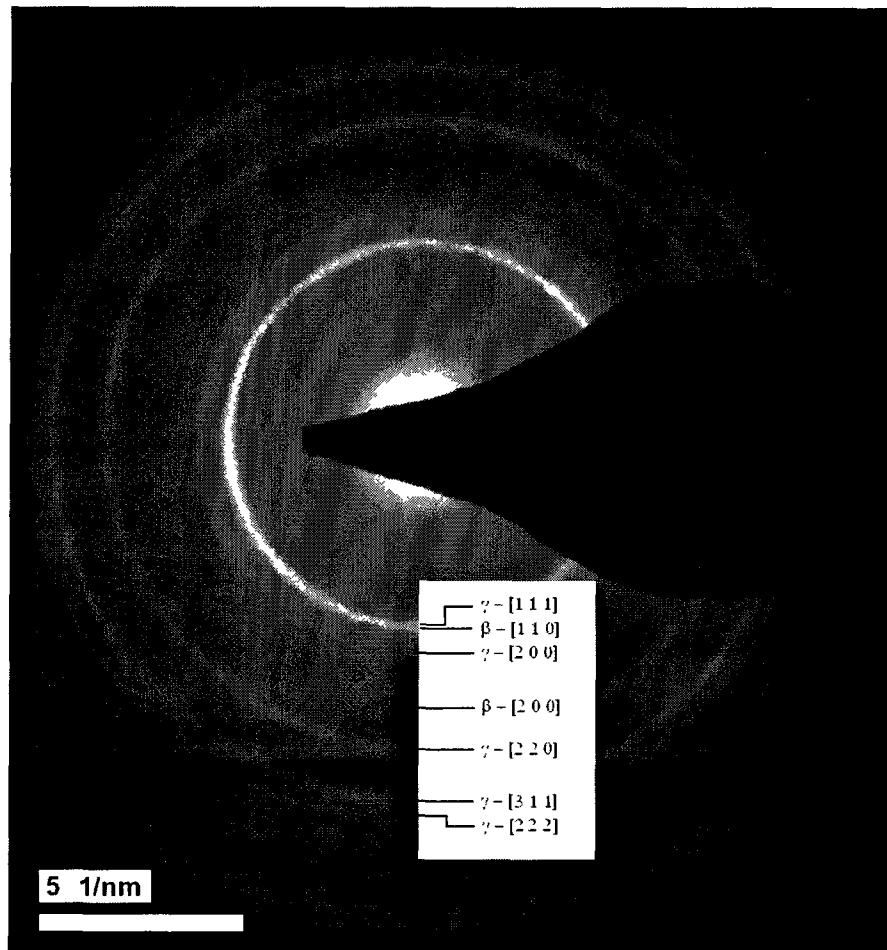


Figure 5.10: SAED pattern of the as-cryomilled CoNiCrAlY powder

BF and DF TEM images of the as-cryomilled powder (shown in Figure 5.11) further confirm that the material has a nanocrystalline microstructure with randomly oriented grains having an average size below 25nm. Findings from the TEM investigation are thus in accordance with results from the XRD analysis and confirm that CoNiCrAlY powder particles with a

nanocrystalline microstructure were successfully synthesized from conventional particles by means of cryomilling.

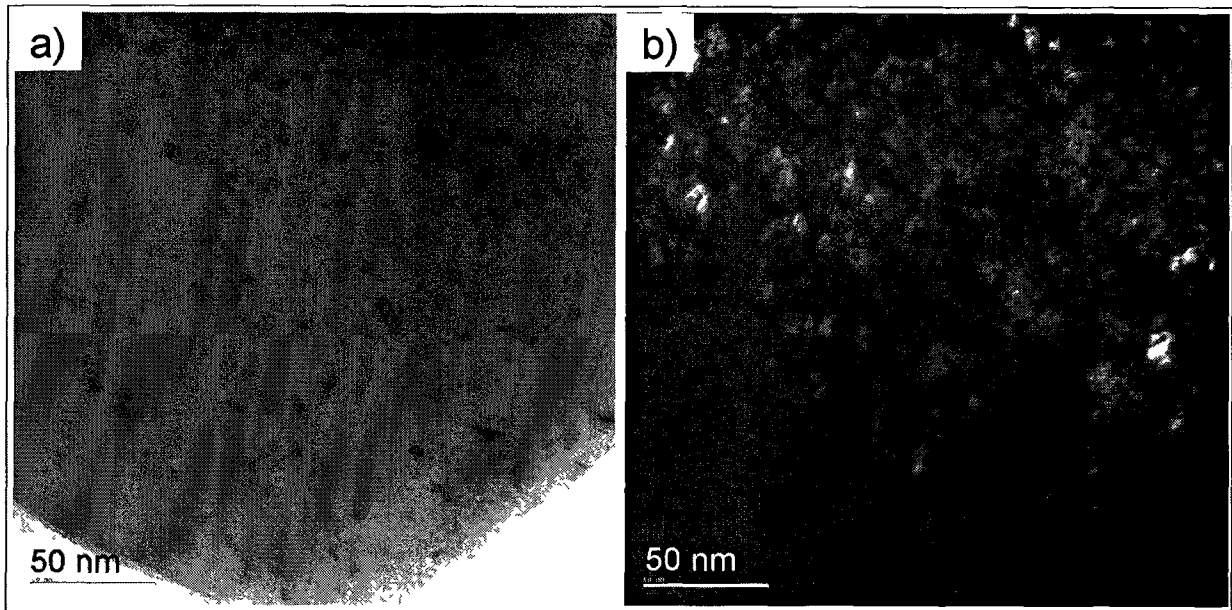


Figure 5.11: BF and DF TEM images revealing the nanocrystalline microstructure of the as-cryomilled CoNiCrAlY powder

5.3 Summary

Results presented in this chapter demonstrated the following important findings:

- a) The as-received CoNiCrAlY powder is characterized with the typical two-phase microstructure and exhibits fine bcc β -NiAl precipitates in the nanocrystalline size range that are dispersed within a coarse-grained fcc γ -matrix Co-Ni-Cr solid solution. The coarse grain structure of the γ -matrix represents the bulk of the material, and therefore the as-received powders can be considered to have a conventional microstructure.
- b) Nanocrystalline CoNiCrAlY powder was successfully synthesized from the as-received conventional powder by means of cryomilling, as demonstrated by XRD and TEM analyses. The as-cryomilled powder exhibits refinement of the γ -phase grains down to the nanoscale size range as well as an important reduction of the β -phase content due to a deformation driven phase dissolution process.

Chapter 6 - Feasibility Study and Optimization of Spray Parameters for CGDS CoNiCrAlY Coatings

The current chapter of this thesis aims to present the theoretical and experimental approaches that were used to demonstrate the feasibility and optimization of CGDS CoNiCrAlY coatings. The first part of this chapter is dedicated to the work that was performed to show the feasibility of manufacturing conventional and nanocrystalline CoNiCrAlY coatings using spraying conditions that had been previously used to successfully deposit other materials using the CGDS apparatus available at the onset of this study. The second part of this chapter will examine the approach considered for the optimization of the CGDS spray parameters. This optimization was achieved by a combination of experimental trials and numerical simulations, which are both detailed in this second part of the chapter.

6.1 CGDS CoNiCrAlY Coatings Feasibility Study

The feasibility study was performed at the very early stages of this work in order to explore the potential and possibility of manufacturing CoNiCrAlY coatings with the CGDS deposition process. This was achieved by carrying out a series of preliminary trials with the conventional as-received powders (AMDRY 9951 and AMDRY 9954) as well as the nanocrystalline as-cryomilled powder. The formation of any coating build-up, regardless of the coating properties and porosity level, would be considered a successful test as it would demonstrate that sufficient plastic deformation was achieved during CGDS to at least cause bonding of some CoNiCrAlY particles. Improvement of the coating characteristics could then be achieved by further optimization of the spraying parameters.

As discussed in section 2.2.3, CoNiCrAlY is a material characterized with properties such as high strength at high temperature, and it has therefore been shown to have a high critical velocity [18]. This material was thus expected to be relatively difficult to deposit using CGDS. Previous work had been carried out on the deposition of nanocrystalline pure nickel particles, which were also characterized with high strength and hardness, and had therefore also been difficult to deposit. Despite their elevated mechanical properties, the

nanocrystalline nickel particles had been successfully deposited using CGDS apparatus at the University of Ottawa facility [53]. In addition, these nanocrystalline nickel particles had a similar density to CoNiCrAlY, and it was thus expected that similar momentum transfer and behaviour of the particles in the flow could be achieved by using the same spraying conditions. As such, in order to maximize the likelihood of any successful deposition of the CoNiCrAlY particles during the preliminary spray attempts, the same spraying conditions as those that were used for the nanocrystalline nickel particles were considered. These spraying conditions are identified below.

6.1.1 Preliminary Trials: Spray Conditions

The nozzle that was considered for these preliminary trials was developed and used by a previous researcher as detailed in section 4.2.1.3. This nozzle features an axisymmetric converging-diverging profile with a 2mm diameter throat and 7.3mm exit diameter. When using this particular nozzle, powders are fed into the nozzle through an axial injection port located at the inlet of the nozzle. A drawback to this powder injection configuration is that the driving gas pressure at the nozzle inlet also reaches the powder feeder canister by flowing through the injection line. Since the powder feeder is rated for a maximum allowable pressure of 1100 kPa and that a positive pressure difference between the powder feeder canister and nozzle injection port must exist in order to generate the powder carrier flow, this effectively limits the maximum operating driving gas pressure to approximately 1050kPa. For this reason, the driving gas pressure at the nozzle inlet was set at 980kPa (the same as the nanocrystalline nickel trials). The pressure difference between the powder feeder canister and powder injection port on the nozzle, hereby referred to as pressure differential, was set at 60 kPa. Helium was used as both the driving and carrier gases. It should be noted that at the time when this portion of the study was performed, the available CGDS apparatus at the University of Ottawa Cold Spray Laboratory featured various limitations. Firstly, the gas heater from this original system was only capable of increasing the driving gas temperature up to 350-400°C. As such, a temperature of 350°C at the nozzle inlet was used for the driving gas during these preliminary trials (also the same as the nanocrystalline nickel trials). Secondly, the motorized substrate displacement mechanism did not allow for precise control or repeatability of the substrate traverse speed. As such, a traverse speed of approximately 4

to 5mm/s was used for this series of trials. Finally, other parameters that were borrowed from the previous trials carried out on the nanocrystalline nickel powder included the spraying stand-off distance and powder feeder wheel rotation speed (to control the powder feedrate), which were set at 5mm and 4 RPM respectively. All coatings prepared in these preliminary trials were done in a single pass of the Al-6061 alloy substrate under the spray jet.

6.1.2 Preliminary Trials: Results

The CGDS spraying parameters mentioned above were used to produce both conventional and nanocrystalline CoNiCrAlY coatings for the purpose of the feasibility study. Results from these preliminary trials are now presented.

6.1.2.1 *Coatings Produced from the Conventional Feedstock Powders*

For the conventional coatings, preliminary trials were performed using both the AMDRY 9954 and AMDRY 9951 as-received CoNiCrAlY powders. Figure 6.1 shows backscattered SEM images of the cross-section of the coatings manufactured from both these powders, respectively. As can be seen from these images, the CGDS process was successful in manufacturing coatings from both these powders, thereby demonstrating the feasibility of conventional CoNiCrAlY coatings by CGDS. As expected however, the quality of the coatings is not satisfactory, and therefore optimization of the spraying parameters is necessary. Observation of both coatings also shows significant differences as a result of the different feedstock particle sizes. The coating prepared with the coarse AMDRY 9954 powder (Figure 6.1a) shows that coating build-up was limited to an approximate thickness of 100 μ m, which is insufficient for the current study (free-standing coating flakes for oxidation testing are to be prepared from the samples, and therefore a thickness of approximately 500 μ m is desirable). Also, this coating features the presence of relatively large defects such as pores and cracks, which are attributed to insufficient plastic deformation of the particles. The presence of insufficiently deformed particles in the vicinity of these defects can actually be identified in the coating structure. Conversely, the coating manufactured with the fine AMDRY 9951 powder shows better promise (Figure 6.1b). This coating was successfully built-up to a thickness of approximately 300 μ m, which is much better than the AMDRY 9954

coating but still too thin in comparison to the desired thickness of 500 μ m. The coating also exhibits porosity in the range of 8 to 10%. Although this porosity is well above the allowable limit, the larger coating build-up thickness suggests that the finer feedstock particles offer better potential for the production of thick and dense conventional CoNiCrAlY coatings by CGDS. Further discussion of the influence of particle size ranges on coating quality will be addressed in the spraying parameter optimization section.

The results obtained from these preliminary trials demonstrate that although conventional CGDS CoNiCrAlY coatings can be produced using the aforementioned spraying parameters, optimisation of these parameters is necessary to improve coating quality. Looking back at these spraying parameters, a value of 4 RPM for the powder feeder wheel rotation speed is very high (in comparison to latter trials) and represents a large powder feeding rate. Based on the SEM images from Figure 6.1, the combination of such high powder feedrates and the limited coating build-up thickness observed is an indication of low deposition efficiency, thereby suggesting that only few particles actually have sufficient velocity to adequately deform and bond to the substrate to form a coating. Optimization of the spraying conditions is therefore necessary to ensure that most particles are accelerated beyond their critical velocity.

Finally, it is interesting to note that clogging of the nozzle was observed towards the end of these preliminary trials. Clogging was found to occur inside the nozzle in the vicinity of the throat where the profile diameter is smallest. This was attributed to excessive amounts of powder particles in the flow due to high powder feedrates. Nozzle clogging in the throat area is another potential drawback of feeding the powder particles axially at the nozzle inlet. At the time when these trials were carried out, the procedure for unclogging the nozzle involved the injection of fine BT-6 glass beads (210-300 μ m in diameter) in the nozzle using compressed air at low pressure (~600kPa). Erosion from the glass beads would eventually dislodge the sprayed material accumulation in the nozzle and remove the obstruction. Although this technique proved to be an effective approach to unclog the nozzles, it was later found that repeated treatments also caused erosion of the nozzle geometry near the throat, thereby affecting the flow characteristics and decreasing the nozzle performance.

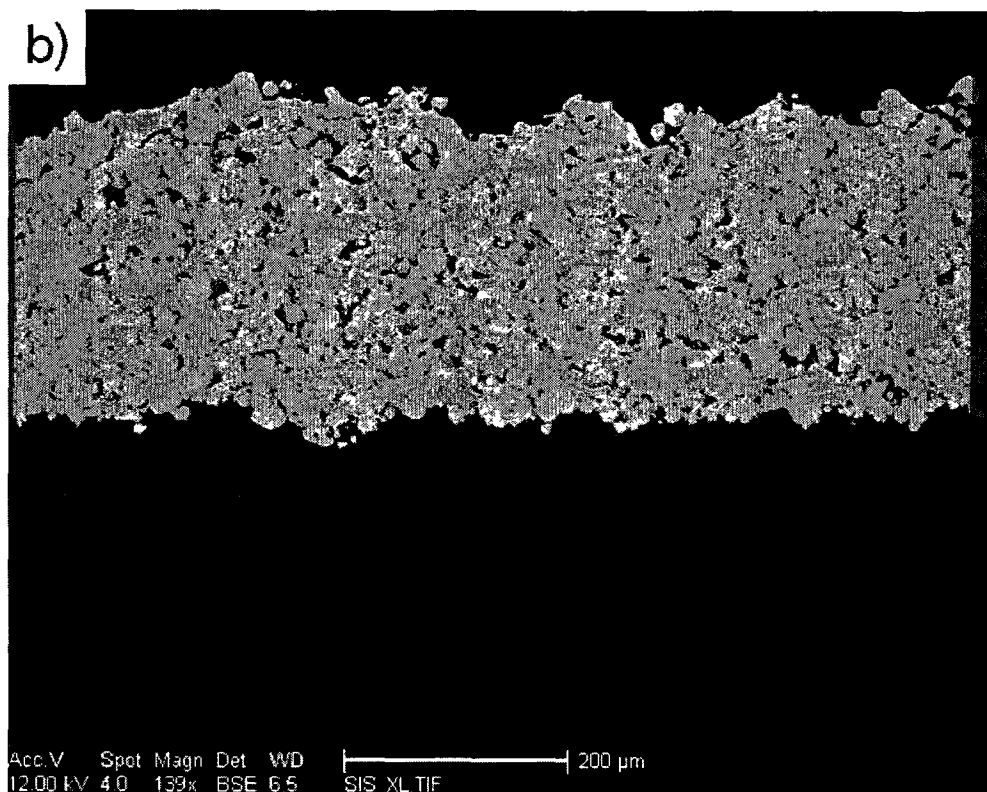
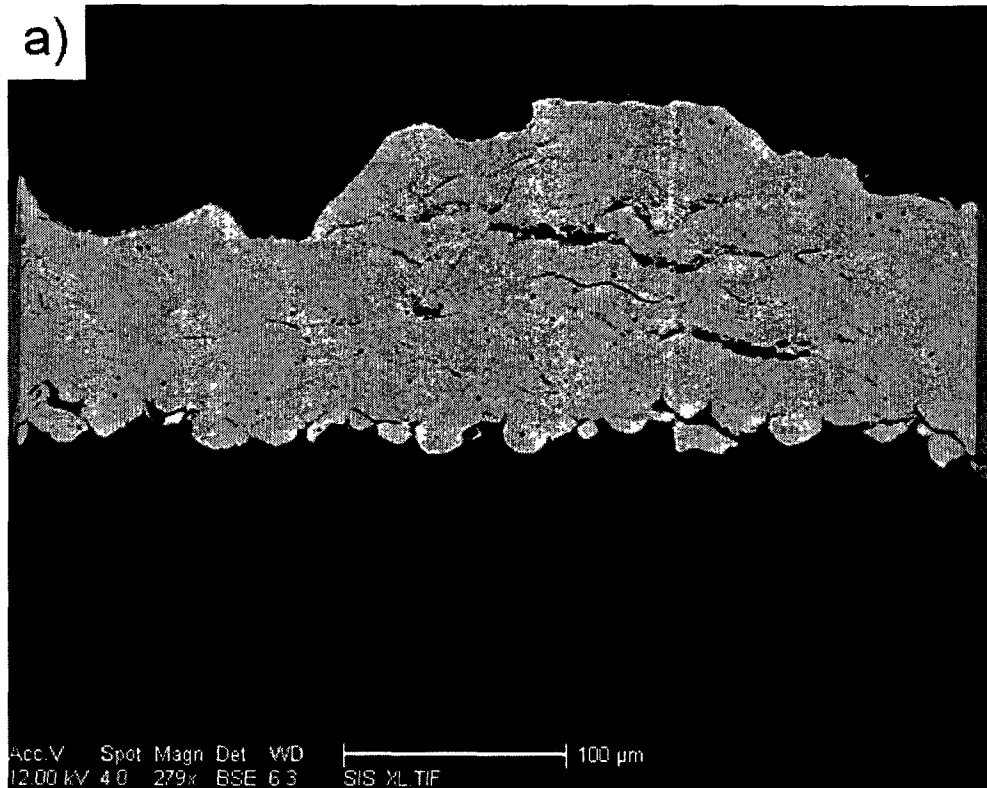


Figure 6.1: SEM images showing the cross-section of coatings obtained from preliminary trials using (a) the AMDRY 9954 and (b) AMDRY 9951 conventional CoNiCrAlY powders

6.1.2.2 Coatings Produced from the Nanocrystalline Feedstock Powder

Preliminary trials were also carried out to verify the feasibility of nanocrystalline CoNiCrAlY coatings by means of CGDS deposition. This was done by performing another series of spray trials using the as-cryomilled feedstock powder and the same spraying parameters as for the conventional coatings.

Figure 6.2 shows two cross-section images at different magnifications of a nanocrystalline coating manufactured during these preliminary trials with the as-cryomilled feedstock powder. As can be seen from this figure, deposition of a coating with a measurable build-up thickness was successful, thereby demonstrating the feasibility of nanocrystalline CoNiCrAlY coatings manufactured by CGDS. Nevertheless, as can be seen from these images, the nanocrystalline coatings obtained feature large defects and extensive crack content. Furthermore, the coating exhibits limited build-up with a thickness of approximately 200µm. Given the relatively poor quality of the conventional coatings obtained with the AMDRY 9954 powder, these types of results were somewhat expected. Firstly, the nanocrystalline feedstock particles are characterized with increased mechanical strength and hardness in comparison to the conventional particles as a result of their fine grain structure. It was thus expected that their critical velocity would be higher and that their CGDS deposition would be more difficult. Secondly, the as-cryomilled feedstock powder features a broad particle size range comparable to the AMDRY 9954 powder. It thus seems appropriate that coating build-up would be limited for the nanocrystalline coating due to the presence of larger particles, as was the case for the conventional coating prepared from the AMDRY 9954 powder. Finally, it is worth mentioning that some reduction in the performance level of the nozzle may have occurred as a result of the clogging incident described previously. These factors may all have contributed to the formation of large visible defects in the nanocrystalline coating structure. Despite these issues, the coating cross-section images show some regions of the coating that are in fact quite dense, thereby suggesting that some particles have achieved sufficient velocity and plastic deformation. This is believed to be attributed to the fact that the irregular flake-like geometry of the cryomilled particles promotes their acceleration in the nozzle as a result of a larger drag coefficient in comparison to the spherical conventional particles [35].

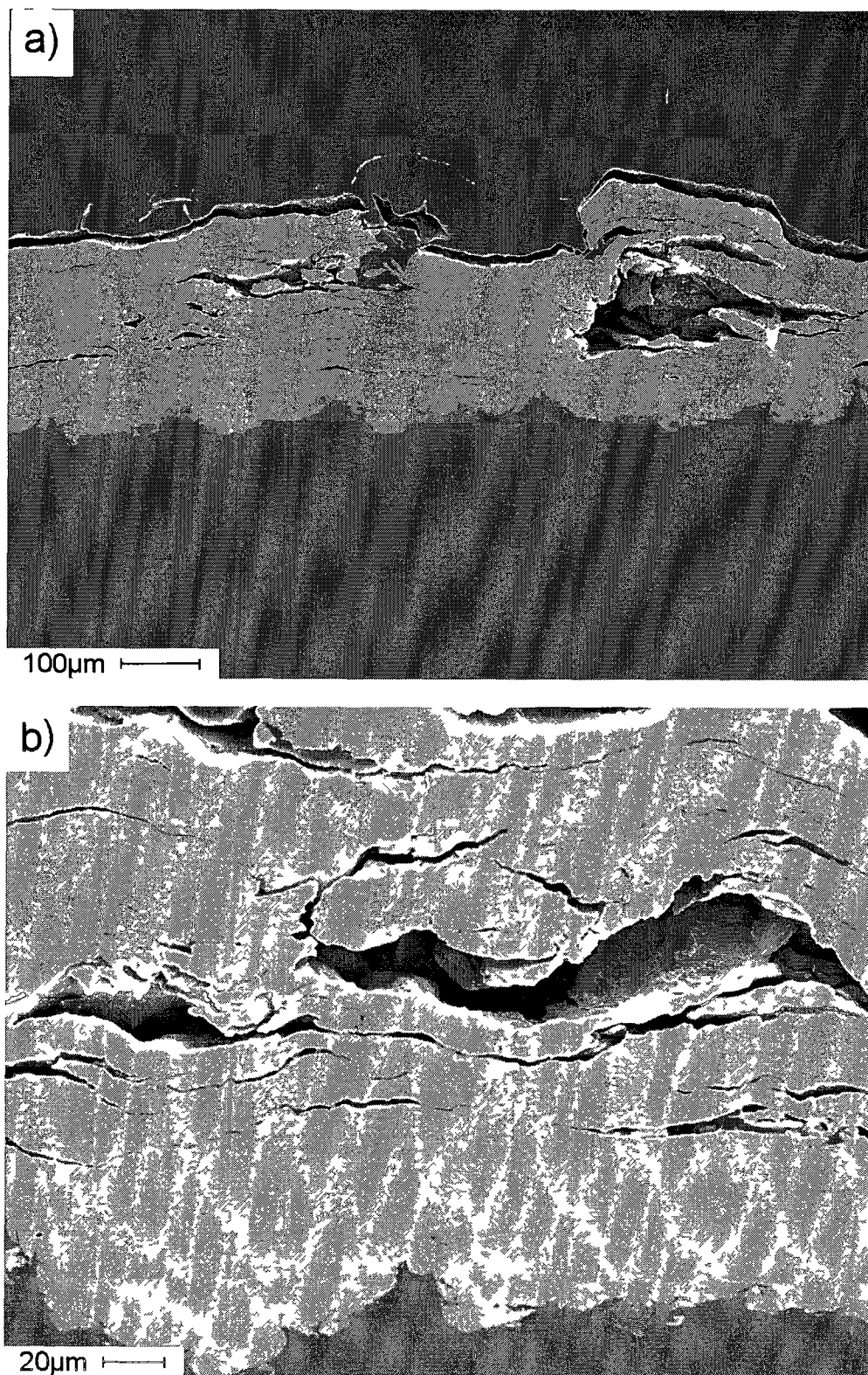


Figure 6.2: SEM images showing the cross-section at various magnifications of a coating obtained from preliminary trials using the nanocrystalline as-cryomilled CoNiCrAlY powder

6.2 CGDS Spray Parameter Optimization

The present section of this report aims to describe the approach that was considered to optimize the CGDS spraying parameters for the deposition of CoNiCrAlY coatings. This process was achieved by a combination of theoretical and experimental trials that were performed in order to investigate the influence of the various spraying parameters on the resulting coating quality. An existing numerical model was used to investigate the influence of various spraying parameters on the supersonic gas flow and its influence on particle acceleration in the nozzle. The use of this model was limited to the study of the gas flow in the nozzle and its interaction with the injected powder particles. Experimental trials were carried out to verify and confirm findings obtained from the numerical model. These experimental trials were also performed to investigate the influence of other spraying parameters that do not affect the gas flow in the CGDS nozzle. As such, the first part of this section will provide a brief description of the numerical model used in this study, namely the underlying assumptions, conservation equations solved, numerical scheme used and other numerical details. The second part of this section will present the influence of the various spraying parameters on the coating quality as evidenced by results obtained from both the numerical and experimental trials.

6.2.1 Numerical Model for the Gas Flow and Particle Acceleration in a CGDS Nozzle

Numerical simulations were performed using a two-dimensional model developed and validated by a previous researcher at the University of Ottawa Cold Spray Laboratory [102]. It should be noted that the numerical simulations were carried out only to compare the predicted particle velocities when changing various spraying conditions in order to identify general trends and provide insight on the expected influence of each spray parameter on particle acceleration. While modelling can be used to determine the precise spray parameters that would be required to achieve a specific desired particle velocity, discrepancies with actual experimental results are always necessarily present and therefore this approach was not used in this work. As such, the model was used as a theoretical comparative tool to

investigate particle behaviour as a function of the various spraying parameters. Details concerning this numerical model are now presented.

6.2.1.1 Model Assumptions

The existing numerical model considered in this study was previously developed using various assumptions to describe the gas flow and particle acceleration [102, 105, 106]. These assumptions can be summarized as the following:

1. The flow behaves as a viscous Newtonian fluid.
2. The local behaviour of the fluid is assumed to be that of a fluid at thermodynamic equilibrium. As such, Stokes relation is valid ($3\lambda + 2\mu = 0$) and strains in the fluid may be expressed by the tensor $2\mu S_{ij}$, where $S_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$.
3. The gas can be modeled by the perfect gas law, which is expressed as $P = (\gamma - 1)\rho E$.
4. The gas flow is assumed to be compressible and turbulent.
5. The geometry of the nozzle is modeled as a two-dimensional axisymmetric profile.
6. Morkovin's hypothesis is used: it is assumed that the turbulent structures in the flow are not significantly influenced by fluctuations of the gas density and therefore this effect can be considered negligible. As a result, the Navier-Stokes equations are used to define the flow field and turbulence models remain valid for empirical values obtained for incompressible flows.
7. The triple velocity correlation functions for turbulence are assumed to be negligible in comparison to the double correlations.
8. Boussinesq's hypothesis is used. As such, turbulent momentum and heat fluxes resulting from the Reynold's averaging process have the same form as laminar flows and are therefore linked to the average flow by eddy viscosity and conductivity.

9. The $k - \varepsilon$ turbulence model is used, despite its inadequacies with adverse pressure gradient flows. For the current work, expansion of the flow in the nozzle represents a region with a favourable pressure gradient, however the region of the gas jet outside the nozzle exit is expected to lead to adverse pressure gradients. Nevertheless, given the short stand-off distances considered in comparison to the length of the nozzle profile, the influence of the adverse pressure gradient is expected to be negligible on the computational results for particle acceleration. Furthermore, the size and mass of the particles injected in the flow are sufficiently large to prevent any $k - \varepsilon$ model limitations from introducing significant numerical errors. The $k - \varepsilon$ turbulence model is thus assumed to be valid for the current modeling work.
10. The presence of particles in the flow is assumed to have negligible influence on the behaviour of the flow field itself. Given the relatively low powder feedrates considered in the present work, this assumption is believed to be valid.
11. Acceleration of the particles is assumed to be caused solely by the forces resulting from momentum transfer between the gas flow and injected particles. All other forces, such as body forces due to gravity, are neglected.
12. All particles injected in the flow are assumed to have a spherical morphology and a density equal to that of nickel.

6.2.1.2 Conservation Equations

Based on the previously listed assumptions, the numerical model aims to solve simultaneously the continuity, momentum and energy conservation equations. These equations are presented in their general Reynolds conservative form to ensure the local conservation of properties as well as to account for turbulence effects in the flow field. These equations are given as follows:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i}(\rho u_i) = 0 \quad (\text{Eq. 6.1})$$

$$\frac{\partial}{\partial t}(\rho u_i) + \frac{\partial}{\partial x_j}(\rho u_j u_i) = -\frac{\partial P}{\partial x_i} + \frac{\partial}{\partial x_j}[2\mu S_{ji} + \tau_{ij}] \quad (\text{Eq. 6.2})$$

$$\frac{\partial}{\partial t}(\rho E) + \frac{\partial}{\partial x_j}(\rho u_j H) = \frac{\partial}{\partial x_j}[-q_{Lj} - q_{Tj}] + \frac{\partial}{\partial x_j}[u_i(2\mu S_{ij} + \tau_{ij})] \quad (\text{Eq. 6.3})$$

where $\tau_{ij} = -\overline{\rho u'_i u'_j}$ and $q_{Tj} = -\frac{\mu_T}{Pr_T} \frac{\partial H}{\partial x_j}$.

A two-equation model (the $k - \varepsilon$ model) is used to complete the equation system. The model uses Boussinesq's turbulent viscosity ($\tau_{ij} = 2\mu_T S_{ij}$) and takes into account non local effects as well as flow history. The turbulent kinetic energy equation is given as:

$$\frac{\partial(\rho k)}{\partial t} + \frac{\partial(\rho u_j k)}{\partial x_j} = \tau_{ij} \frac{\partial u_i}{\partial x_j} - \rho \varepsilon + \frac{\partial}{\partial x_j} \left[\left(\mu + \frac{\mu_T}{\sigma_k} \right) \frac{\partial k}{\partial x_j} \right] \quad (\text{Eq. 6.4})$$

where $k = \frac{1}{2} \overline{u'_i u'_i}$ and $\varepsilon = \nu \overline{\frac{\partial u'_i}{\partial x_k} \frac{\partial u'_i}{\partial x_k}}$.

The rate of dissipation of turbulence is given by the following expression:

$$\frac{\partial(\rho \varepsilon)}{\partial t} + \frac{\partial(\rho u_j \varepsilon)}{\partial x_j} = C_{\varepsilon 1} \frac{\varepsilon}{k} \tau_{ij} \frac{\partial u_i}{\partial x_j} - C_{\varepsilon 2} \rho \frac{\varepsilon^2}{k} + \frac{\partial}{\partial x_j} \left[\left(\mu + \frac{\mu_T}{\sigma_\varepsilon} \right) \frac{\partial \varepsilon}{\partial x_j} \right] \quad (\text{Eq. 6.5})$$

Finally, the turbulent viscosity is given as $\mu_T = \frac{\rho C_\mu k^2}{\varepsilon}$.

Modeling of the behaviour of a powder particle in the flow is achieved using Newton's second law of motion in an Euler-Lagrangian system. The equation of motion used to describe the velocity of a particle is given as:

$$m_p \frac{du_p}{dt} = \frac{C_D A_p \rho (u - u_p)^2}{2} \quad (\text{Eq. 6.6})$$

The drag coefficient considered in this equation is taken from previous work and is generally used for modeling of the particle/flow interactions in CGDS.

6.2.1.3 Numerical Details

Transformation of the physical domain into a computational domain is achieved by means of the commercially available Gambit software. This software allows for the creation and construction of an investigation area having a geometry that matches that of the CGDS nozzle. The software also contains a powerful mesh generator capable of creating meshes that properly adapt to various geometries. Given that the nozzle geometry considered in this work is composed only of straight edges and is therefore relatively simple, the mesh considered for the present numerical model was chosen to be structured. As a result, the cells within the mesh are represented as parallelograms oriented with the main direction of the flow. This approach has been successfully used elsewhere for modeling of CGDS nozzle flows [102, 105].

The flow field is divided into two numerical investigation zones: the first is the flow field inside the nozzle, while the second corresponds to the free jet at the nozzle exit. These zones are delimited by various types of surfaces: an inlet, an outlet, a series of solid wall surfaces and a centerline about which flow is assumed to be symmetric (based on the axisymmetric flow assumption). Two-dimensional modeling of the flow requires that a number of boundary conditions be attributed to the inlet, outlet and wall type delimiting surfaces. These boundary conditions are listed in Table 6.1. For the particle acceleration model, particles are injected along the centerline of the nozzle axis with negligible axial and radial velocities.

Table 6.1: List of boundary conditions for the various delimiting surfaces

Boundary	Inlet	Outlet	Wall
u	Extrapolated	Extrapolated	0
v	0	Extrapolated	0
P	Known	Known	Extrapolated
T	Known	Known	Extrapolated
k	Known	Extrapolated	Known
ε	Known	Extrapolated	Known

Simultaneous solution of the conservation equations is achieved by means of the commercially available Fluent software. Discretization of the conservation equations is done using a technique based on the control volume approach. The resulting equation system is linearized and solved iteratively using a Gauss-Seidel type solver [106]. Convergence of the solution is deemed acceptable when the three following criteria have been respected:

1. The mass flow rates at the inlet and outlet of the computational domain are equivalent. This is verified by comparing the sum of the mass flow rates of every computational cell at both the inlet and outlet boundaries. For the present work, a relative difference in mass flow rate $\left(\frac{\Delta \dot{m}}{\dot{m}}\right)$ smaller than 10^{-6} was considered satisfactory for convergence of the solution.
2. Throughout the iterative solution of the conservation equations, the numerical residuals are observed to decrease by many orders of magnitude. Numerical residuals represent the variation of a given property's value from one computational iteration to the next. Convergence of the solution was considered satisfactory when the residuals had decreased below a relative threshold of 10^{-6} .
3. The solution is independent of the cell size resulting from mesh generation. Once a solution appears to have converged (based on the previous two criteria), the mesh was refined and the computational process was repeated. Comparison of both solutions allowed determining whether the mesh size influenced the solution. This process was repeated until the solutions no longer changed as a result of mesh refinement.

Investigation of the acceleration of particles by means of Eq. 6.6 was performed using the converged solution of the flow field in the CGDS nozzle. This portion of the numerical modeling was once again performed using the Fluent software.

6.2.2 Influence of Various Spray Parameters

The present section aims to discuss the influence of various spray parameters on the resulting coating quality. The spraying parameters for the CGDS system that were considered as variables for this work are the following: the nozzle inlet temperature, the nozzle inlet pressure, the particle size distribution, the particle injection pressure differential (ΔP), the nozzle stand-off distance (SOD), the substrate traverse speed and the powder feedrate as determined by the powder feeder wheel rotation speed. These different spray parameters can be grouped into two distinct categories. The first four can be considered as spraying parameters that influence the coating quality by means of affecting the flow behaviour and consequently the particle velocities. The influences of these parameters have thus been investigated both numerically and experimentally. The remaining parameters can be viewed as those that do not significantly influence the flow behaviour or particle acceleration, but rather play a more important role with respect to the actual deformation and bonding mechanisms upon deposition. These parameters have thus been studied using only experimental approaches. The influence of each spraying parameter for the purpose of their optimization is now discussed.

6.2.2.1 Nozzle Inlet Temperature

As discussed extensively in section 2.2.4, the influence of the gas temperature on the acceleration of particles in a CGDS nozzle is well known. From a particle velocity perspective, higher process gas temperatures are desirable based on Eq. 2.4 which shows that for a specific gas expansion (i.e. fixed nozzle geometry with fixed exit Mach number), the gas velocity increases with increasing temperature, thereby more effectively accelerating the powder particles. Furthermore, it was argued in section 2.2.3 that higher gas temperatures can provide some level of particle heating which in theory can somewhat reduce the critical velocity of the sprayed particles. Although the extent of particle heating has been shown to be quite limited, higher gas temperatures would certainly not be unfavorable from this point of view. While higher gas temperatures are theoretically desirable, physical limitations with the experimental equipment are typically observed to be the main constraining factor.

As discussed in the preliminary spray trials from section 6.1, the existing gas heater for the CGDS equipment at the onset of this project could only heat the gas to a temperature of 350-400°C. A new gas heater was therefore designed which would be capable of providing a gas temperature at the nozzle inlet of up to 650°C. More details of this gas heater are provided in section 4.2.1.4. It is important to note that this new gas heater was originally designed to be used with the existing CGDS nozzle, which was limited to an inlet gas pressure of approximately 1MPa as a result of the axial powder injection configuration. As discussed in the following section, modifications were later made to this nozzle which allowed for higher gas pressures to be used. These higher gas pressures resulted in higher mass flow rates through the gas heater, thereby adding a significant load on the power supply system. Through a series of experiments, it became evident that a steady maximum temperature of 650°C could not be maintained throughout the spraying trials under these conditions. From these experiments, it was determined that a maximum temperature of 550°C would ensure sufficient stability of the gas heating system throughout the spray trials. With these physical limitations in mind, a gas temperature of 550°C was thus determined to be optimal for this study. As such, the numerical modeling trials which will be presented in the upcoming sections have all been performed using a nozzle inlet gas temperature of 550°C.

6.2.2.2 Nozzle Inlet Pressure

The nozzle inlet pressure proved to be one of the more important spraying parameters considered in this study. As discussed in section 2.2.4, the gas pressure plays a major role on the flow behaviour inside the nozzle, which necessarily influences the interactions between the particles and the gas flow. Furthermore, examination of Eq. 2.12 shows that the acceleration of a particle in the flow is directly proportional to the density of the flow, which is linked to the gas pressure according to the perfect gas law. The influence of the nozzle inlet pressure as a CGDS spray parameter is thus highly relevant.

Investigation of the particle and flow behaviour in the nozzle as a function of the nozzle inlet pressure was achieved by means of a series of numerical modeling trials. All numerical trials were performed with the same nozzle geometry (see section 4.2.1.3) and considered helium as the propellant gas. Four various nozzle inlet pressure settings were considered which ranged

from 1 MPa to 2.5 MPa. The lower limit of 1 MPa was selected as a reference given that preliminary trials conducted at this pressure were met with mixed levels of success and therefore higher pressures were likely required to increase the particle velocities. The upper limit of 2.5 MPa for the gas pressure was selected for safety considerations (based on predicted pressure ratings of the CGDS system) as well as to set a self-imposed limit for the consumption of helium due to higher mass flow rates. A nozzle inlet temperature of 550°C was considered for all cases.

Figure 6.3 shows the velocity of the helium gas flow along the centerline axis of the nozzle for different nozzle inlet pressures. As can be seen from this graph, the axial velocity is not influenced by the gas pressure in the converging section of the nozzle, which demonstrates that the nozzle is choked for all pressures considered. In the diverging section of the nozzle, increasing the gas pressure is observed to cause a slight increase of the gas velocity, however the variation is not significant. The most important influence of the nozzle inlet pressure on the gas behaviour is observed near the nozzle exit plane. For each nozzle inlet pressure considered, strong fluctuations of the gas velocity occur at a certain point inside the nozzle. Following these fluctuations, the velocity is seen to steadily decline. These strong fluctuations represent the onset of a series of compression and expansion waves in the flow which eventually revert the supersonic flow back to the subsonic regime. Increasing the nozzle inlet pressure is seen to delay the onset of these shockwaves and reduce their intensity, thereby resulting in higher subsonic velocities in the free jet zone.

This is further evidenced in Figure 6.4 which shows the axial velocity contours of the gas flow in the nozzle as a function of the nozzle inlet pressure. For each trial, shocks are observed inside the nozzle, as evidenced by a series of alternating velocity regions (seen as yellow spots) near the nozzle outlet. The presence of shockwaves inside the nozzle can be viewed as undesirable as they represent strong velocity fluctuations in the flow that can interfere with the successful acceleration of the particles. The presence of such shockwaves in the nozzle demonstrates that in all cases, the inlet/outlet pressure ratios are insufficient to support supersonic flow throughout the diverging length of the nozzle. In reference to Figure 2.12, this corresponds to case d) of the flow behaviour in a converging/diverging nozzle. As the nozzle inlet pressure is increased, the shocks are seen to move downstream in the nozzle,

thus approaching the optimal matched flow behaviour. It can be seen that for an inlet pressure of 2.5 MPa, the shockwaves occur closest to the nozzle exit plane. This is desirable from a particle acceleration perspective as it allows for a longer exposure of the particles in the high velocity portion of the flow, thereby optimizing momentum transfer. The displacement of these shockwaves is not necessarily significant however when compared to the shockwave locations in the case of a 2.0 MPa nozzle inlet pressure. Conversely, nozzle inlet pressures below 2.0MPa reveal that the onset of shockwaves occurs further inside the nozzle, thereby causing greater velocity reductions. These results demonstrate that higher nozzle inlet pressures (upwards of 2.0MPa) are likely to improve the flow behaviour in the nozzle and may allow for higher particle velocities to be achieved. Also, it is important to recall that a higher nozzle inlet pressure results in higher gas densities throughout the flow, which according to Eq. 2.12 is expected to promote acceleration of the particles. As such, the numerical model is now used to investigate the predicted behaviour of powder particles injected in the nozzle as a function of the inlet gas pressure.

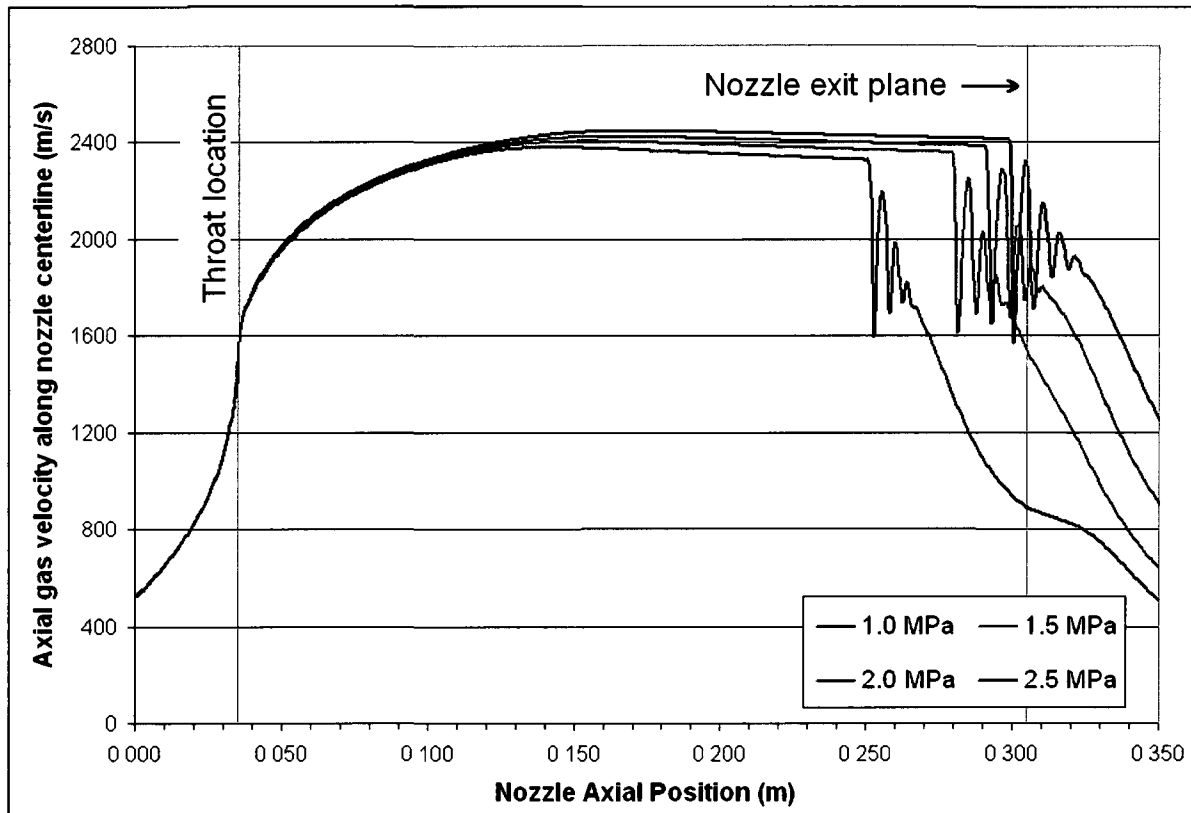


Figure 6.3: Flow velocity along the centerline axis of the CGDS nozzle as a function of nozzle inlet pressure

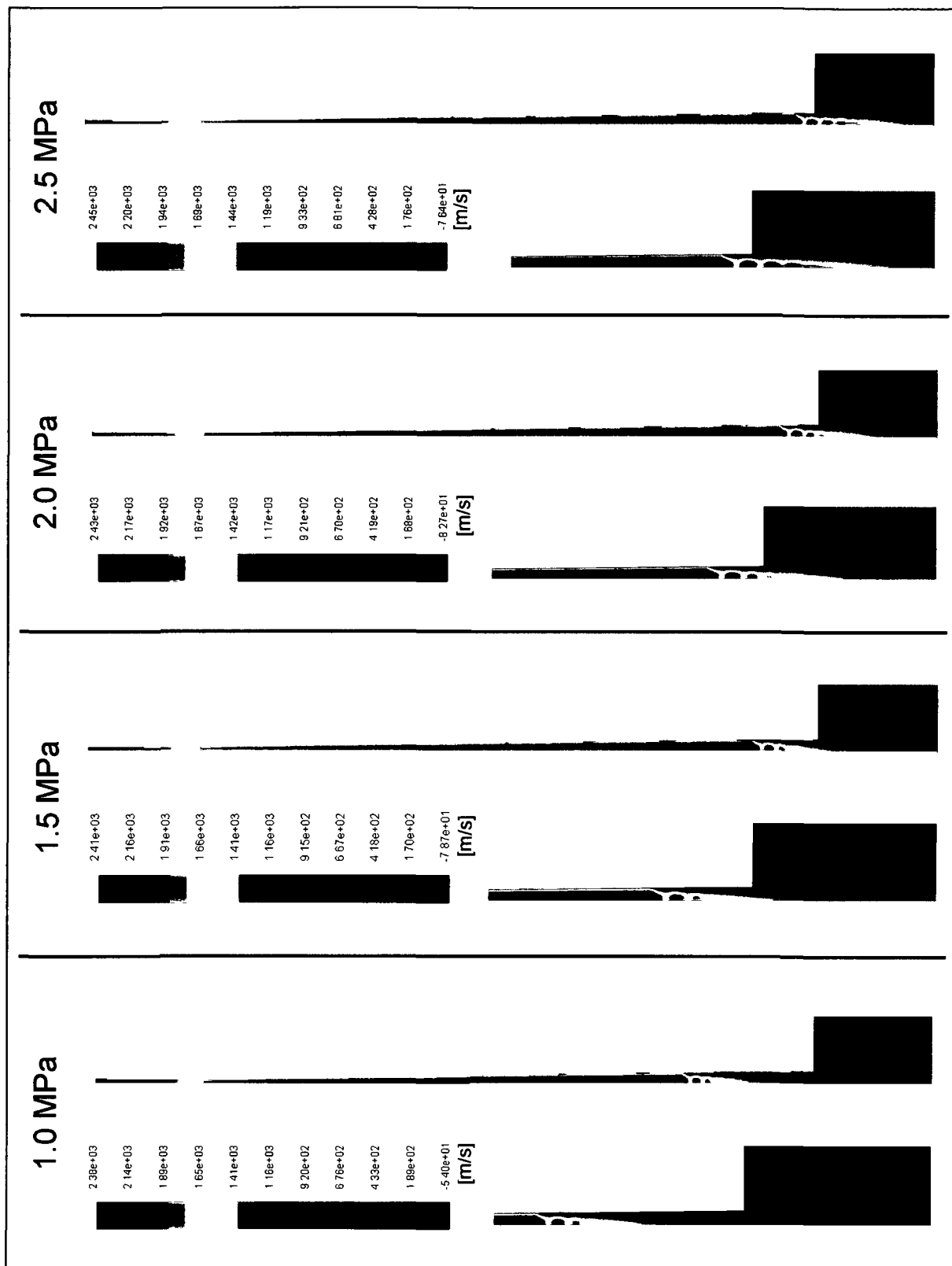


Figure 6.4: Axial velocity contour plots of the CGDS nozzle gas flow as a function of nozzle inlet pressure

Prior to presenting modeling results for the predicted particle velocities using different nozzle inlet pressures, certain issues needed to be considered. As discussed in section 6.1.1, the nozzle used for this work was originally limited to an inlet pressure of approximately 1 MPa as a result of the axial powder injection configuration. The axial powder injection configuration implies that particles are injected parallel to the flow upstream of the nozzle inlet where the pressure is highest. Given the limited pressure rating of the commercial powder feeder and the requirement of a positive pressure differential for the powder to flow from the feeder to the injection port, a maximum allowable nozzle inlet pressure must be respected (approximately 1MPa in this case). As such, the increased nozzle inlet pressure scenarios outlined previously could not be realized using this axial powder injection configuration. To counter this problem, it was envisioned to add a new injection port to the nozzle so that powder could be injected radially into the nozzle downstream of the throat. This approach provides interesting advantages. Most importantly, given that the pressure decreases rapidly as the gas expands in the nozzle, the pressure in the downstream vicinity of the throat is significantly lower than the nozzle inlet pressure. As such, much larger nozzle inlet pressures can be used without the physical constraints imposed by the powder feeder. Also, radial injection eliminates the onset of clogging at the throat or in the converging portion of the nozzle. However, various considerations needed to be taken into account with this new powder injection configuration. Firstly, injecting the powder radially downstream of the throat implies that the particles are deprived of any momentum transfer that could be achieved in the converging section of the nozzle. This results in a trade-off where one must verify whether the benefits of higher nozzle inlet pressures can outweigh the drawbacks of losing momentum transfer in the converging section of the nozzle. For this reason, all modeling work carried out with nozzle inlet pressures higher than 1.0 MPa assumed that particles were injected at a specific location downstream of the throat rather than at the entrance of the nozzle. Secondly, the precise injection location needed to be optimized in order to ensure that maximum particle acceleration is achieved.

The optimal location for radial injection was first considered. For these modeling trials, an arbitrary particle size of 20 μ m was considered in the previously discussed helium flow obtained with a nozzle injection pressure and temperature of 2.0 MPa and 550°C respectively.

The behaviour of a particle injected at 15mm, 20mm, 25mm and 65mm downstream of the throat location was considered (the throat is located 35mm from the inlet of the nozzle). Predicted particle velocities resulting from these modeling trials are presented in Figure 6.5. As expected, it can be seen that particles injected closest to the throat are predicted to achieve higher velocities when they reach the exit of the nozzle. This is attributed to the slightly longer dwell time of these particles in the flow, thereby allowing more momentum transfer with the gas and resulting in higher particle velocities. While these results suggest that the injection port should be placed closer to the throat, in practice a minimal distance is required given the fixed diameter of the injection port (2.5mm) which must be equal in size or smaller than the nozzle channel at the injection site. Based on the nozzle geometry, it was therefore determined that the optimal location for the radial powder injection port was 20mm downstream of the throat. Finally, verification of the pressure distribution for the gas flow along the nozzle revealed that even in the case of the highest nozzle inlet pressure (2.5 MPa), the static pressure at the proposed injection site remained well below the maximum allowable pressure imposed by the powder feeder.

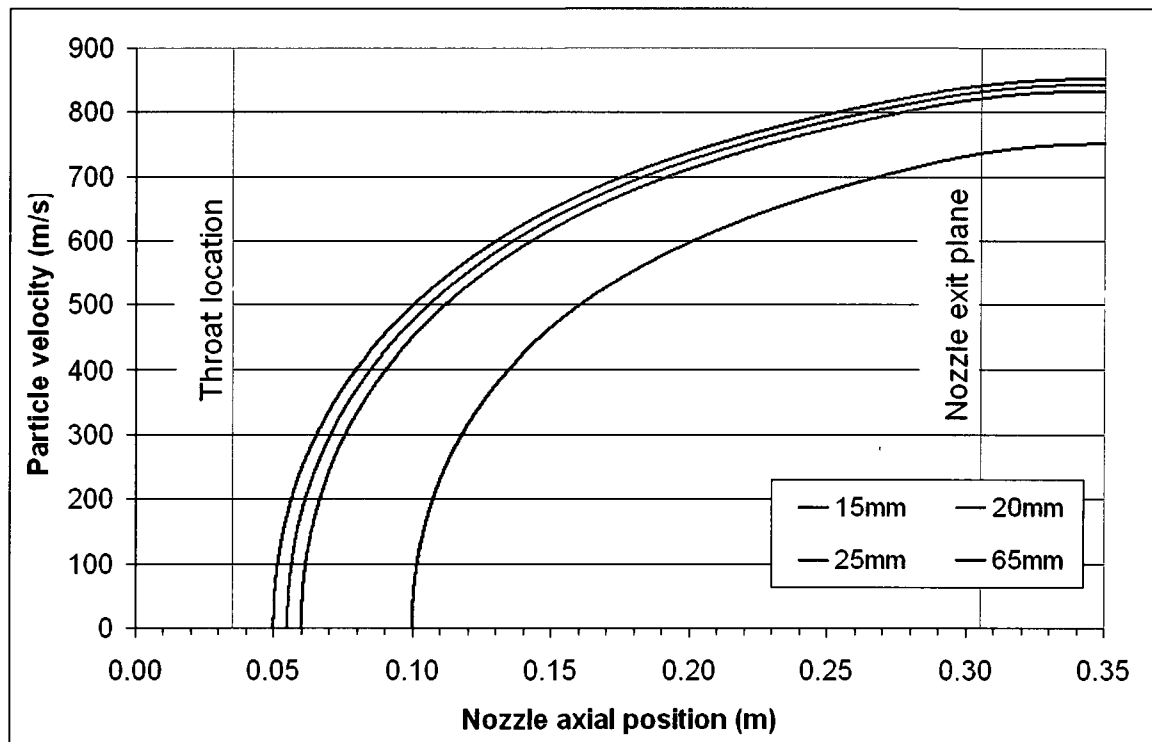


Figure 6.5: Predicted velocity of a 20 μ m particle as a function of the radial injection location (nozzle inlet gas pressure and temperature of 2.0MPa and 550°C respectively)

Having identified a preferred radial powder injection location along the nozzle, numerical modeling was carried out to verify the predicted velocity of the particles when sprayed using different nozzle inlet pressures. The particle diameter and nozzle inlet gas temperature were maintained constant at 20 μ m and 550°C respectively for all these trials. Results are presented in Figure 6.6.

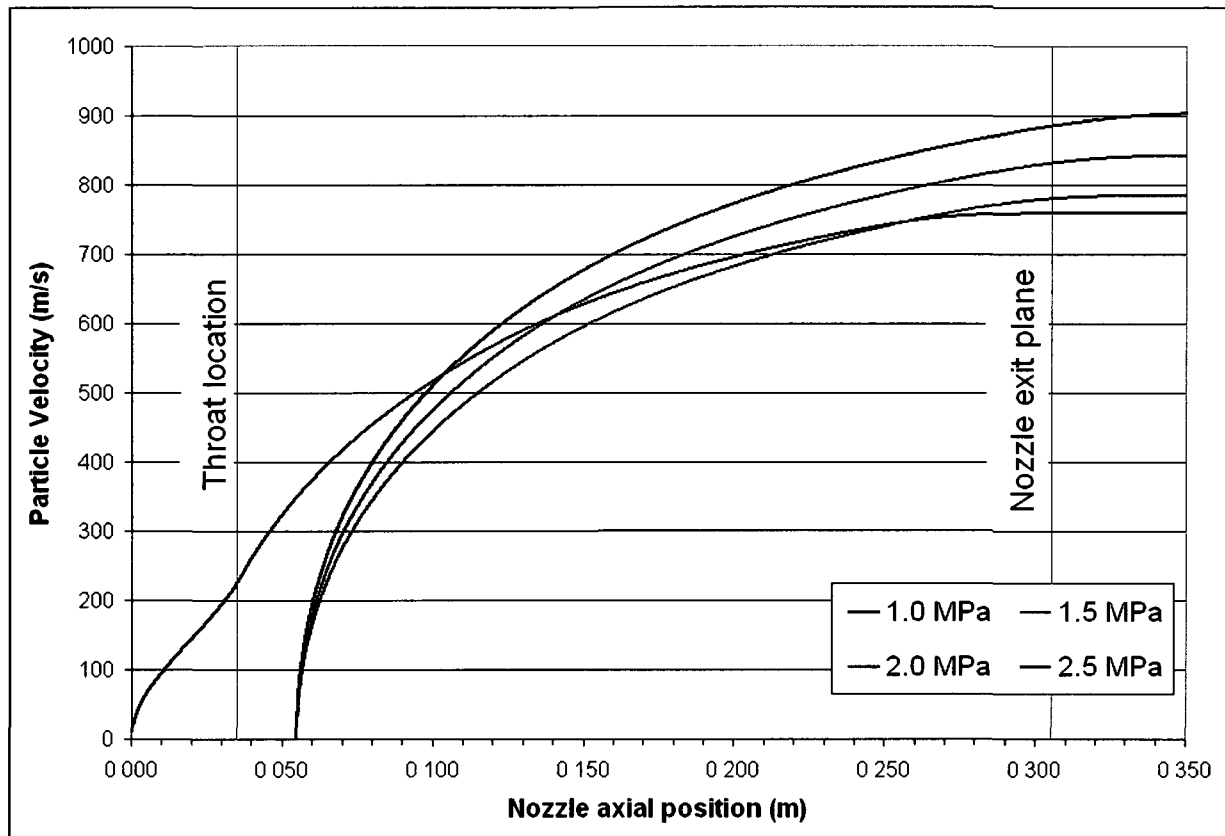


Figure 6.6: Predicted particle velocity as a function of nozzle inlet pressure (20 μ m particle, gas temperature 550°C)

As can be seen from this figure, higher particle velocities are achieved with increased nozzle inlet pressure. Based on these findings, a 20 μ m particle is likely to achieve an increase in velocity by more than 100m/s if injected radially with a nozzle inlet pressure of 2.5 MPa as opposed to 1.0MPa with axial injection. These results demonstrate that the benefits of using higher pressures outweigh the loss of momentum transfer in the converging section of the nozzle. Given that some deposition and coating build-up was previously achieved during the

preliminary trials using a nozzle inlet pressure of 1.0 MPa, it is expected that this increase in particle velocity will result in significant improvement of the coating structure.

To validate the trends observed in the numerical trials, numerous experimental tests were also carried out. For conciseness purposes, only one sample image of a coating cross-section is provided as an example of the influence of increased nozzle inlet pressures. Figure 6.7 shows the cross-section of a CoNiCrAlY coating manufactured using the conventional AMDRY 9951 powder and a nozzle inlet gas pressure and temperature of 2.0 MPa and 550°C respectively. As can be seen in this figure, the use of a higher nozzle inlet pressure and temperature has reduced the porosity down to $2.7 \pm 0.8\%$. Also, this coating featured a thickness of just over 2 mm, which is substantially larger than the coating obtained during the preliminary trial and is therefore an indication of improved deposition efficiency.

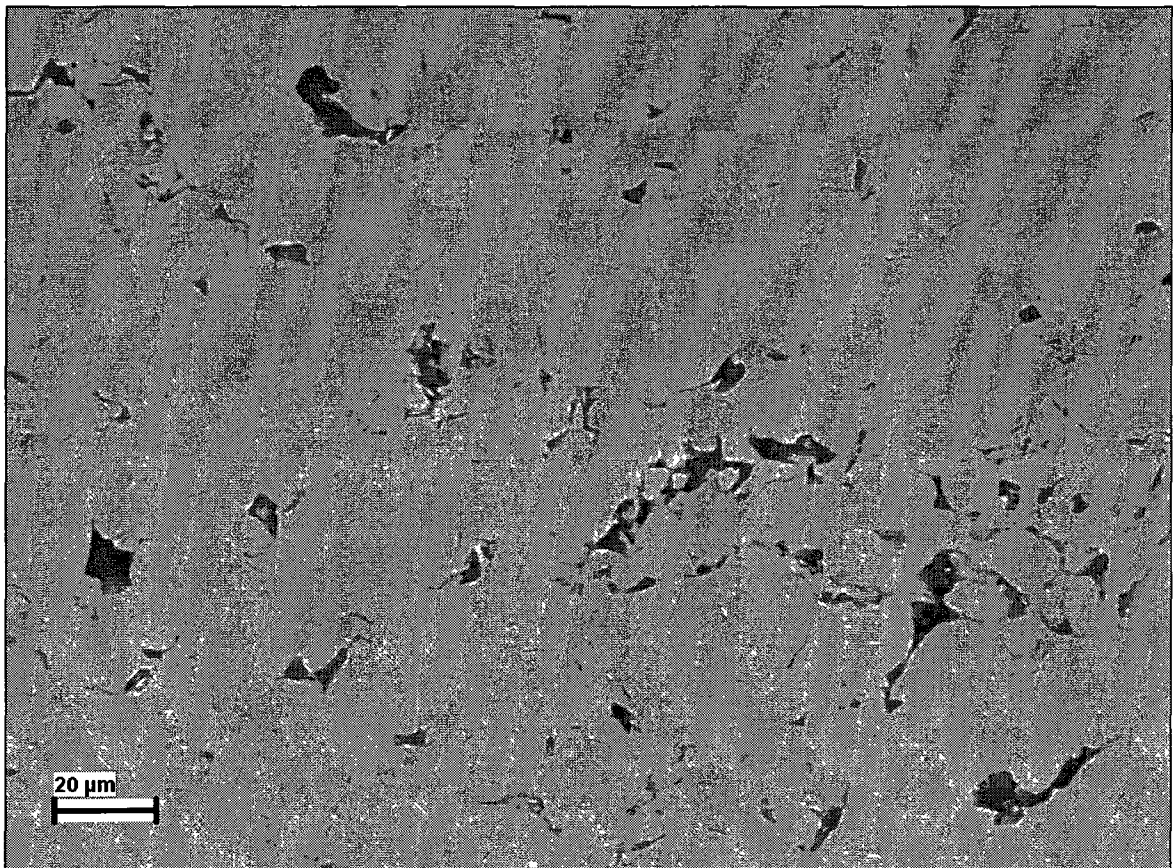


Figure 6.7: SEM image showing the cross-section of a CoNiCrAlY coating manufactured from the AMDRY 9951 feedstock powder using helium with a nozzle inlet pressure and temperature of 2.0 MPa and 550°C, respectively

Results from this series of experimental trials revealed interesting findings. For the conventional coatings, as can be seen in Figure 6.7, significant improvement of the coating structure was observed when varying the pressure from 1.0 MPa to 2.0 MPa. As will be discussed later, further optimization of other spray parameters allowed for the production of conventional coatings with very low porosity while using a nozzle inlet pressure of 2.0 MPa. For this reason, it was determined unnecessary to further increase the gas pressure (which would lead to higher helium consumption rates) and therefore an optimized nozzle inlet pressure of 2.0 MPa was selected for the conventional feedstock material. Conversely, in the case of the cryomilled feedstock material, it was not possible to achieve coatings with the required porosity level using a 2.0 MPa nozzle inlet pressure. This was attributed to the inherent increased strength of the material as a result of its nanocrystalline microstructure, thereby resulting in a higher critical velocity. As such, higher pressures were required to promote momentum transfer to these particles, and therefore the minimal nozzle inlet pressure for deposition of the cryomilled powder was determined to be 2.5 MPa.

6.2.2.3 Particle Size Distribution

The influence of the particle size distribution as a spray parameter on the resulting particle velocities and coating quality has been touched upon on various occasions throughout this report. Upon examination of Eq. 2.12 (see section 2.2.4.7), it was previously discussed that the acceleration of a particle is inversely proportional to its diameter. As such, small particles are expected to undergo greater accelerations and achieve higher velocities than larger particles. This was also evidenced throughout the preliminary trials (see section 6.1.2.1) as coatings manufactured with the as-received powder having a finer size distribution (AMDRY 9951) showed much better promise than the coatings produced with the coarser powder (AMDRY 9954). To further verify the influence of particle size distribution, experimental particle velocity measurements were taken using the Cold Spray Meter for both these powders during the preliminary trials. Results of these velocity measurements are presented in Figure 6.8. Once again, limited availability of the Cold Spray Meter only allowed for velocity measurements to be taken during these preliminary trials, and as such this tool could not be used for further spray parameter optimization.

As can be seen from this figure, the particle velocity measurement histograms for both powders overlap, which was to be expected given that their particle size distributions also overlap. Measurements reveal that particles in the finer AMDRY 9951 powder achieved higher average velocities by nearly 50 m/s when compared to the coarser AMDRY 9954 powder. Based on the results from the preliminary trials, it appears that this increase in average particle velocity makes a significant difference on coating quality as a larger fraction of particles reach the necessary velocity for deposition. Given that successful coating build-up was achieved with the AMDRY 9951 and not as much with the AMDRY 9954, these results also suggest that the critical velocity of this specific CoNiCrAlY alloy powder is likely in the range of 600 m/s.

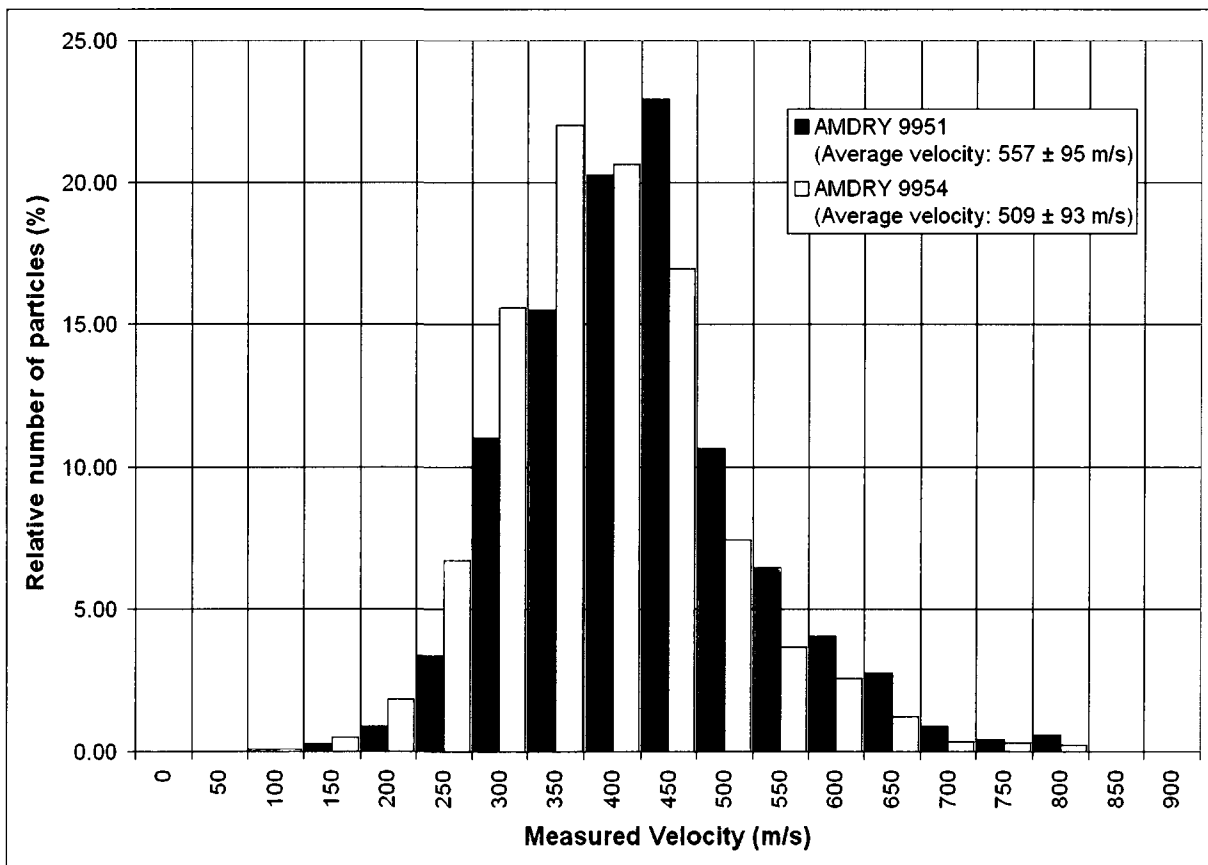


Figure 6.8: Particle velocity measurement histograms obtained during the preliminary spraying trials for the conventional as-received AMDRY 9951 and AMDRY 9954 CoNiCrAlY powders

Given that the improvement in coating quality due to finer particle sizes appeared to be significant throughout the preliminary trials, numerical modeling was also carried out to verify the extent to which particle sizes influence their predicted velocity in improved flow conditions. For these modeling trials, the optimized flow conditions for conventional particles were considered (helium, 2.0 MPa, 550°C), as determined in the previous sections. Once again, the behaviour of particles injected 20mm downstream of the throat location was considered. Particles with various diameters ranging from 5 μ m to 37 μ m were considered. Results of these modeling trials are shown in Figure 6.9. As can be seen from this figure, finer particles clearly undergo greater acceleration in the flow and achieve higher velocities when they reach the exit plane of the nozzle. Velocities above 800 m/s are expected to be achieved with particles having a diameter equal to or finer than 20 μ m. These results are therefore in accordance with the experimental findings observed during the preliminary trials.

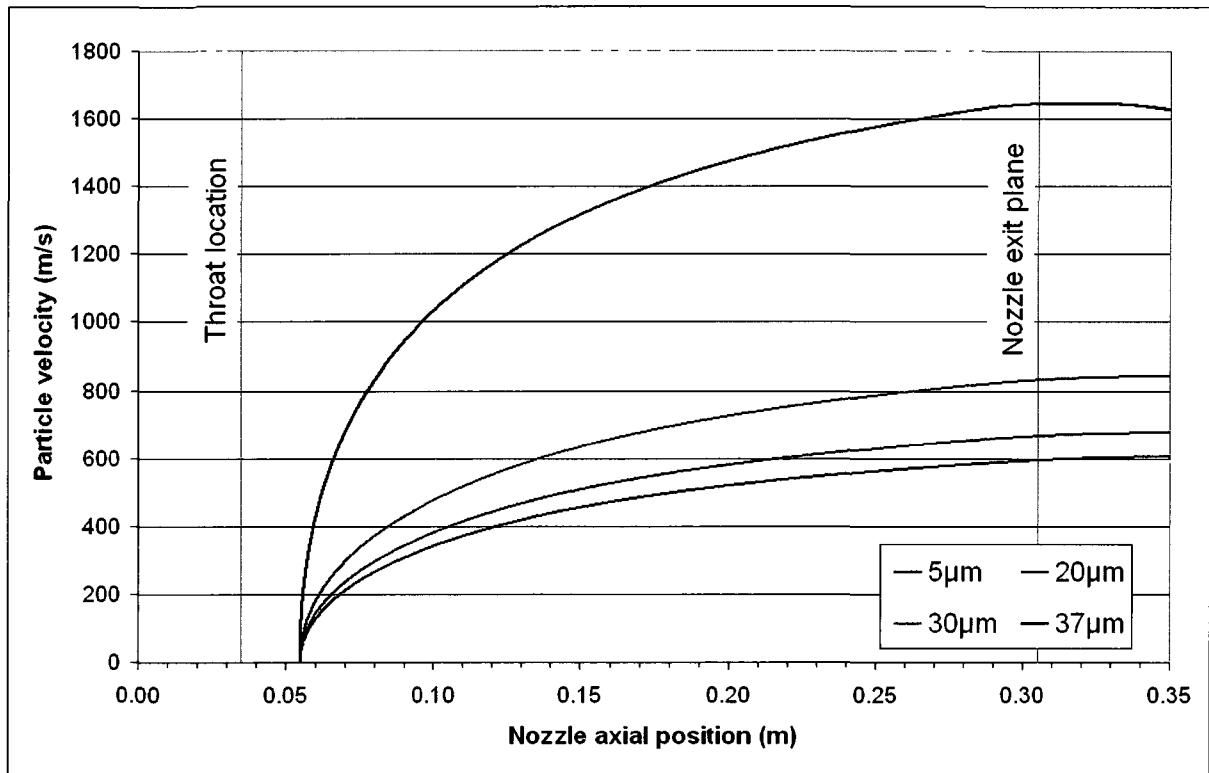


Figure 6.9: Predicted particle velocity as a function of particle diameter in a helium flow using a nozzle inlet pressure and temperature of 2.0 MPa and 550°C, respectively

Based on the findings presented in this section, it is evident that finer particles sizes are desirable for CGDS deposition. For this reason, no further trials were performed using the coarse AMDRY 9954 powder feedstock. Furthermore, it is important to recall that the AMDRY 9951 feedstock powder ranges in size from 5-37 μm . According to the previous modeling results, this means that the largest particles in this powder batch are likely to reach a nozzle exit velocity of nearly 600 m/s, which approximately corresponds to the critical velocity of this alloy as determined in the preliminary trial velocity measurements. However, it is important to note that the results offered by the model represent a best-case scenario for particle acceleration as particles are tracked along the centerline of the nozzle where the gas velocity is highest. Most typically, this is not the actual behaviour of particles in the nozzle, and therefore particle velocities in reality will be lower. Furthermore, smaller particles with higher velocities are likely to collide with the slower-moving large particles found in the feedstock, which ultimately reduces the overall average velocity of the powder batch. As such, a narrower particle size range is also desirable in order to minimize detrimental interactions between the particles. For these reasons, the AMDRY 9951 powder was sieved using a commercial Ro-Tap sieve shaker (Model RX-29) and a standard ASTM #500 sieve with nominal opening size of 25 μm (smallest available for this type of sieve shaker). The resulting sieved AMDRY 9951 powder was therefore characterized with particles ranging from 5 μm to 25 μm in size. Finally, the cryomilled powder, which was measured to have particle sizes ranging from 1 μm to 70 μm , was also sieved below 25 μm using the same technique and equipment as the AMDRY 9951 powder.

6.2.2.4 *Injection Pressure Differential*

The injection pressure differential is a spray parameter used to ensure that powder is successfully supplied along the feeding line from the powder feeder to the nozzle injection port. Generally, the injection pressure differential must be sufficiently large to overcome any friction losses in the feeding line and also to provide just enough momentum for the particles to be injected into the nozzle's main gas flow. Given the optimal nozzle inlet pressures determined previously, powder injection is to be achieved through a radial injection port. Therefore, it is also desirable to keep the injection pressure differential as low as possible in order to prevent any significant disturbance of the main flow which may occur with larger

carrier gas pressures and flow rates. Furthermore, higher injection pressures may lead to excessive radial particle velocities at the injection site. This may cause the particles to travel across the centerline axis of the nozzle and rebound along the wall surfaces, thereby limiting the desired acceleration of the particles. Optimization of the required injection pressure differential was determined experimentally by generating the main flow in the nozzle and then progressively increasing the injection pressure differential until a constant supply of powder particles were observed to exit the nozzle. Results from these experiments showed that the required injection pressure differential increased with increasing nozzle inlet pressures. This is believed to be caused by higher densities in the main flow which would imply that particles require slightly more radial velocity for successful injection. The optimized injection pressure differential values were thus determined to be 175 kPa and 225 kPa for the flows characterized with nozzle inlet pressures of 2.0 MPa and 2.5 MPa respectively.

6.2.2.5 *Nozzle Stand-Off Distance*

The influence of the nozzle stand-off distance (SOD) on the resulting coating quality was investigated indirectly by means of numerous experimental trials. For the present study, the nozzle SOD was varied from 5mm to 20mm from the surface of the substrate, which is within the range of common practice for CGDS deposition. Results of these experimental trials were mainly inconclusive and no specific SOD value was identified as being clearly advantageous. However, it was observed that most coatings manufactured with a SOD of 20mm exhibited a lower thickness and slightly larger porosity. This may be explained by the modeling results presented in Figure 6.3 which shows that even when using a nozzle inlet pressure of 2.5 MPa, shockwaves occur near the exit plane of the nozzle which then results in a significant reduction of the gas velocity. The greater SOD would thus represent a longer dwell time for the particles in the lower velocity flow, which could lead to some deceleration of the particles. Given these observations and the mainly negligible influence of the SOD within this range, a SOD of 10mm was selected as the optimal value for the purpose of this study.

6.2.2.6 *Substrate Traverse Speed*

The substrate traverse speed is one of two spray parameters that were found to have an important influence on the density of the deposited coating through means of a compaction

mechanism known as impingement. Compaction by means of impingement is a process by which previously deposited particles undergo further plastic deformation as a result of the subsequent impacting of newly deposited particles, as first proposed by Van Steenkiste et. al. [26]. As the deposition process is carried out, the cumulative plastic deformation resulting from the numerous individual particle impacts results in a refinement of the pore structure and ultimately causes densification of the coating. This naturally occurring mechanism is particularly useful when producing coatings with a powder material having a high critical velocity, as is the case in the present work. The extent of compaction by means of impingement is determined by the number of particle impacts at a given location per unit time. This can be adjusted by varying the substrate traverse speed, which effectively changes the duration for which the substrate remains under the impinging particle jet. Low traverse speeds are expected to increase the impingement effect and result in lower porosity coatings. Numerous experimental trials were conducted to verify this assumption. Results from these trials demonstrated that the substrate traverse speed had a strong influence on the resulting coating porosity. For example, Table 6.2 shows the measured coating porosity as a function of substrate traverse speed for conventional coatings manufactured with a nozzle inlet pressure and temperature of 2.0 MPa and 550°C respectively.

Table 6.2: Influence of substrate traverse speed on coating porosity for CGDS deposition using helium with 2.0 MPa and 550°C nozzle inlet conditions

Substrate Traverse Speed	Measured Coating Porosity
5.0 mm/s	$7.7 \pm 2.1 \%$
3.0 mm/s	$4.1 \pm 1.1 \%$
1.0 mm/s	$1.0 \pm 0.3 \%$

Based on these findings, a low substrate traverse speed is desirable as it produces coatings with low levels of porosity. The optimal substrate traverse speed for both the conventional and nanocrystalline coatings was therefore determined to be 1.0 mm/s.

6.2.2.7 Powder Feedrate

The second spray parameter that was observed to influence the degree of compaction by means of impingement is the powder feedrate. Intuitively, higher powder feedrates result in more particles impacting on the substrate surface per unit time, thereby increasing the extent of impingement. While more impingement could theoretically be achieved with elevated powder feedrates, it is important to recognize that certain restrictions must be considered. Unlike the substrate traverse speed, the powder feedrate also influences the behaviour of the particles in the flow. Firstly, as was observed during the preliminary trials (see section 6.1.2), excessive powder feedrates can result in nozzle clogging and must therefore be avoided. Secondly, as discussed in section 2.2.6, elevated feedrates may also saturate the flow and result in particle loading effects, thereby preventing adequate acceleration of each particle. For these reasons, a relatively large powder feedrate is desirable (greater compaction by impingement and higher coating build-up thickness), however it must also be kept sufficiently low to prevent any undesirable influence on the flow behaviour. Investigation of the influence of this spray parameter was performed experimentally by adjusting the powder feeder wheel rotation speed (measured in RPM), which acts as a reference for the relative amount of particles injected in the flow per unit time. During the optimization trials conducted with the radial injection configuration, the RPM value was varied within the range of 0.5 to 1.5. As a first observation, it was noticed that when using the radial injection configuration, the flow was more susceptible to particle loading effects than previously determined with the axial injection configuration. For example, a series of experimental trials revealed that reducing the powder feedrate from 1.5 to 1.0 RPM resulted also in decreases in porosity from $7.1 \pm 1.7\%$ to $4.3 \pm 0.8\%$, respectively (these specific tests were done using helium with a nozzle inlet pressure and temperature of 1.5 MPa and 550°C for the deposition of AMDRY 9951 particles). Further reduction of the powder feedrate (below 1.0 RPM) resulted in coatings with insufficient build-up thickness for the desired application and was thus determined unsatisfactory. Based on these results, it was determined that a powder feedrate corresponding to a powder feeder wheel rotation speed of 1.0 RPM was optimal for this study.

6.2.3 Optimized Spray Parameters Summary

The influence of various spray parameters on particle velocity and resulting CGDS coating quality were investigated by means of numerical modeling trials and systematic experimental testing, as detailed in section 6.2.2. From this investigation, optimized spraying parameters were identified for the deposition of both conventional and nanocrystalline CoNiCrAlY CGDS coatings. The optimized spraying parameters, as considered in this research work and within restrictions imposed by physical limitations, are summarized in the following table. A detailed analysis of the morphology and microstructure of the CGDS coatings manufactured from these optimal spraying conditions will be presented in Chapter 7.

Table 6.3: Optimal spraying parameters for conventional and nanocrystalline CoNiCrAlY CGDS coatings

Spray Parameter	Conventional Coatings	Nanocrystalline Coatings
Feedstock Powder	AMDRY 9951, sieved <25 μ m	As-cryomilled powder, sieved <25 μ m
Substrate	Aluminum T-6061 alloy	Aluminum T-6061 alloy
Driving Gas Type	Helium	Helium
Nozzle Inlet Pressure	2.0 MPa	2.5 MPa
Nozzle Inlet Temperature	550°C	550°C
Carrier Gas Type	Helium	Helium
Injection Pressure Differential	175 kPa	225 kPa
Powder Injection Configuration	2.5mm dia. radial injection port, 20mm downstream of nozzle throat location	2.5mm dia. radial injection port, 20mm downstream of nozzle throat location
Nozzle Stand-Off Distance	10 mm	10 mm
Substrate Traverse Speed	1 mm/s	1 mm/s
Powder Feeder Wheel Rotation Speed (Powder Feedrate)	1.0 RPM	1.0 RPM

Chapter 7 - Characterization of As-Sprayed CoNiCrAlY Coatings Manufactured by Various Deposition Techniques

Having successfully characterized the feedstock materials microstructures in Chapter 5 and determined their optimal CGDS spraying parameters in Chapter 6, it is now fitting to investigate and characterize the morphology (coating structure, presence of defects and oxide content) and microstructure (phase composition and grain structure) of the as-sprayed CoNiCrAlY coatings manufactured with the optimized spraying conditions. Evaluation of the coating morphology was carried out to assess the general quality of the as-sprayed CGDS coatings (both conventional and nanocrystalline) as well as the thermal sprayed coatings (APS and HVOF) for comparison purposes. In depth analysis of the conventional and nanocrystalline CGDS coating microstructures was also performed in order to compare their microstructures to those of the original feedstock particles and determine whether any changes have occurred during the deposition process. Firstly, this investigation is intended to either confirm or refute the claims that CGDS has the ability to preserve a material's microstructure throughout the deposition process as a result of the relatively low processing temperature [7, 15, 53]. Secondly, microstructural changes such as grain growth and oxide inclusions in thermal spray bond coats have been shown to be detrimental to their oxidation behaviour. Part of the incentive to manufacture bond coats using the CGDS deposition technique is because it is expected to offer better control of the material's microstructure during the spraying process by reducing microstructural changes. It is therefore important to assess whether any microstructural changes occur during the CGDS deposition process, and if so, identify the changes in order to later determine their influence on the coating oxidation behaviour.

7.1 Conventional CoNiCrAlY Coatings

The present portion of the report will provide an analysis of the as-sprayed coatings manufactured from the conventional CoNiCrAlY feedstock powder using various deposition techniques. The coating characteristics such as morphology and microstructure are presented.

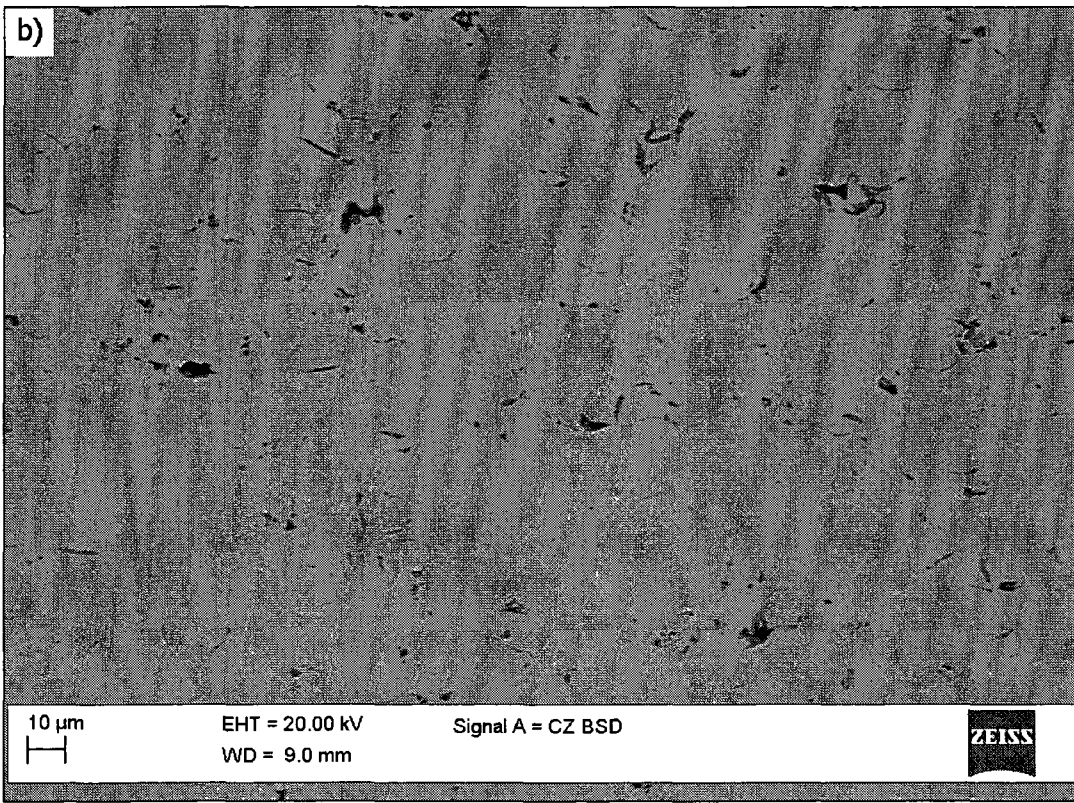
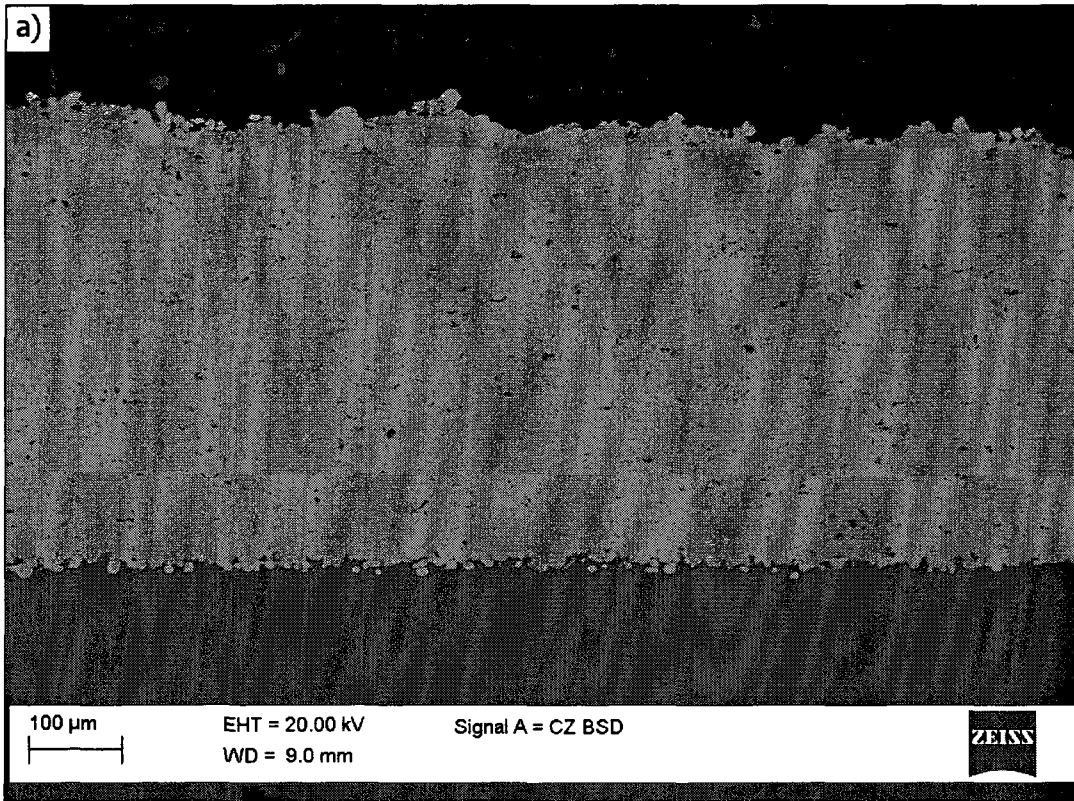
7.1.1 Conventional CGDS Coatings

This section of the thesis will investigate the as-sprayed CGDS coatings manufactured from the conventional feedstock powder sieved below 25 μ m using the optimized spraying parameters.

7.1.1.1 *As-Sprayed Coating Morphology*

The cross-section structure and morphology of the as-sprayed conventional CGDS coating manufactured using optimized spraying conditions can be seen in Figure 7.1. As can be seen from this figure, the coating exhibits limited porosity and no visible defects such as interlamellar cracks. Porosity measurements for this coating resulted in an average porosity of $1.0 \pm 0.3\%$, which is well within the acceptable limits and objectives outlined in this work. The pores found within the CGDS coatings are typically small in size with an average equivalent diameter of 1.5 μ m. This level and type of porosity may be attributed to insufficient localized plastic deformation of impinging particles upon impact, thus resulting in the formation of small voids between two adjacent particles. Conversely, the limited porosity, large coating build-up thickness achieved in a single spray pass and absence of cracks within the coating structure demonstrate that most impinging particles have sufficient kinetic energy to achieve adequate plastic deformation. EDS analysis revealed that the as-sprayed CGDS coating had an oxide content of 0.10 ± 0.05 (wt. %). When compared to the oxide content of the original feedstock powder, which was measured to be 0.03 ± 0.03 (wt. %), it can be concluded that the CGDS deposition process has caused very little oxidation of the sprayed material. This was expected given that CGDS uses inert gases and low process temperatures, thereby reducing the rate and likelihood of oxidation during deposition.

Observation of the cross-section images in Figure 7.1c also reveals that the typical γ/β two-phase microstructure that was originally present in the conventional feedstock powder (see Figure 5.2) has not been retained during CGDS deposition. This is evidenced by the apparent absence of the β -phase precipitates in the coating cross-section which suggests that microstructural changes have occurred during the deposition process. To further verify this, a thorough investigation of the as-sprayed conventional CGDS coating microstructure is now presented.



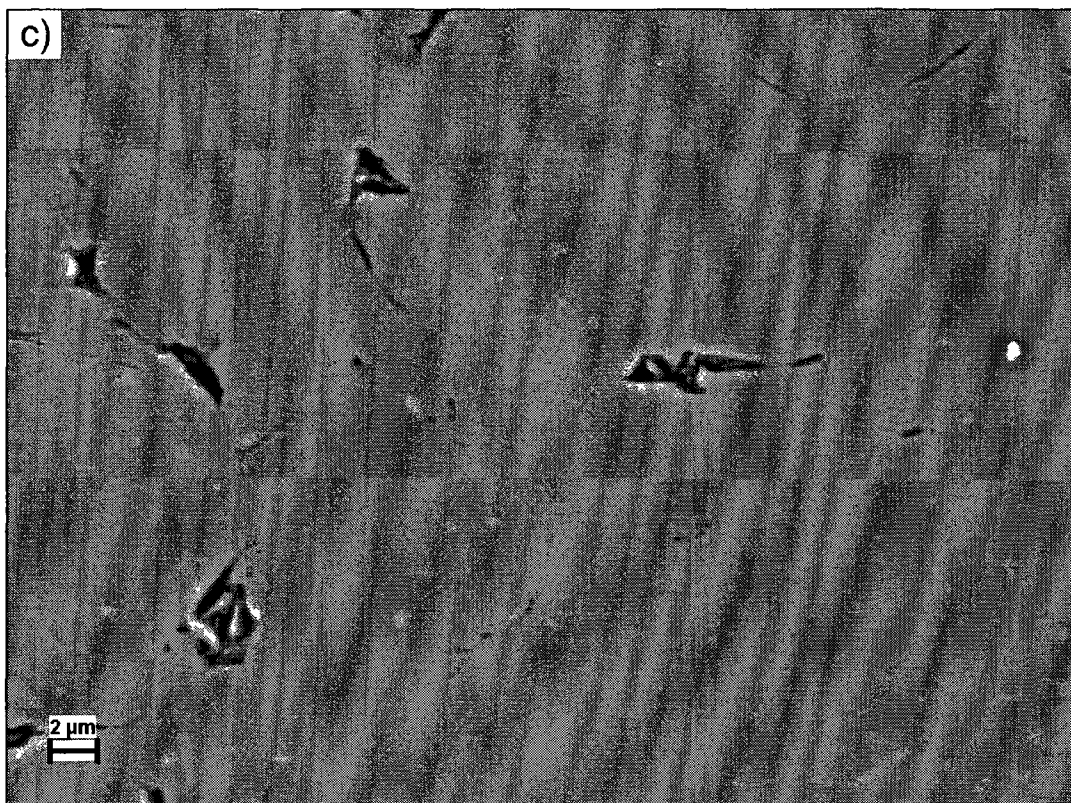


Figure 7.1: Backscattered SEM images at (a) 100x, (b) 400x and (c) 2500X magnifications showing the cross-section of the as-sprayed conventional CGDS coating manufactured using optimal spraying conditions

7.1.1.2 As-Sprayed Coating Microstructure

The microstructure of the conventional CoNiCrAlY coatings was characterized by the same approach as the one used for the original feedstock powders. XRD and TEM analyses were performed on the coatings to investigate their phase content and grain structure. Figure 7.2 shows the XRD scan of a conventional CoNiCrAlY coating as well as that of the original as-received powder. When comparing these two XRD spectra, significant differences can be observed. The first important observation is that peak broadening has occurred for the γ -phase peaks which could be attributed to grain refinement and/or induced micro-stresses caused by the deposition process. A second observation is that the peaks associated to the β -phase are no longer distinguishable. This might once again be the result of grain refinement of this phase, which would cause peak broadening as well as reduced diffraction intensity, thereby making β -phase peaks difficult to identify. However, given the very fine grain size of the β -phase precipitates in the original feedstock powder and the apparent complete absence of β

peaks in the resulting CGDS coating, this explanation does not seem likely. Rather, it is believed that the β -phase may have dissolved into the γ -matrix in a process similar to what had been previously observed in the as-cryomilled powder. The differences between the two XRD spectra demonstrate that the CGDS deposition process has indeed altered the bond coat material microstructure. It is also interesting to note that there are no visible peaks attributed to oxides having formed during the CGDS deposition process, thereby suggesting a low concentration of oxides in the as-sprayed coating. This observation agrees with the low oxide content previously reported for this coating.

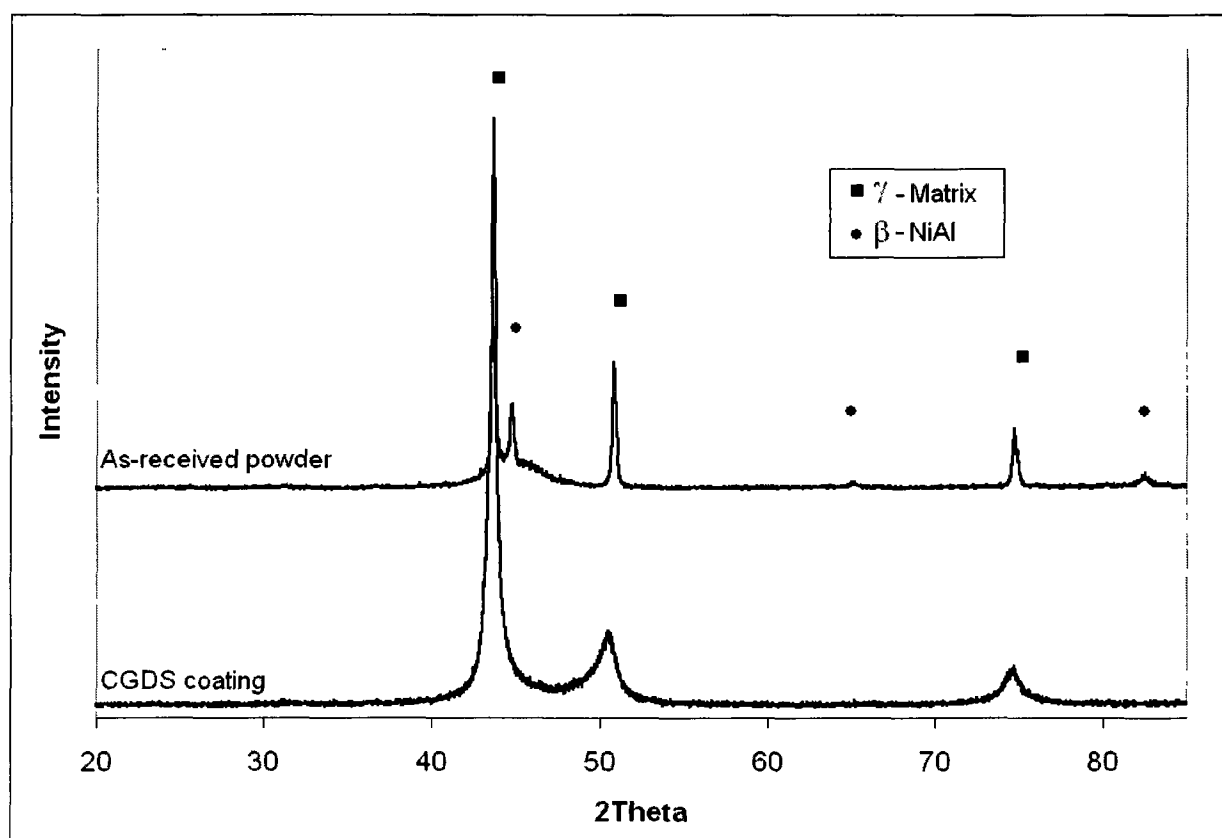


Figure 7.2: XRD spectra of as-sprayed CoNiCrAlY CGDS conventional coating and original as-received feedstock powder

TEM analysis of the conventional CGDS coating was carried out in order to better assess its microstructure and gain a clearer understanding of its behaviour upon deposition. Figure 7.3a shows the SAED pattern of the conventional CoNiCrAlY coating. This diffraction pattern is considerably different to that of the original feedstock powder (see Figure 5.4) as it clearly reveals multiple diffractions rings associated to the γ -phase Co-Ni-Cr solid solution. The

presence of these diffraction rings as opposed to diffraction spots (as were observed in the as-received powder diffraction pattern) demonstrates that the grains in the γ -matrix have undergone considerable refinement. Smaller ring fragments can also be observed (although they are faint) and are attributed to diffractions of β -phase precipitates. These β -phase diffractions are much weaker than those obtained for the as-received powder, thus suggesting a lower β -phase content in the coating when compared to the original powder. These results are in accordance with the XRD analysis, further confirming that grain refinement of the γ -phase and some level of dissolution of the β -phase has occurred during the CGDS deposition process. Figure 7.3 also shows bright field and dark field TEM images of the CGDS coating. These images confirm that in this area of the coating, the microstructure is composed of fine γ -phase grains of approximately 20-30nm in diameter. Interestingly, further inspection of the sample revealed the presence of larger γ -phase grains with equivalent diameters of approximately 100-200 nm in other regions of the coating, as shown in the TEM images from Figure 7.4. The SAED pattern obtained in this region of the coating shows the presence of strong diffraction spots (as opposed to rings), thereby also suggesting the presence of larger sized grains. Further analysis of the CGDS coating sample confirmed the existence of a bimodal grain size distribution for the γ -matrix, thus revealing that refinement of the γ -matrix grains is not uniform throughout the coating.

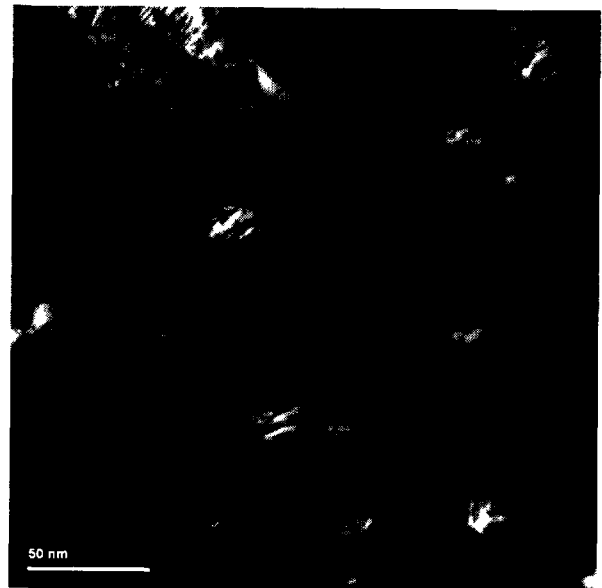
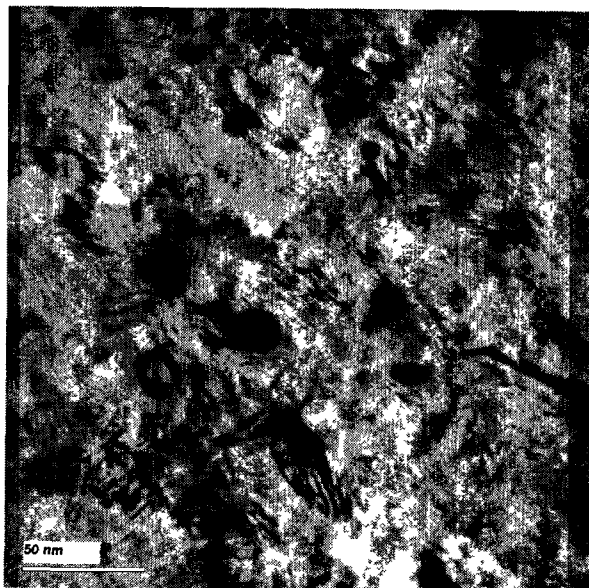
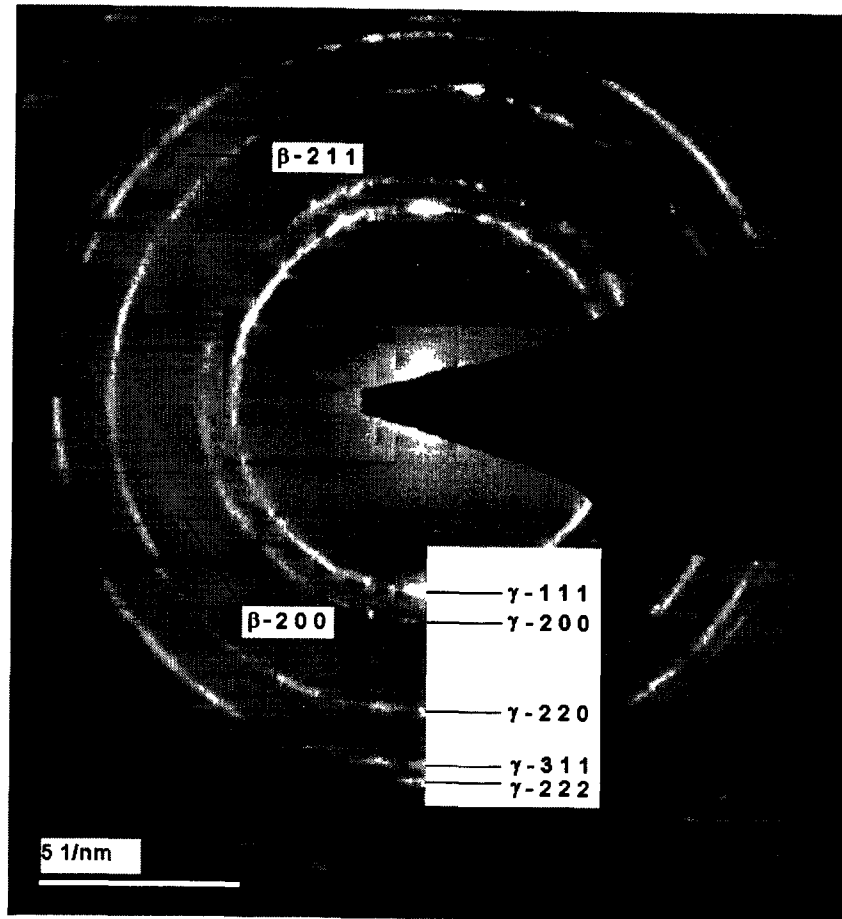


Figure 7.3: TEM images showing (top) the SAED pattern of the conventional as-sprayed CGDS coating as well as the corresponding BF (bottom left) and DF (bottom right) images depicting the fine grain structure in some regions of the coating

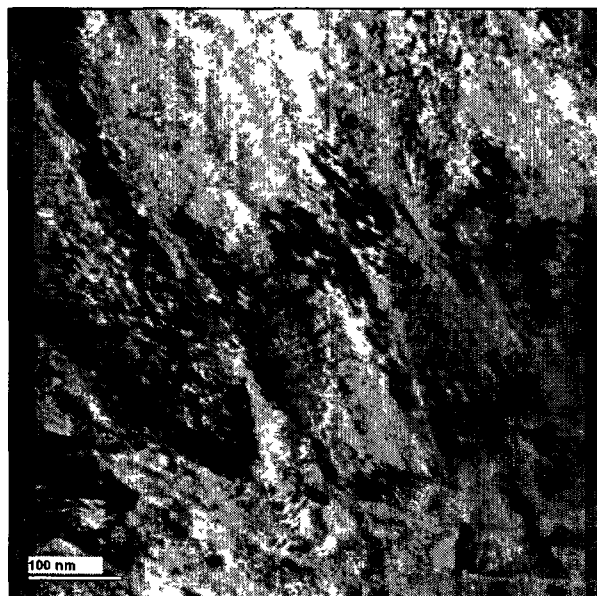
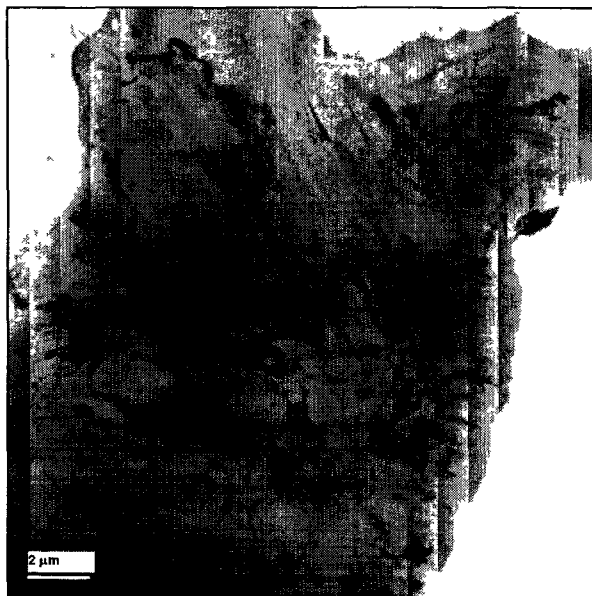
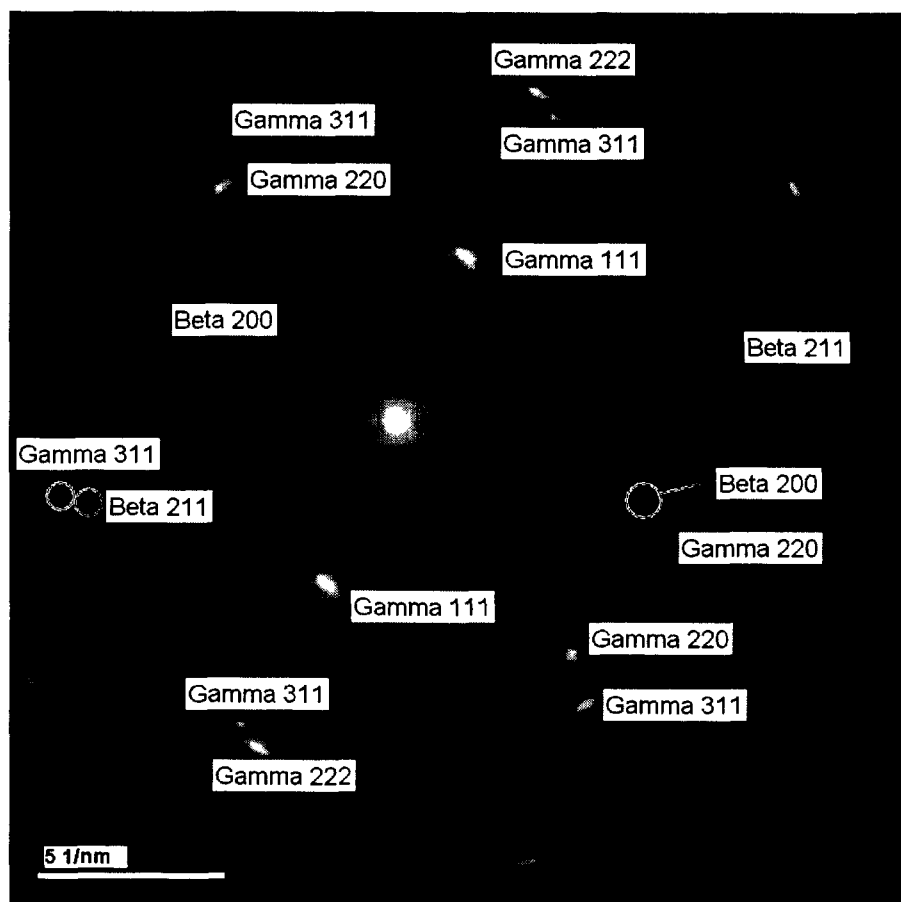


Figure 7.4: SAED pattern (top) and BF TEM images at various magnifications (bottom) showing the presence of a coarser grain structure in other regions of the conventional CGDS coating

γ - Phase Grain Refinement Process

The XRD and TEM analysis performed on the conventional powder and resulting CGDS coating revealed that the γ -matrix underwent grain refinement during the CGDS deposition process. Given the absence of significant heating of the particles in CGDS as well as the use of inert gases in the process, it is expected that changes in the microstructure be solely caused by the intense plastic deformation of the sprayed material upon deposition. Grain refinement resulting from severe plastic deformation is a well known phenomenon that has been studied and applied extensively [107, 108]. In fact, the process of subjecting materials to severe plastic deformation has been shown to be one of many effective methods for producing nanocrystalline materials [89, 100, 109]. Processes such as high-pressure torsion and equal-channel angular pressing have been used for the production of bulk nanocrystalline solids [109], whereas mechanical milling and alloying has been used for the synthesis of nanocrystalline particles [89, 101]. In mechanical milling, the plastic deformation of the milled material occurs as particles are crushed by the larger fast-moving grinding media particles. The nature of plastic deformation in mechanical milling is thus attributed to the impact of the powder particles with the higher momentum grinding media, and therefore it can be envisioned that it is not extensively different to the plastic deformation mechanism of powder particles impacting on a substrate during the CGDS deposition process.

To further verify this, the microstructures of the conventional CGDS coating and the as-cryomilled CoNiCrAlY powder are now compared. Figure 7.5 presents the XRD spectra of the as-cryomilled powder as well as the conventional CGDS coating and illustrates how they both have a similar microstructure. When compared to the spectrum of the original feedstock powder, both these spectra show the occurrence of peak broadening of the γ -matrix, as well as the attenuation/disappearance of the peaks associated to the β -phase. Discrepancy with respect to spectrum intensity between the two scans is attributed to the different physical condition of the samples (powder form and solid form for the as-cryomilled powder and CGDS coating sample respectively). These findings seem to demonstrate that the impact of powder particles on the substrate during the CGDS process is similar to plastic deformation in a material caused by mechanical milling, thus leading to similar microstructural evolutions in

the material. It is therefore hypothesized that the concepts and mechanisms of grain refinement and phase transformations/dissolution observed in a material subjected to mechanical milling (severe plastic deformation) can thus be extended to explain the behaviour of a material deposited by CGDS.

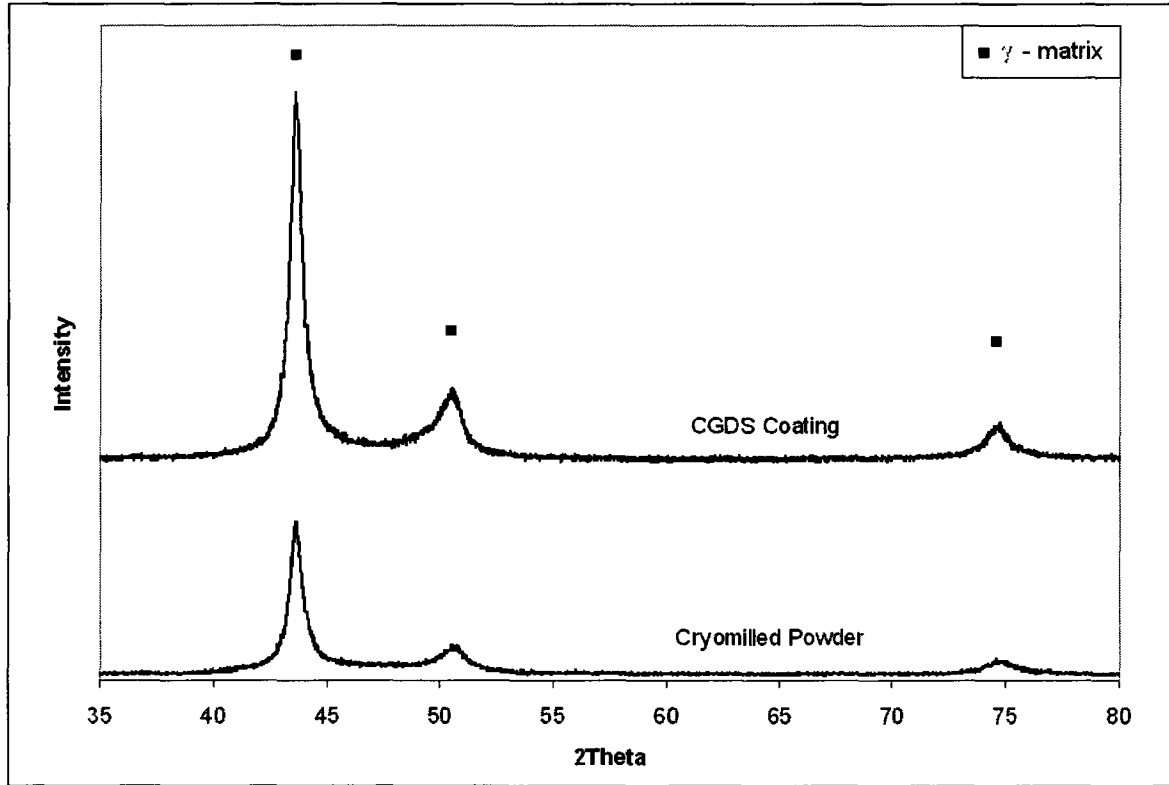


Figure 7.5: XRD spectra of the conventional CoNiCrAlY CGDS coating and the as-cryomilled feedstock powder

As discussed in a previous section of this report, grain refinement and the mechanism of formation of nanostructures in mechanical milling initiates from the formation of shear bands resulting from the high deformation rates encountered in mechanical milling [101]. These shear bands have a high dislocation density, and with continued milling time, the increasing dislocation density leads to higher atomic level strains. When a given dislocation density is reached in the highly strained region, the crystal breaks down into smaller subgrains separated by low-angle grain-boundaries, resulting in a decrease of the lattice strain. As milling continues and the material undergoes further plastic deformation, shear bands form in areas that were previously unstrained. As this process is carried on, grain sizes steadily decrease and the shear bands coalesce. The low-angle grain boundaries are replaced by higher angle

grain boundaries, thus implying grain rotation. The result is the formation of dislocation-free nanocrystalline grains with random orientations. It is believed that this grain refinement mechanism can also be used to explain the reduction of the γ -phase grain sizes in the CoNiCrAlY material during the CGDS deposition process. In CGDS, shear bands are formed at the particle/substrate and particle/particle interfaces [22, 23] as a result of the high deformation rates encountered upon impact, thus allowing the grain refinement mechanism to be initiated. The impingement from the subsequent impacting particles provides additional plastic deformation of the sprayed material, therefore introducing additional shear bands and dislocations and assisting the grain refinement process. Since the evolution of plastic deformation in CGDS coatings is restricted to the short exposure time of the coating under the impinging jet of particles, it is expected that grain refinement in the CGDS coating material would be less extensive than in a mechanically milled material. Mechanical milling is typically carried out for numerous hours, which ensures that the material has been uniformly plastically deformed and that grain refinement has been achieved equally throughout the material. This is not the case for CGDS coatings: different extents of plastic deformation are undergone by the impacting particles due to the varying particle impact velocities (and consequently impact force) from one particle to the next. Additionally, different degrees of plastic deformation within various regions of a single particle exist due to the formation of shear bands upon impact. These varying levels of plastic deformation in the deposited material explain the reason for the existence of a bimodal γ -phase grain size distribution in the CGDS coating. It is believed that the particles that achieve a greater impact velocity will undergo a more important reduction in grain size. Also, the regions of the particles having undergone the most plastic deformation upon deposition (shear bands at the impacting surfaces) will likely experience more significant grain refinement, as suggested in Figure 7.3 by the existence of 20-30nm γ -phase grains. Conversely, central regions of larger particles with lower impact velocities are expected to encounter less plastic deformation and will experience little or no grain refinement, as observed in Figure 7.4 by the presence of larger 100-200nm grains. It is also interesting to note that Figure 7.4 shows the presence of grains separated by low-angle grain boundaries, thus suggesting that the grain refinement process has been initiated but the level of plastic deformation in this area of the coating is insufficient to cause further refinement or grain rotation. Conversely, Figure 7.3 shows fine grains with

high-angle grain boundaries, which suggests that this area of the coating has been subjected to enough plastic deformation to cause substantial grain refinement and grain rotation. As such, areas in the coating subjected to less plastic deformation will exhibit limited grain refinement, resulting in coarser grains with low-angle grain boundaries, whereas areas subjected to more plastic deformation will exhibit increased grain refinement, leading to fine grains with high-angle grain boundaries. It was not possible to verify specifically which areas of the coating had undergone more grain refinement based on the TEM analysis performed in the present study. However, the level of grain refinement is believed to be directly linked to the extent of plastic deformation as discussed previously.

β - Phase Dissolution Process

The XRD and TEM investigations of the as-received powder and resulting conventional CGDS coating also revealed transformations of the β -phase. Results suggest that the fine β -phase precipitates in the sprayed material undergo a dissolution process into the γ -matrix during CGDS deposition. Once again, it is believed that this type of microstructural evolution is the result of intense plastic deformation encountered by the sprayed material throughout the CGDS process. Phase transformations and dissolution resulting from severe plastic deformation have been observed elsewhere [108, 110], and the occurrence of deformation driven dissolution of the β -phase during the CGDS process would explain the results observed in this study. Dissolution of the intermetallic β -phase in the CoNiCrAlY alloy due to severe plastic deformation is believed to be attributed to instabilities in the crystal lattice because of its high strain levels and energy state. Similarly to the grain refinement mechanism, the severe plastic deformation of the sprayed particles leads to high dislocation densities in the material, resulting in high average strains at the atomic level. This increased energy state within the material can compromise the stability of the crystal lattice. Upon increased energy and strain levels, it becomes energetically favourable for the crystal structure to change in order to better accommodate the energy and strain levels. As discussed previously, this may be done by breaking down larger grains into finer subgrains, which eventually results in grain refinement. However, if the grains are already very fine (as is the case for the β -phase precipitates in this study), the process of grain refinement reaches a limit and is no longer

favourable. Rather, the increased density of line and point defects in the material as a result of severe plastic deformation extends the solubility of Al in the γ -matrix, thereby prompting changes in the Al-rich β -phase crystal lattice structure itself and leading to its dissolution. Figure 7.6 shows the lattice stability as a function of the average valence electrons per atom (Z) for two common crystal structures (adapted from [111]). The β -phase was shown to be composed of NiAl which has an average number of valence electrons per atom of $Z = 6.5$. According to Figure 7.6, this intermetallic naturally forms as a bcc crystal lattice at equilibrium since this is the crystal structure that has the lowest energy state for the given average number of valence electrons per atom. Conversely, the γ -phase was shown to consist of a Co-Ni-Cr solid solution with an fcc lattice structure for which the average number of valence electrons per atom is $Z = 8.25$. According to Figure 7.6, this phase would likely form as an fcc crystal lattice at equilibrium. These observations are in accordance with the findings and results presented in this work. Figure 7.6 also shows that the bcc NiAl β -phase observed in the CoNiCrAlY material is less stable than its fcc γ -matrix Co-Ni-Cr solid solution counterpart. It can be observed that an energy increase equal to Δ_1 (~ 7.1 kJ/mol) in the β -phase bcc lattice would be sufficient to favour a crystal lattice transformation from bcc to fcc. Alternatively, an energy increase equal to Δ_2 (~ 21.4 kJ/mol) in the γ -phase fcc lattice would be required to favour the transformation of the fcc crystal structure to bcc. The high velocity impact of the sprayed particles results in a large energy increase in the deposited material, which is seemingly sufficient to cause dissolution of the bcc β -phase into the fcc matrix, but not sufficient to cause transformation of the fcc matrix into a bcc lattice structure. This is attributed to the fact that the large γ -matrix grains absorb a significant amount of energy during the plastic deformation and grain refinement processes, whereas the initially fine β -precipitates cannot undergo the same extent of deformation or refinement. It is therefore apparent that the initial fine grain structure of the β -precipitates as well as their relative lattice instability when compared to the fcc γ -matrix are two factors that tend to favour the deformation-driven dissolution process.

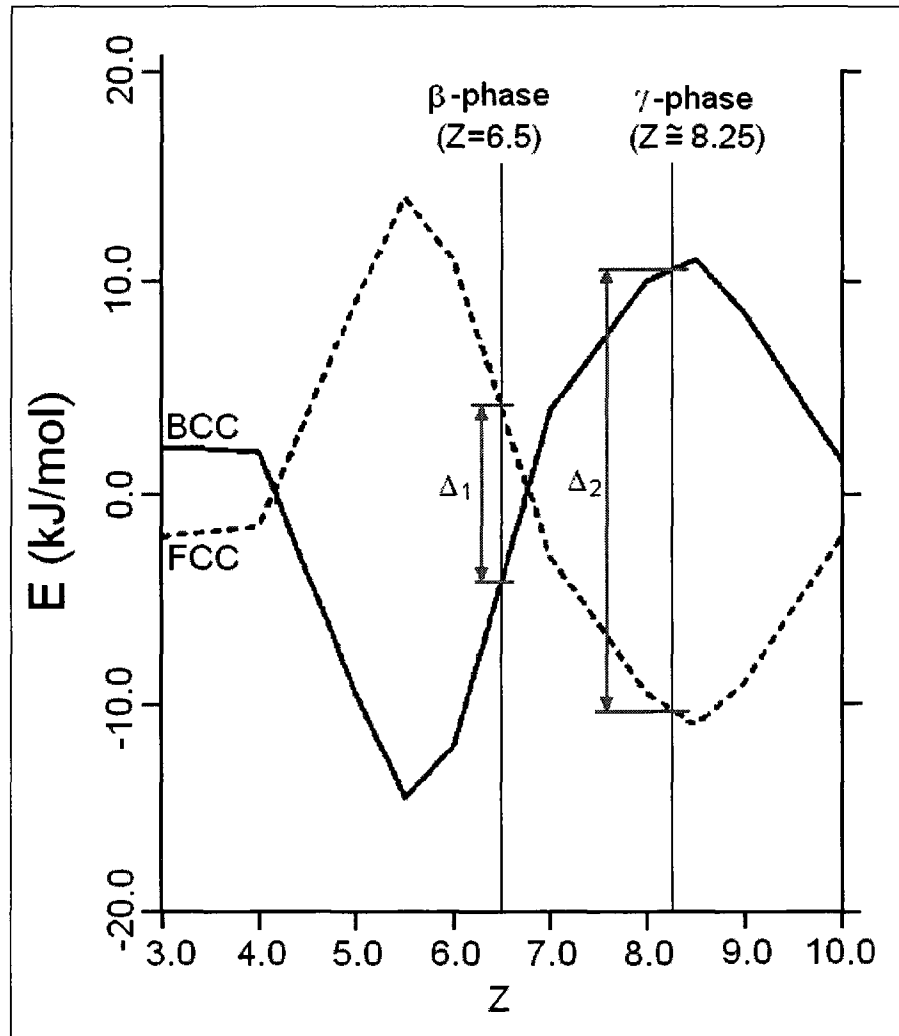


Figure 7.6: Lattice stability as a function of the average number of valence electrons per atom (Z) for two types of crystal structure: BCC (solid curve) and FCC (dashed curve).
(Adapted from [111])

7.1.2 Conventional APS Coatings

The following section will investigate the general features of the as-deposited APS coatings manufactured from the conventional AMDRY 9954 feedstock powder. Characteristics of these coatings such as morphology and microstructure are presented. It should be noted that due to limited resources and microscope availability, no TEM characterization of these thermal spray coatings was performed.

The cross-section structure and morphology of the as-sprayed conventional APS coating can be seen in Figure 7.7.

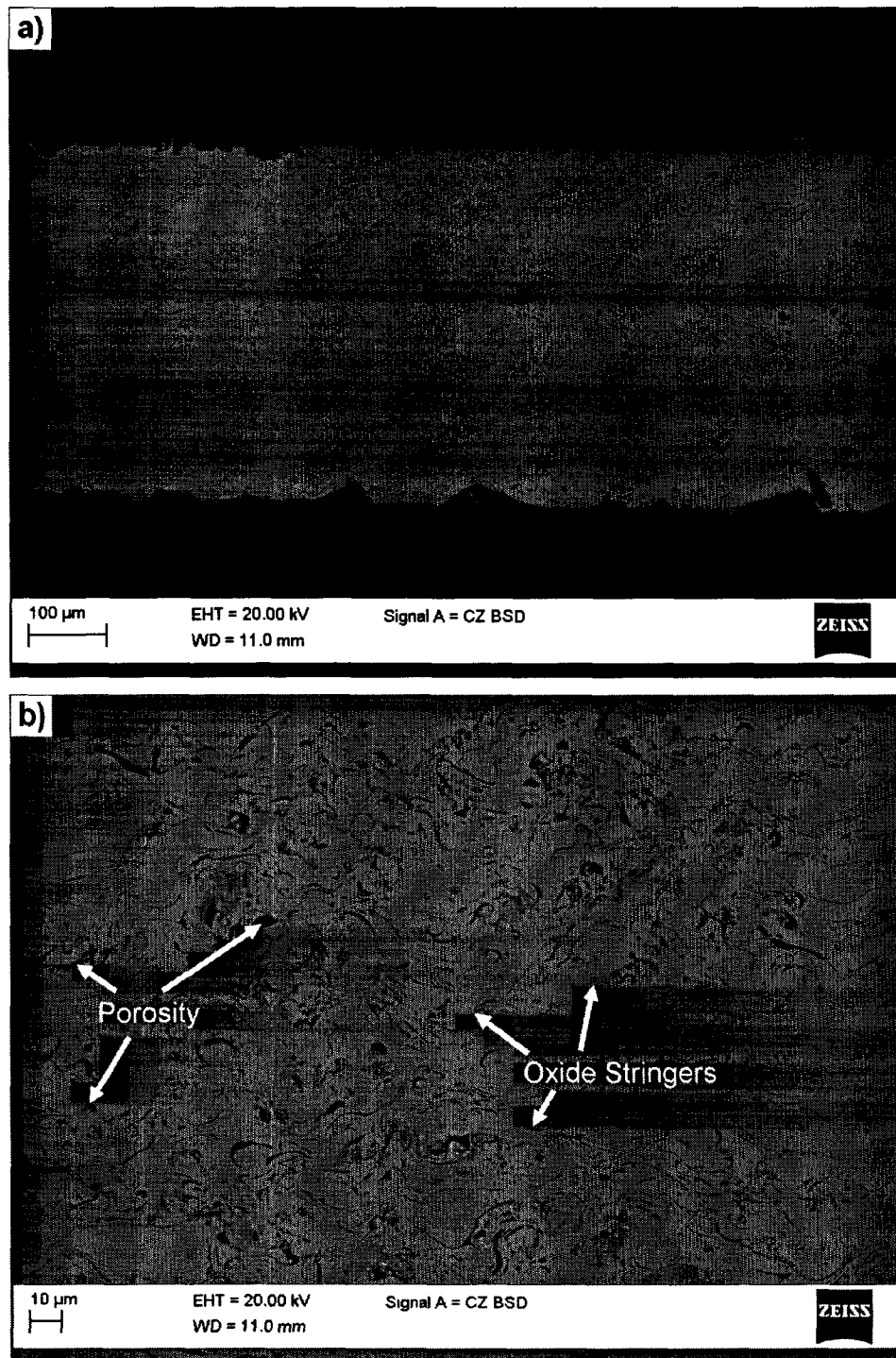


Figure 7.7: Backscattered SEM images at (a) 100x and (b) 400x magnifications showing the cross-section of the as-sprayed conventional APS coating

As can be seen from these images, the coatings deposited by APS exhibit a large amount of visible defects such as porosity and inter-splat cracks. The average porosity of these coatings was measured to be $5.3 \pm 0.5\%$, which is substantially larger than that of the CGDS coatings. One of the main causes of increased porosity and visible defects in APS coatings is related to the rapid solidification of the molten droplets as they splatter onto the substrate to form the coating. This solidification process causes shrinkage and contraction of the deposited particles which can result in the formation of elongated cracks between each splat. Such inter-splat cracks are easily seen within the coating cross-sections in Figure 7.7. Also, it is possible that some of the sprayed particles may not have undergone complete melting during the deposition process. Given the relatively low particle impact velocity in APS, the deposition of unmelted particles results in insufficient particle deformation and causes an increase in porosity. Evidence of such defects caused by insufficient deformation is also visible in the APS coating cross-section in the form of equiaxed pores. These two types of porosity are typically not encountered as frequently in the HVOF and CGDS techniques given the lower process temperatures causing limited to no melting of the particles and thus resulting in minimal shrinkage upon cooling. Furthermore, the inherent high particle impact velocities in HVOF and CGDS promote compaction of the particles thus typically resulting in high-density coatings. Numerous oxide stringers (identified in Figure 7.7b as dark grey streaks) are also visible within the APS coating microstructure, suggesting that significant particle oxidation occurred throughout the deposition process. The average oxide content for the APS coatings was evaluated at 3.82 ± 0.70 (wt. %), which is a significant increase in comparison to both the original feedstock powder and the CGDS coatings.

Closer inspection of the cross-section images in Figure 7.7 also shows the absence of visible β -phase precipitates, thereby suggesting that microstructural transformations have taken place throughout the APS deposition processes. Shibata *et al.* [75] also observed the absence of β -precipitates in their APS coatings and suggested that in-spray oxidation of the sprayed particles had been significant enough to cause depletion of aluminum within the coating to the extent where the β -phase precipitates could no-longer form. The high oxide content observed in the APS coatings in the present work would support this theory.

An XRD analysis was also carried out in order to further investigate the APS coating microstructure, as shown in Figure 7.8. The spectrum for the APS coating in the as-sprayed condition shows evidence of a single-phase microstructure composed of only the γ -matrix without the presence of β -phase precipitates. A significant difference with the CGDS deposition technique is that peaks associated to undesirable spinel-type oxides are visible in the as-sprayed condition, prior to any oxidation testing. As suggested by Tang et al. [92], peaks indicated as “spinel” represent either a mixture of some/all of other spinel mixed oxides such as NiCr_2O_4 , NiAl_2O_4 , CoAl_2O_4 , CoCr_2O_4 and NiCo_2O_4 , or a substitutional solid solution of $(\text{Ni,Co})(\text{Al,Cr})_2\text{O}_4$. Weak peaks of $\alpha\text{-Al}_2\text{O}_3$ can also be identified in the as-sprayed condition. The formation of mixed spinel-type oxides and alumina in the as-sprayed condition demonstrates the severity of the oxidation of the particles throughout the APS deposition process and further justifies the elevated oxide content and absence of β -precipitates in the as-sprayed coatings. In addition, there is no evidence of peak broadening, as was observed for the CGDS coating, thus suggesting a coarse grain structure which is typical of APS coatings.

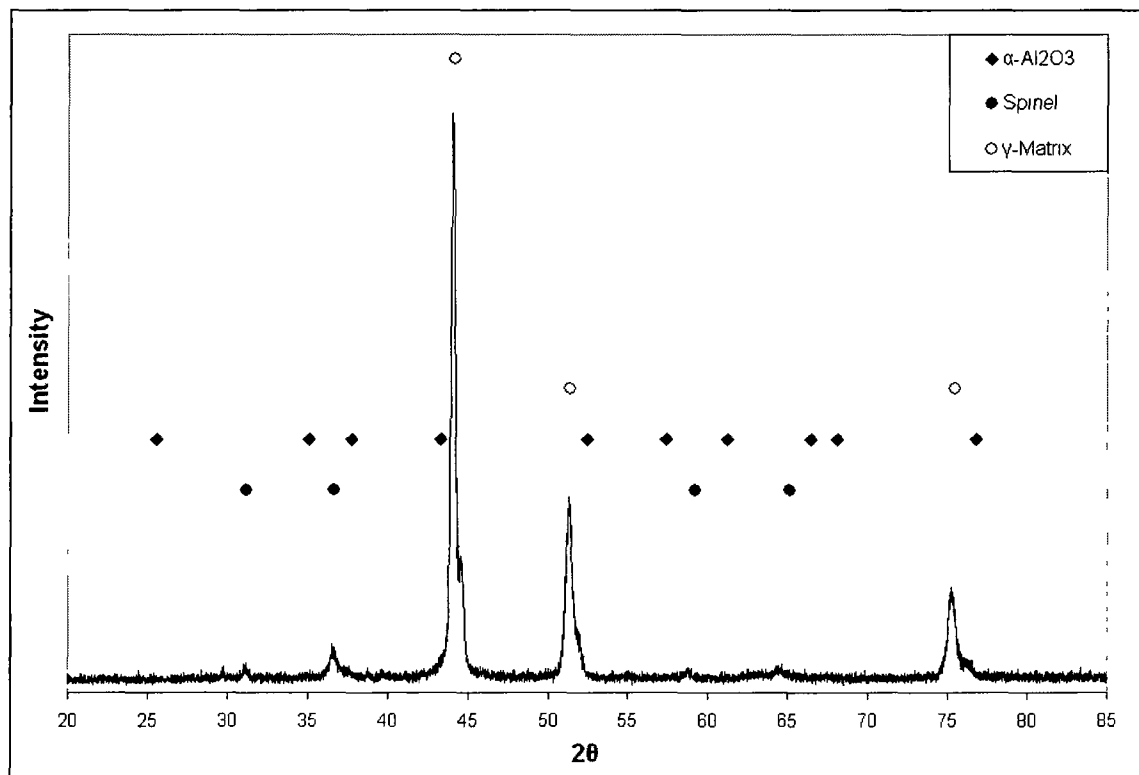
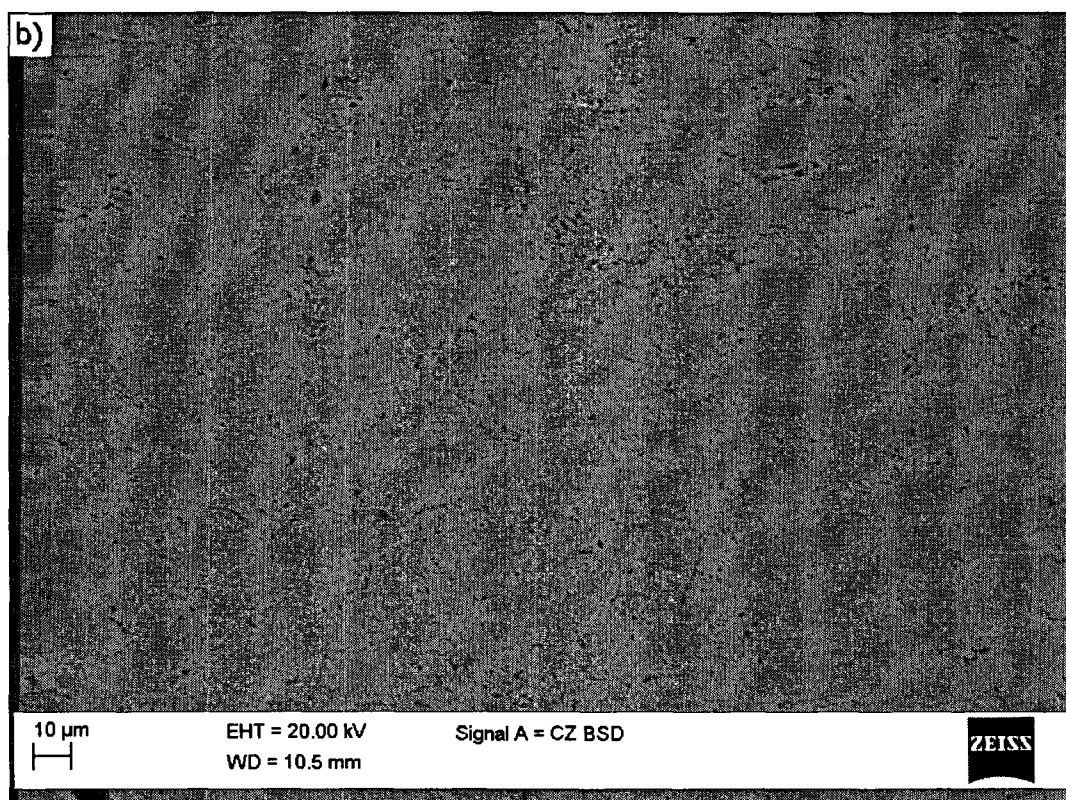
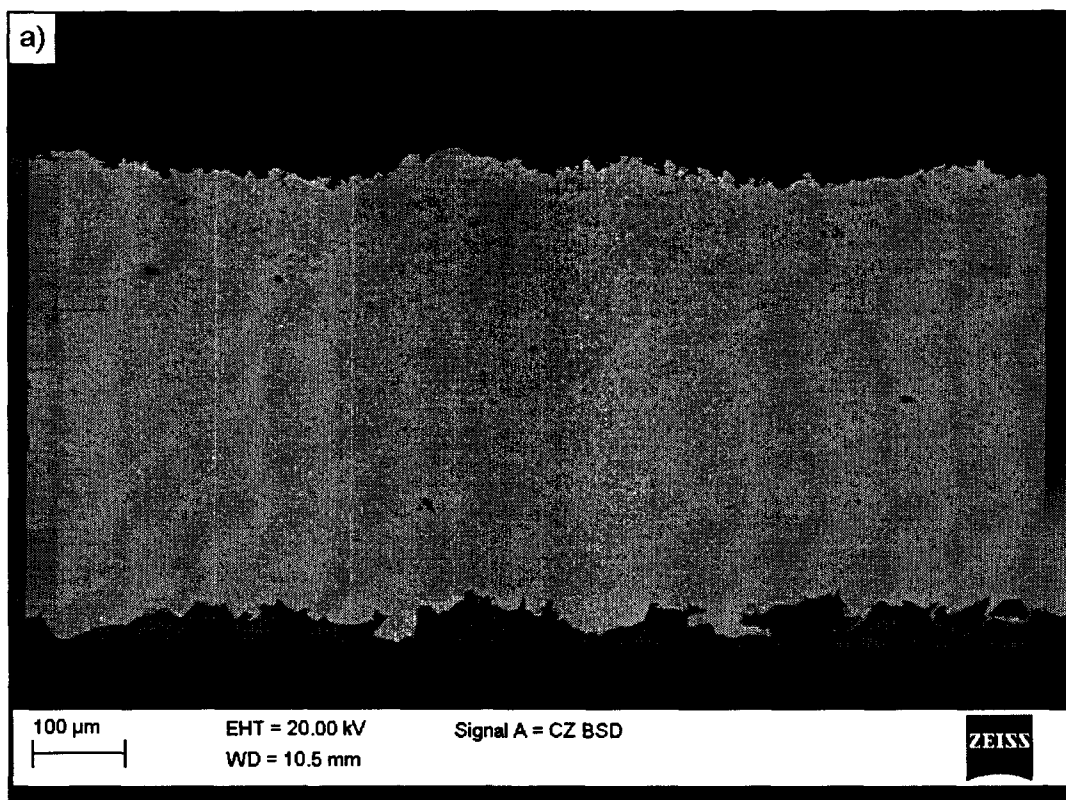


Figure 7.8: XRD spectrum of the as-sprayed APS CoNiCrAlY coating

7.1.3 Conventional HVOF Coatings

This section of the report will investigate the characteristics of the as-sprayed HVOF coatings manufactured from the conventional AMDRY 9954 feedstock powder. Characteristics of these coatings such as morphology and microstructure are presented. Once again, it should be noted that due to limited resources and microscope availability, no TEM characterization of these thermal spray coatings was performed.

The cross-section structure and morphology of the as-sprayed conventional HVOF coating can be seen in Figure 7.9. As can be seen from this figure, coatings deposited by HVOF feature the most desirable structure with minimal porosity, absence of cracks and a clean interface with the substrate. Porosity measurements carried out on these coatings revealed an average porosity of $0.5 \pm 0.1\%$, which represents about half that of the conventional CGDS coatings. The pores found within the HVOF coatings are also finer than those found in the CGDS coatings, thus demonstrating a better compaction effect of the deposited particles during spraying. This is likely attributed to the combined effect of softening of the sprayed particles in the higher temperature flow and the elevated particle velocities inherent to the process. When compared to other CoNiCrAlY coatings deposited by HVOF and reported in the literature [75, 92, 99, 112], the coatings of the current work feature a higher density and fewer visible defects. The average coating oxide content was measured to be 0.75 ± 0.23 (wt %), noticeably higher than CGDS coatings, which is expected given the higher process temperature and exposure to oxygen in the process combustion gases. Conversely, this level of oxide content is within the typical range for MCrAlY coatings deposited by means of HVOF spraying [75].



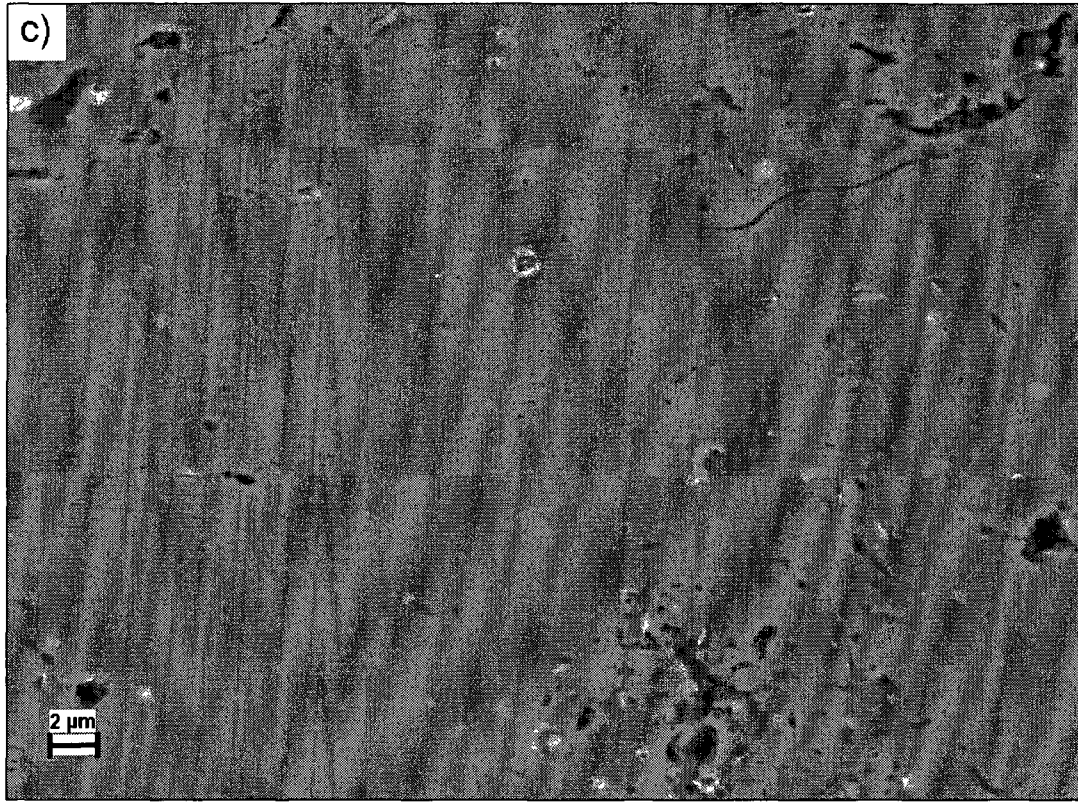


Figure 7.9: Backscattered SEM images at (a) 100x, (b) 400x and (c) 2500x magnifications showing the cross-section of the as-sprayed conventional HVOF coating

The SEM cross-section images of the as-sprayed HVOF coatings also reveal that the typical γ/β two-phase microstructure initially found in the conventional feedstock powder was not retained during deposition. This is evidenced by the apparent absence of the β -precipitates in the coating cross-section. Interestingly, these results differ with those reported in other studies [75, 92, 99]. For example, Saeidi et al. [99] observed a two-phase microstructure in their HVOF coatings and explained that the lower process temperature when compared to plasma spraying resulted in only partial melting of the particles, thus allowing the β -phase to be retained in the coating microstructure. However, this does not appear to be the case in the present study. Also, the low oxide content measured in the HVOF coating does not suggest that in-spray oxidation caused extensive depletion of aluminum as was the case in the APS coating. As such, this mechanism is not believed to be responsible for the single-phase microstructure obtained in the HVOF coating. Therefore, the absence of β -phase precipitates in the HVOF coating microstructure is believed to be caused by a similar deformation driven dissolution mechanism as that observed in CGDS. HVOF spraying is known to combine

warm process temperatures and high particle impact velocities in order to produce a coating. To some extent, HVOF spraying relies on plastic deformation of the warm particles upon impact with the substrate for successful deposition, and therefore the actual coating build-up process can be, in some cases, very similar to that observed in CGDS. Therefore, results obtained in the present work suggest that HVOF sprayed particles were subjected to sufficient plastic deformation to cause dissolution of the β -phase by the same mechanisms as those witnessed in the CGDS coating. Based on these findings, the HVOF coating in the present study appears to have a microstructure more similar to that of CGDS coatings than to that of other HVOF coatings found in the literature.

To further verify this, an XRD analysis was also carried out on the as-sprayed HVOF coating sample in order to investigate its phase content. Results from this analysis are presented in Figure 7.10. As can be seen in this figure, the XRD scan does in fact exhibit a single-phase microstructure composed only of the γ -phase Co-Ni-Cr solid solution, as was the case for the CGDS coating. These results further suggest that the HVOF deposition process has also caused dissolution of the β -phase due to severe plastic deformation of the particles upon impact on the substrate. Furthermore, as observed for the CGDS coating, peak broadening of the γ -phase is also visible, which once again suggests the occurrence of grain refinement of this phase. One may argue that given the fact that the main diffraction peak associated to the β -phase is located very close to that of the γ -phase, peak broadening may have resulted in the β -peak being hidden in the main γ -peak shoulder. However, investigation of the HVOF coating cross-section at high magnification (Figure 7.9c) demonstrates that the β -precipitates have undergone, at the very least, partial dissolution as a result of the deposition process. The occurrence of peak broadening of the γ -matrix phase is quite surprising for a thermal spray deposition process that is typically associated to thermally induced grain growth. However, it is important to recall, as discussed previously, that HVOF is a deposition process that uses a combination of thermal energy to soften and/or partially melt the sprayed material as well as kinetic energy to promote plastic deformation upon impact of the particles on the substrate. While the results observed in the present work may not be common to most HVOF processes, it emphasizes that the selected spray parameters can have a significant influence on the coating microstructure. Based on these findings, it would appear that the HVOF coatings

considered in this study were manufactured using spraying parameters that favored the contribution of plastic deformation as opposed to thermal softening for successful coating deposition. This further reinforces the idea that the HVOF coatings considered in this work are more similar to CGDS coatings in many aspects than to other HVOF coatings reported in the literature.

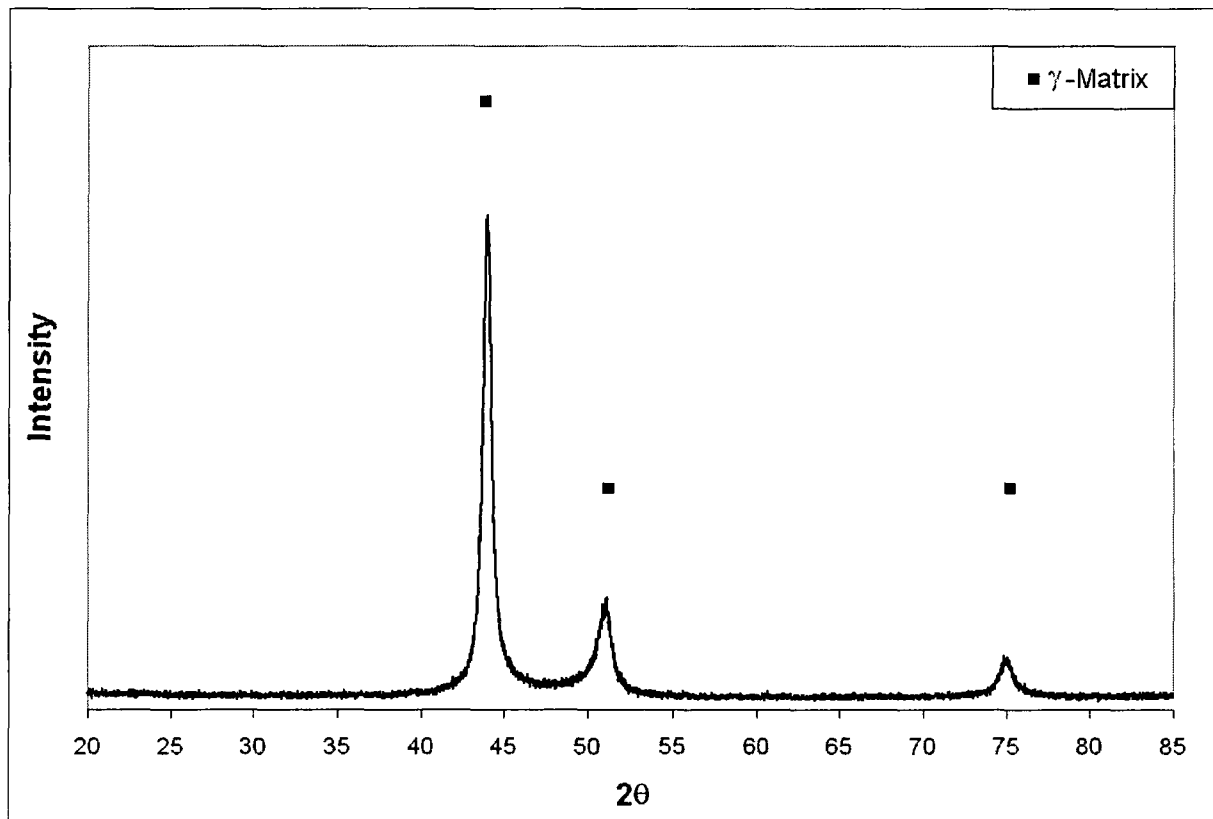


Figure 7.10: XRD spectrum of the as-sprayed HVOF CoNiCrAlY coating

7.1.4 Conventional Coatings Summary

Results from the characterization of the as-sprayed conventional coatings are now summarized for clarity purposes. The average porosity level and measured oxide contents of the as-sprayed coatings deposited using the various spraying techniques are presented in Table 7.1. The oxide content of the original feedstock powder is also presented as a reference for comparison.

Table 7.1: Summary of as-deposited coating properties by various spraying techniques

Material	Coating Porosity (%)	Oxide Content (wt. %)
Feedstock Powder	N/A	0.03 ± 0.03
CGDS Coating	1.0 ± 0.3	0.10 ± 0.05
HVOF Coating	0.5 ± 0.1	0.75 ± 0.23
APS Coating	5.3 ± 0.5	3.82 ± 0.70

As discussed previously, the HVOF coatings exhibit the most desirable structure with very limited porosity and minimal visible defects. The CGDS coatings also feature an acceptable structure with porosity levels slightly higher than the HVOF coatings. However, the APS coatings feature a high level of porosity and visible defects such as inter-splat cracks. As expected, the low processing temperature inherent to the CGDS deposition technique allowed for minimal in-spray oxidation of the particles and resulted in a very low coating oxide content. The negative influence of increasing processing temperature on the coating oxide content is further demonstrated by results obtained for the HVOF and APS coatings.

Investigation of the coating microstructures revealed that all deposition techniques resulted in microstructural transformations when compared to the original feedstock powder. It was observed that the extent of in-spray particle oxidation that occurred during the APS deposition process resulted in the formation of detrimental mixed spinel-type oxides and was sufficient to deplete aluminum to the point where the β -precipitates could no longer form. Such transformations are expected to be detrimental to the oxidation behaviour of the coating.

XRD and TEM investigations of the conventional CGDS coatings demonstrated evidence of grain refinement of the initially large γ -matrix grains in some regions of the coating as well as dissolution of the fine β -phase precipitates. Other regions in the coating did not experience the same extent of grain refinement, thereby resulting in a bimodal grain size distribution. Such transformations of the deposited material's microstructure were attributed to the varying extents of intense plastic deformation resulting from the high-velocity impact of the sprayed particles. These findings contradict the generally accepted claims that the CGDS process does not lead to changes in the deposited material's microstructure. Although transformations in microstructure due to exposure to high temperatures are avoided, results in this work suggest that the CGDS process may still introduce microstructural changes in the material by

means of severe plastic deformation. The influence of these microstructural changes on the bond coat oxidation behaviour will be addressed in Chapter 8.

Surprisingly, the HVOF coatings featured a microstructure very similar to that of the CGDS coatings. Evidence of β -phase dissolution during deposition as well as an apparent refinement of the grain structure suggests that the HVOF coatings considered in this study were manufactured using spraying parameters that favored the contribution of plastic deformation as opposed to thermal softening for successful coating deposition. Based on these observations, it was concluded that the HVOF coatings considered in the present work are more similar to CGDS coatings than to other HVOF coatings reported in the literature.

7.2 Nanocrystalline CoNiCrAlY Coatings

7.2.1 Nanocrystalline CGDS Coatings

The following section will characterize the as-sprayed CGDS coatings manufactured using the optimized spraying parameters and the cryomilled (nanocrystalline) feedstock powder sieved below 25 μ m. Similarly to the conventional CGDS coatings, characteristics such as coating morphology and microstructure are presented. A comparison to the original feedstock powders and conventional CGDS coatings is also provided.

7.2.1.1 As-Sprayed Coating Morphology

The structure and morphology of the nanocrystalline CGDS coatings are presented in the cross-section images shown in Figure 7.11. These images show that the nanocrystalline CGDS coatings exhibit a large build-up thickness achieved in a single pass ($\sim 500\mu$ m) and feature limited visible defects such as porosity and interlamellar cracks. Porosity measurements carried out on these nanocrystalline coatings revealed an average porosity of $2.9 \pm 0.9\%$, which is noticeably higher than the conventional CGDS coatings. The difference in porosity is likely attributed to the higher hardness and mechanical strength inherent to the nanocrystalline feedstock particles, thereby increasing their critical velocity and leading to more particles undergoing incomplete plastic deformation. The difference in porosity may also be partly explained by the different particle morphology of both feedstocks. The flake-like nanocrystalline particles have a higher drag coefficient than the spherical conventional particles, and are therefore more susceptible to natural disturbances in the flow such as bow shocks ahead of the substrate. Similarly to the influence of shock waves on the acceleration of very small particles [34], such disturbances may hinder the actual impact velocity of the nanocrystalline particles upon deposition, thus causing fewer of these particles to have the required velocity to achieve adequate plastic deformation.

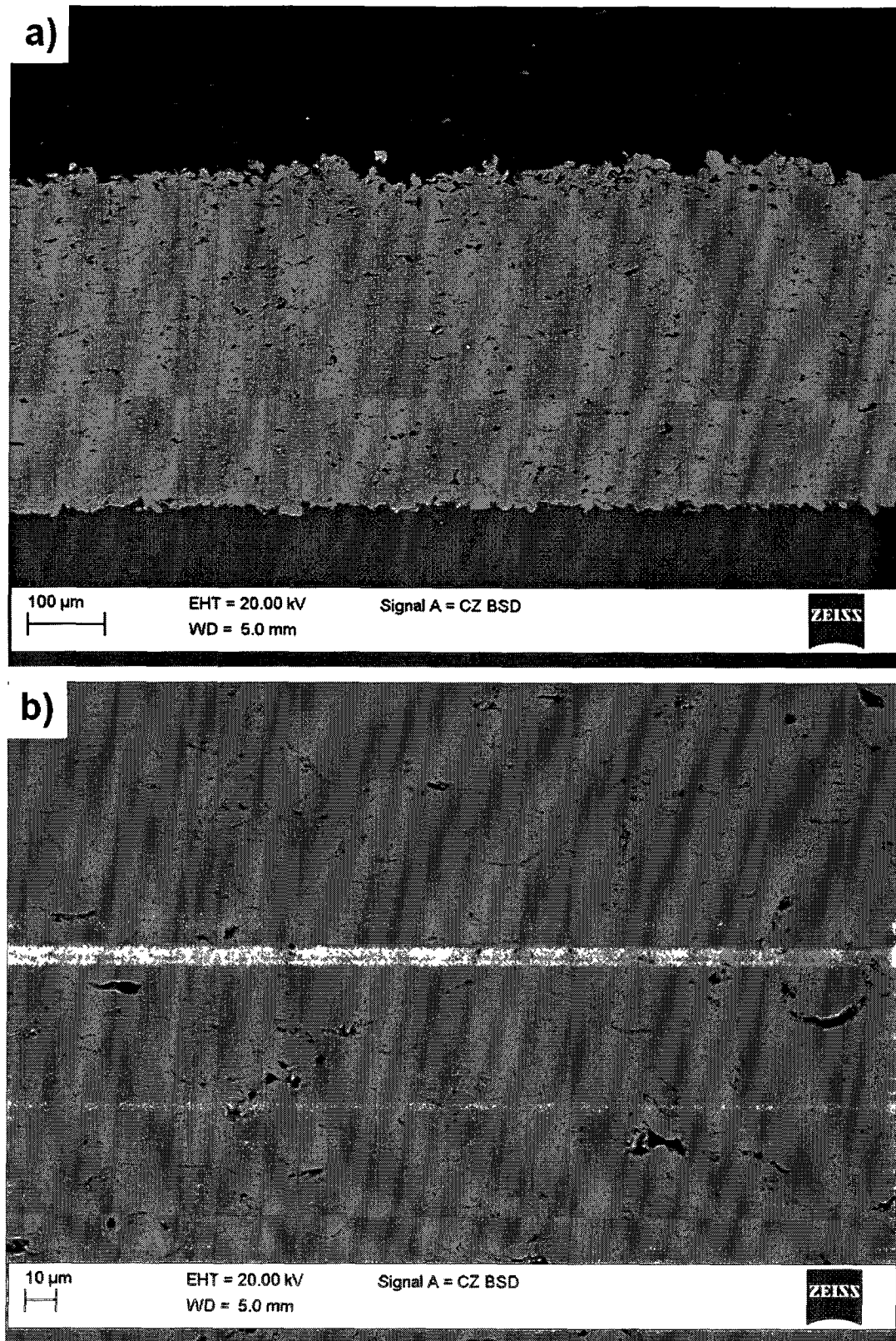


Figure 7.11: Backscattered SEM images at (a) 100x and (b) 400x magnifications showing the cross-section of the as-sprayed conventional HVOF coating

Although the level of porosity observed for the nanocrystalline coatings is below the maximum allowable porosity threshold of 3.0%, there still exists an opportunity to improve the coating structure. While the term “optimized spraying conditions” has been used to describe the conditions used for the manufacturing of these coatings, it is believed that improved levels of porosity may yet be achieved with more advanced nozzle geometry designs. With this in mind, however, it is believed that with the current physical limitations of the experimental CGDS apparatus, it would not be possible to further reduce the porosity level of the nanocrystalline CGDS coatings.

7.2.1.2 As-Sprayed Coating Microstructure

Investigation of the microstructure of the nanocrystalline CGDS coatings was performed in order to compare with the original cryomilled powder as well as the conventional CGDS coatings. Figure 7.12 shows the XRD spectra of the nanocrystalline CGDS coating as well as the original as-cryomilled feedstock powder. As opposed to the conventional CGDS coatings and powders, there are no significant changes in the material microstructure as a result of the CGDS deposition process. Both spectra feature only three peaks, all of which are associated to the γ -phase. These peaks also exhibit similar width, thereby demonstrating that no broadening has occurred from the deposition process and therefore the γ -phase grain structures of the original powder and resulting coating are similar. Also, the peaks normally associated to the β -phase remain absent in both spectra, thus suggesting little change with respect to this phase in the material. The only noticeable discrepancy between the two scans is the varying spectrum intensity which is once again believed to be attributed to the different physical condition of the samples (powder form and solid form for the as-cryomilled powder and CGDS coating sample respectively).

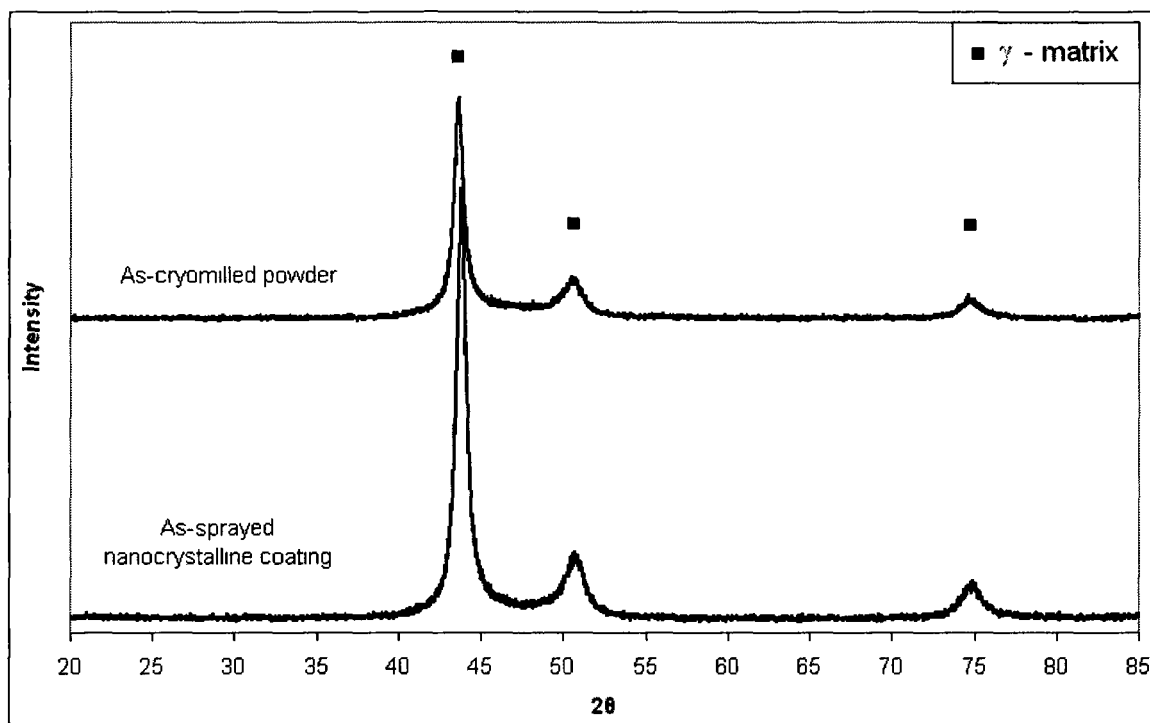


Figure 7.12: XRD spectra of the nanocrystalline CoNiCrAlY CGDS coating and the original as-cryomilled feedstock powder

To further confirm that the nanocrystalline microstructure previously characterized in the as-cryomilled powder had been retained throughout the CGDS deposition process, TEM investigation of the resulting coating was carried out. Figure 7.13 shows the SAED of the nanocrystalline CGDS coating. When compared to the diffraction pattern of the original as-cryomilled powder (Figure 5.10), it can be seen that both materials exhibit similar features including diffraction rings associated to the γ -phase matrix as well as very faint ring fragments associated to the β -phase precipitates. Further similarities between the as-cryomilled powder and resulting CGDS coatings are evidenced in Figure 7.13 which also shows BF and DF TEM images of the nanocrystalline CGDS coating microstructure. Comparison of these images with those obtained from the original as-cryomilled powder (Figure 5.11) reveals that both materials feature similar nanocrystalline grain structures with average grain sizes below 50nm. The apparent absence of microstructural changes induced throughout the CS deposition process for this coating is attributed to the fact that such transformations have already occurred in the material during the cryomilling process, as discussed in section 5.2.2. The extent of grain refinement that can be achieved in a material

by means of induced severe plastic deformation has been investigated in mechanical milling and has been shown to be limited [101]. Given that substantial grain refinement had already occurred in the material during the cryomilling process, further grain refinement by means of additional plastic deformation is not likely to occur. This explains why the additional plastic deformation resulting from the CS deposition process did not cause further grain refinement in the cryomilled powder.

Finally, Figure 7.14 shows a high-resolution TEM image of a single γ -phase fcc grain in the nanocrystalline coating microstructure. This grain features an equiaxed morphology and has an equivalent diameter of approximately 10-15nm, thus further demonstrating the nanocrystalline grain structure of the coating. The figure also demonstrates that the grains in the nanocrystalline CGDS coating exhibit a high density of planar defects (twins), which indicates that twinning is the main deformation mechanism during particle impact. Twinning represents the situation where two crystals share common crystal lattice points in a symmetrical arrangement which can be formed as a result of stacking faults or planar defects caused by slip. The twinning deformation mechanism typically dominates over dislocation-based plasticity under the following conditions: very small grain sizes and high strain rates, both of which are known to be present during CGDS deposition of the nanocrystalline powder. It is thus believed that although the nanocrystalline coating does not exhibit further grain refinement during CGDS deposition, it does show evidence of deformation in the form of twinning.

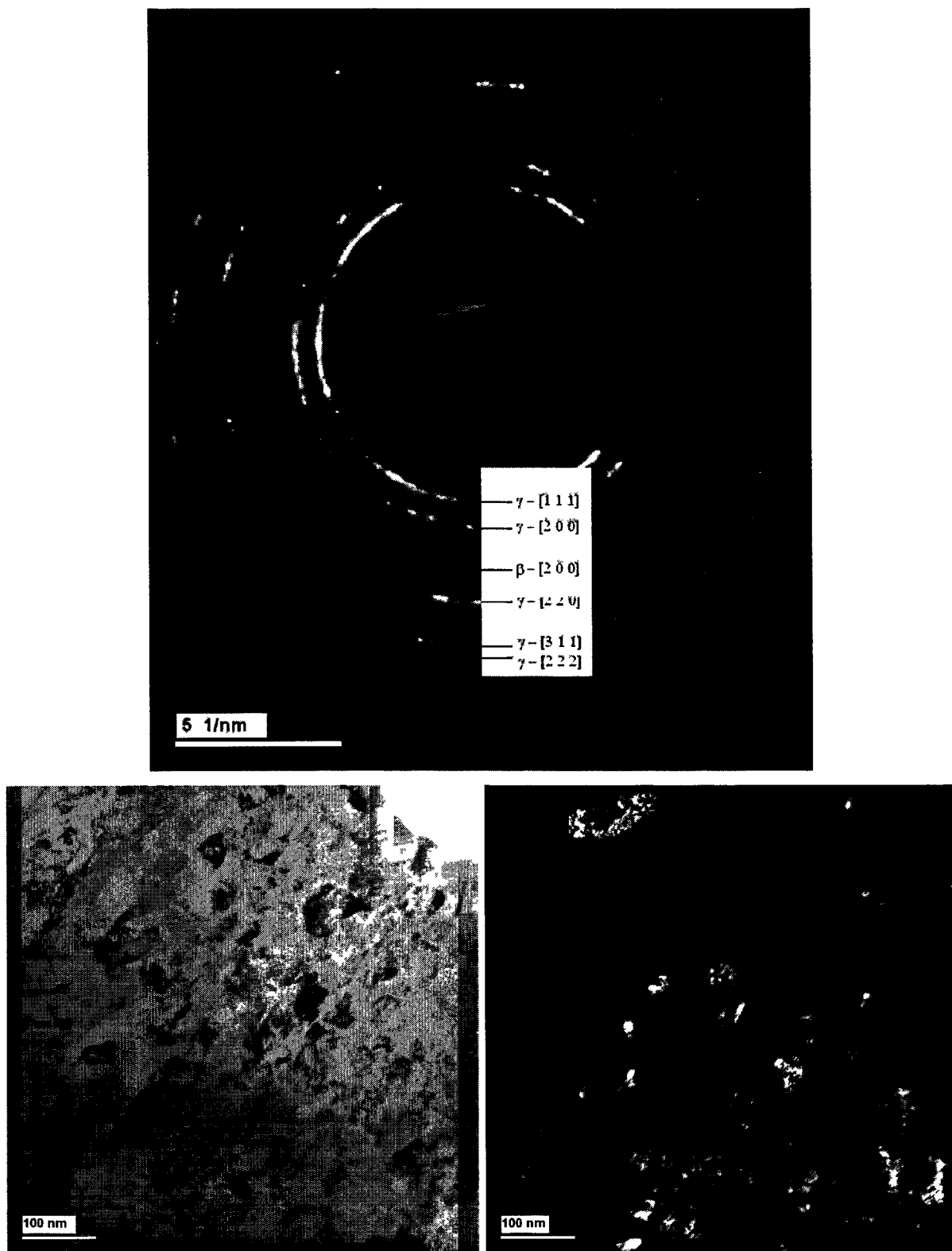


Figure 7.13: TEM images showing the SAED pattern (top) as well as the BF (left) and corresponding DF (right) images of the nanocrystalline CGDS CoNiCrAlY coating microstructure

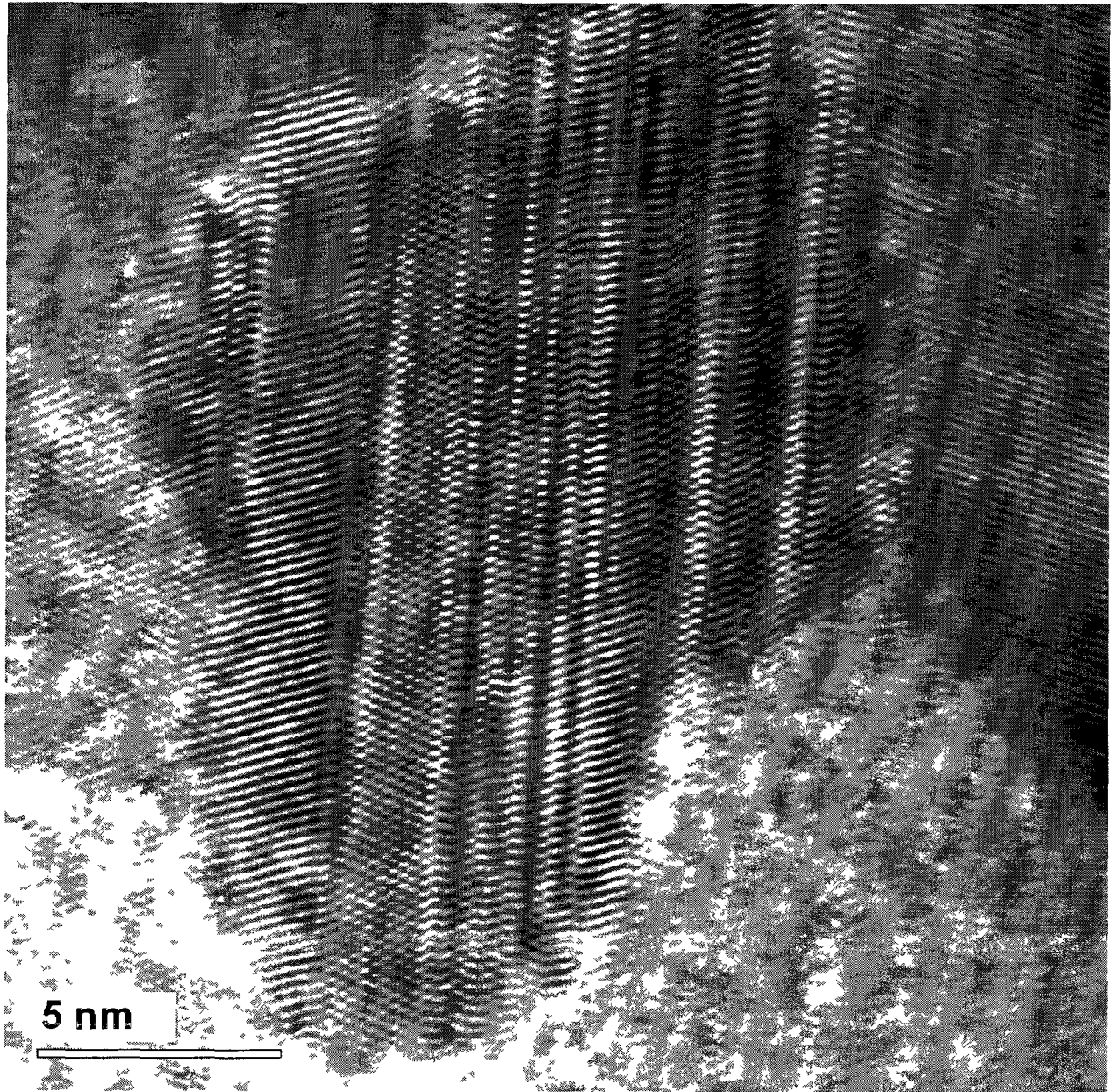


Figure 7.14: HRTEM of a single γ -phase fcc grain in the nanocrystalline CoNiCrAlY CGDS coating

7.2.2 Nanocrystalline Coatings Summary

Characterization of the nanocrystalline CGDS coating structure revealed an acceptable porosity level of $2.9 \pm 0.9\%$, which is noticeably higher than the conventional CGDS coatings. This was attributed to the increased mechanical strength of the nanocrystalline powder particles, thereby requiring higher velocities to achieve sufficient plastic deformation. XRD and TEM investigation of the nanocrystalline coatings showed that the plastic deformation from CGDS deposition did not cause further grain refinement of the γ -phase nor additional dissolution of the β -phase precipitates. This was attributed to the fact that such microstructural transformations had already taken place during the cryomilling process, and therefore no further grain refinement or β -phase dissolution occurred during deposition of the cryomilled powder. However, the nanocrystalline coating did show evidence of other microstructural changes resulting from CGDS deposition in the form of twinning as a deformation mechanism.

Chapter 8 - Oxidation Behaviour of CoNiCrAlY Bond Coats Manufactured by Various Deposition Techniques

This chapter aims to present the experimental results obtained from a series of oxidation experiments carried out to investigate the oxidation behaviour of CoNiCrAlY bond coats. The first series of trials involved the characterization of the oxidation behaviour of conventional coatings manufactured by the CGDS deposition technique. For comparison purposes, coatings were also manufactured from the same feedstock powders by thermal spray techniques, namely APS and HVOF, and subjected to identical sample preparation and oxidation testing procedures. The second series of trials focused on the assessment of the oxidation behaviour of nanocrystalline coatings produced by CGDS. The oxidation behaviour of these coatings is then compared with that of the previously discussed conventional CGDS coatings. The purpose of these trials is to determine how the various deposition techniques and more specifically the resulting microstructures of the coatings (grain structure and oxide content) influence the oxidation behaviour of the bond coat material.

8.1 Conventional CoNiCrAlY Coatings Oxidation Behaviour

The present section of this report presents the experimental results of the oxidation tests carried out on the conventional CGDS CoNiCrAlY coatings. As a basis for comparison, results from the oxidation tests performed on the HVOF and APS coatings are also presented. For conciseness purposes, oxidation results obtained from all three different deposition techniques are presented and discussed simultaneously. Comparison of the experimental results with values published in the literature has also been included in the discussion as a reference to support the validity of the experimental approach considered in this work.

8.1.1 Oxide Growth Rates

In order to assess the overall oxide growth rate, oxidation samples were weighed prior to and following every isothermal heat treatment using a digital weighing scale (Sartorius Extend - model ED124S). These measurements were recorded in order to determine the mass gain of the samples due to the formation of oxides during the oxidation tests (isothermal heat treatments in atmospheric air at 1000°C for 5h, 25h, 50h and 100h durations). Given that oxidation is a surface phenomenon, the mass gain measurements are reported as a gain in mass normalized per unit area for each sample. Results from this analysis for the conventional coatings manufactured by CGDS, HVOF and APS are presented in Figure 8.1. For clarity purposes only, experimental data points were linked by means of solid black lines. For all three deposition techniques, results are presented as the average mass gain for five coating samples. Error bars have been included to show the experimental standard deviation obtained for the mass gain measurements. Three curves generated from data available in the literature are also presented (dashed lines) for comparison purposes. These curves show the mass gain measurements obtained from the isothermal oxidation testing of CoNiCrAlY coating samples manufactured by HVOF and APS using the same feedstock powder as the one considered in the present study. However, it should be noted that the values used to generate these reference curves were evaluated graphically and therefore should only be considered as approximate trend lines. For further precision, the reader should consult the corresponding references directly.

Figure 8.1 shows that of the three deposition techniques considered in this study, the HVOF coating exhibits the lowest overall oxide growth rate. The curve for the HVOF coating presents a parabolic trend and appears to somewhat stabilize after 100 hours of oxidation time. Conversely, the APS coating exhibits a much higher initial oxide growth rate which further accelerates after 50 hours of oxidation time. In general, the trends observed from the experimental data obtained from these two thermal spray techniques agree with the literature quite well. The two reference curves plotted in Figure 8.1 for the HVOF deposition technique also present parabolic trends and the values for the mass gain measurements are of comparable orders of magnitude. However, it is evident from these results that the HVOF coating considered in this study appears to be of particularly high quality as the mass gain

measurements obtained from this coating are noticeably and consistently lower than those from the two references. This is also apparent for the APS coating considered in this study. Despite having a much higher oxide growth rate than the HVOF coating, the mass gain measurements obtained experimentally for the APS coatings are noticeably lower than those from Shibata et al. [75]. Additionally, Shibata et al. [75] reported to have observed spalling of the oxide scale from their APS coating sample after 50 hours of oxidation time as well as from their HVOF coating after 100 hours of oxidation time. No oxide scale spallation was observed for either the APS or HVOF coatings considered in this study.

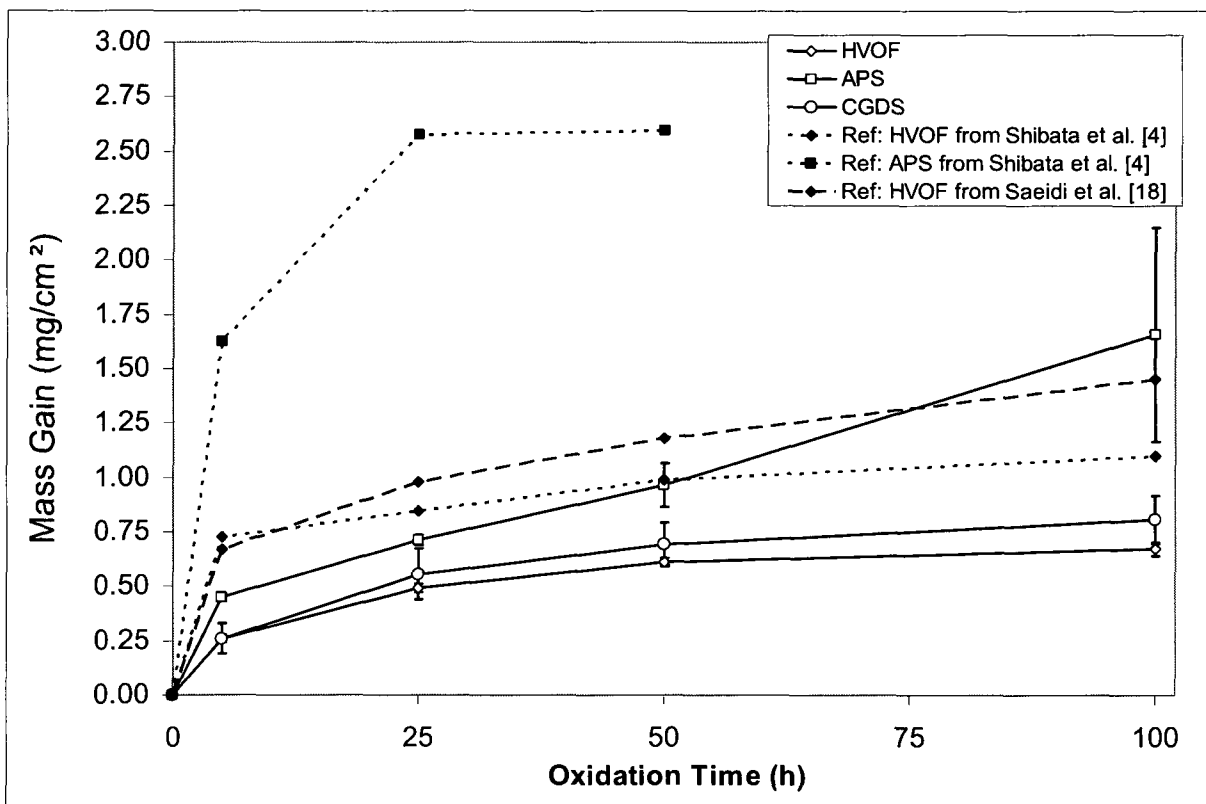


Figure 8.1: Mass gain measurements normalized per surface area as a function of oxidation time at 1000°C for CoNiCrAlY coatings deposited by APS, HVOF and CGDS spraying

The significant differences in mass gain measurements and oxidation behaviour between the experimental results presented in the current work and data from the literature are mainly attributed to the fact that a higher isothermal oxidation temperature was used by Shibata et al. [75] and Saeidi et al. [99] (1100°C as opposed to 1000°C in this study). It is well known that a temperature difference of 100°C can have a significant influence on the oxide growth rate

dynamics and oxide scale compositions. However, given the absence of data in the literature for the oxide growth rates of the specific CoNiCrAlY material considered in this study at 1000°C, it seems appropriate to include the data from Shibata et al. [75] and Saeidi et al. [99] for reference purposes. While the oxidation temperature difference is expected to be the main source of discrepancy between the results, it is also believed that the lower porosity and oxide content observed in the coatings of the present study play an important role on the oxide growth rates, as will be discussed further in following sections.

The oxide growth rate of the CGDS coating follows that of the HVOF coating very closely, but the mass gain consistently remains slightly higher. These results are somewhat surprising given that various reference papers suggest that greater oxide contents in the as-sprayed coating favour the formation of fast-growing undesirable oxides, thus leading to higher oxide growth rates. However, despite having a lower as-deposited oxide content, the CGDS coatings exhibit a higher oxide growth rate during isothermal oxidation when compared to HVOF. The reason for this observation may be a combination of various factors. Firstly, elevated process temperatures such as those inherent to HVOF have been known to cause in-spray oxidation of the sprayed material [87], thus forming a fine oxide layer on a particle's surface. These oxides are then embedded into the coating microstructure upon deposition, thus resulting in higher as-sprayed oxide contents, as observed in this work. In coatings having a two-phase microstructure composed of a γ -matrix and β -precipitates, such as the CoNiCrAlY coatings considered in this study, the Al-rich β -phase acts as an aluminum reservoir [75, 113]. As oxidation of the coating progresses, aluminum diffuses from the β -precipitates and reacts to form the α -Al₂O₃ scale, thereby causing dissolution of the β -precipitates and resulting in a β -phase depletion zone near the oxidized surface. It has been suggested that the presence of in-spray oxides embedded in the coating microstructure can act as obstacles to the diffusion of aluminum, and therefore inhibit the oxide scale growth rate [99, 114]. It is important to recall here that even though both the CGDS and HVOF coatings in the as-sprayed condition do not exhibit a two-phase microstructure, they still contain a sufficiently high Al concentration to ensure its selective oxidation by means of Al diffusion. As such, the theory that Al diffusion may be inhibited due to the presence of embedded oxides might partially explain the reason for which the HVOF coatings were observed to have a

slightly lower oxide growth rate than the CGDS coatings. Secondly, given that oxidation is considered to be a surface phenomenon, mass gain measurements for each sample presented in this study, as well as those from selected references, have been normalized with respect to the sample surface area. For the present study, the reported mass gain measurements represent a highest-possible value for the two following reasons: (1) the influence of surface roughness and irregularities were assumed to have negligible effect on the measured surface area and (2) it was not possible to evaluate the additional surface area associated to porosity within the coating. Taking into account the influence of surface roughness and irregularities would lead to an increased value for the measured surface area, meaning that the normalized mass gain of a sample per unit area would in reality be even lower than the currently presented values. Nevertheless, to ensure consistency in the measurements, all free-standing coating samples were polished on both sides to the same surface finish prior to oxidation testing. As such, errors associated to surface area measurements due to surface roughness would be minimal and ultimately equivalent from one sample to the next. In addition, this polishing step eliminates the presence of any oxides having formed on the outer surface of the coating (surface exposed to air during processing), thereby concentrating the oxidation experiments on the effect of the coating microstructure and internal oxide content. While surface roughness effects have thus been mitigated, it is believed that the influence of coating porosity on the mass gain measurements is far more significant as it represents additional surface area for oxidation to occur.

In order to verify this, isothermal oxidation tests were carried out on CGDS coatings manufactured with non-optimized spraying conditions and characterized with higher average porosity levels. Two different coatings were considered, each manufactured by different spraying parameters. When compared to the optimal spraying conditions, the first non-optimized coating was deposited using axial powder injection with a lower nozzle inlet gas pressure (1MPa rather than 2MPa) and a lower gas temperature (400°C rather than 550°C), which resulted in a coating with a porosity level evaluated at 7.5%. All other spraying parameters remained identical to those of the optimal conditions. For the second non-optimized coating, all conditions were identical to the optimal spraying parameters with the exception of the substrate traverse velocity which was increased to 3mm/s (as opposed to

1mm/s), thereby reducing the level of particle impingement and causing a slight increase in porosity, which was measured to be 4.1%. As shown in Figure 8.2, results of the mass gain measurements for these coating samples during oxidation testing show a significant increase in the oxide growth rate with increasing coating porosity. These results demonstrate the strong influence of coating porosity on the measured overall oxide growth rate. Such a finding in itself is quite interesting given that results from mass gain analyses reported in the literature are not typically presented as a function of coating porosity.

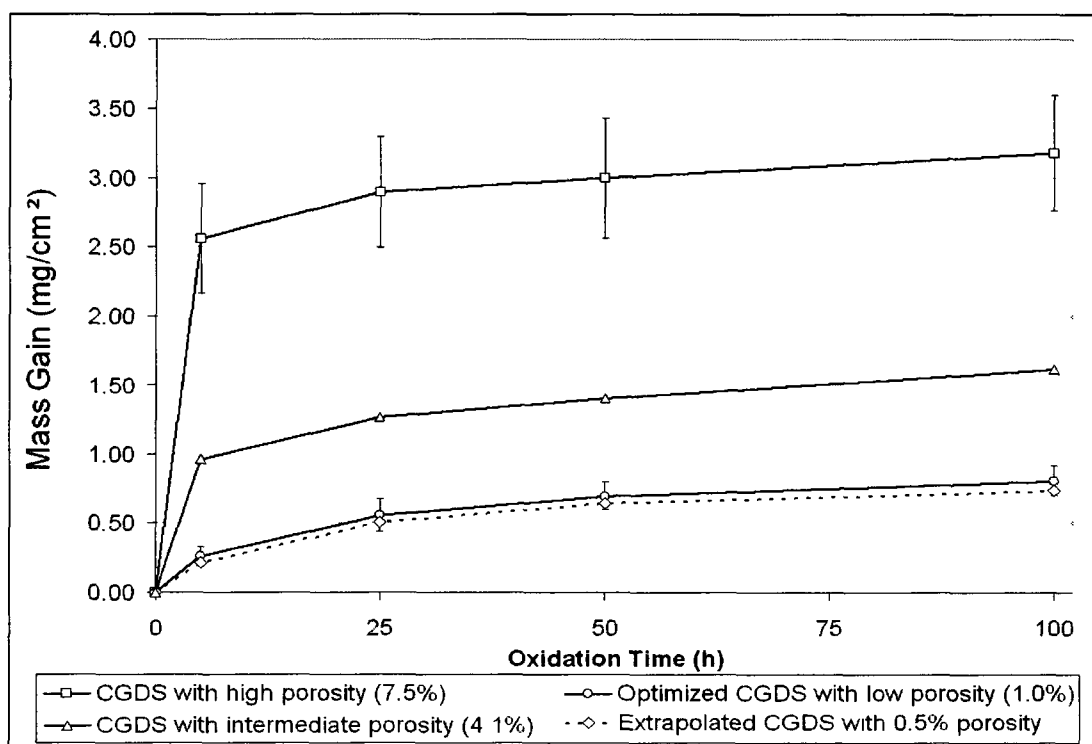


Figure 8.2: Mass gain measurements as a function of oxidation time at 1000°C for CGDS CoNiCrAlY coatings showing the influence of coating porosity on the overall oxidation rate

Results from these latest trials were then correlated with respect to porosity using a polynomial curve fit for each given oxidation time. This curve fit was then used to extrapolate the predicted mass gain for a CGDS coating with a theoretical porosity equal to that of the HVOF coatings (0.5%). Results of this extrapolation are also presented in Figure 8.2. It was found that the extrapolated curve fits closely to that of the HVOF coating, thus suggesting that the difference in porosity between the HVOF and CGDS coatings may also partly explain the discrepancies in oxide growth rates.

The influence of porosity on the mass gain is believed to be strongly dependant not only on the extent of porosity, but also on the morphology of the pore structure. In the case of high-porosity coatings, voids typically form large networks of pores that communicate with the coating surface (open-porosity). This pore structure allows for oxygen to penetrate deep into the coating and reach the inner cavities to form oxides, resulting in enhanced mass gain measurements. Conversely, for coatings with lower porosity levels such as the HVOF and CGDS coatings considered in this study, pores do not form networks nor communicate with the surface (closed-porosity). Such coatings are still susceptible to oxidation along the surface of voids due to their reaction with oxygen entrapped inside the pores (even if it is at low concentration) due to enhanced reactivity at elevated temperatures [99]. Although such oxidation is expected to occur, it should not influence the mass gain measurements since oxygen initially entrapped in the coating contributes equally to the total mass of the sample before and after the oxidation test. While this is true for closed-pores located near the center of the bond coat thickness, closed-pores near the coating surface may be subjected to inward diffusion of oxygen [92] which has been shown to lead to the formation of internal oxides near the bond coat surface. It is believed that oxygen is selectively supplied to the inner surfaces of pores located near the surface of the coating by means of inward diffusion, thereby promoting the oxidation reaction within the porosity. It is thus hypothesized that this latter mechanism may explain the differences in mass gain measurements between the CGDS and HVOF coatings.

Figure 8.3a shows a large oxide scale that has formed along the surface of a communicating cavity located near the surface of a non-optimized CGDS coating. This demonstrates that higher porosity levels, notably open-porosity networks, provide a substantial increase in surface area for oxidation to occur, thereby affecting the mass gain measurements. The figure also shows that the β -phase precipitates are now visible in some areas of the coating, which will be addressed in more detail in a following section. For now, it is simply interesting to note that the β -phase has been depleted in areas close to the communicating cavity, which suggests that the internal oxidation mechanism is similar to that happening on the coating surface. Conversely, Figure 8.3b shows an oxide scale formed along the surface of non-communicating voids found within the optimized low-porosity CGDS coating further

suggesting that inward diffusion of oxygen into the coating is mostly responsible for the formation of this internal oxide scale. These findings all demonstrate that three-dimensional considerations within the coating structure, namely coating porosity, clearly have an influence on the recorded mass gain during coating oxidation.

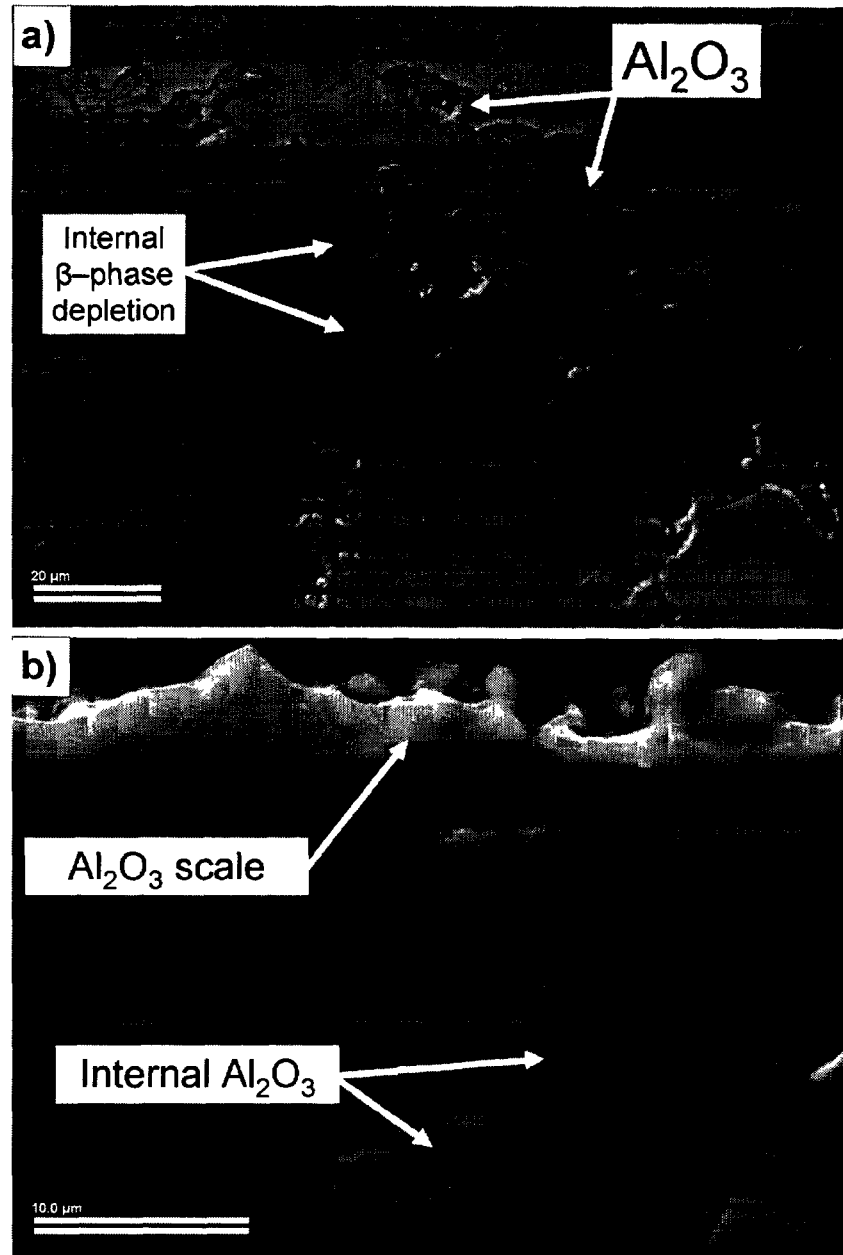


Figure 8.3: SEM images showing CoNiCrAlY coating cross-sections after 100h of oxidation at 1000°C. Image a) shows the development of oxides along the surface of communicating porosities in a coating deposited with non-optimized spraying conditions. Image b) shows the formation of internal oxides along the surface of closed porosities located near the surface due to inward oxygen diffusion.

Figure 8.4 shows the evolution of the oxide scale and depletion zone in the CoNiCrAlY coatings manufactured by the various deposition techniques as a function of oxidation time. From this figure, the similarities in microstructure for the CGDS and HVOF coatings become further evident.

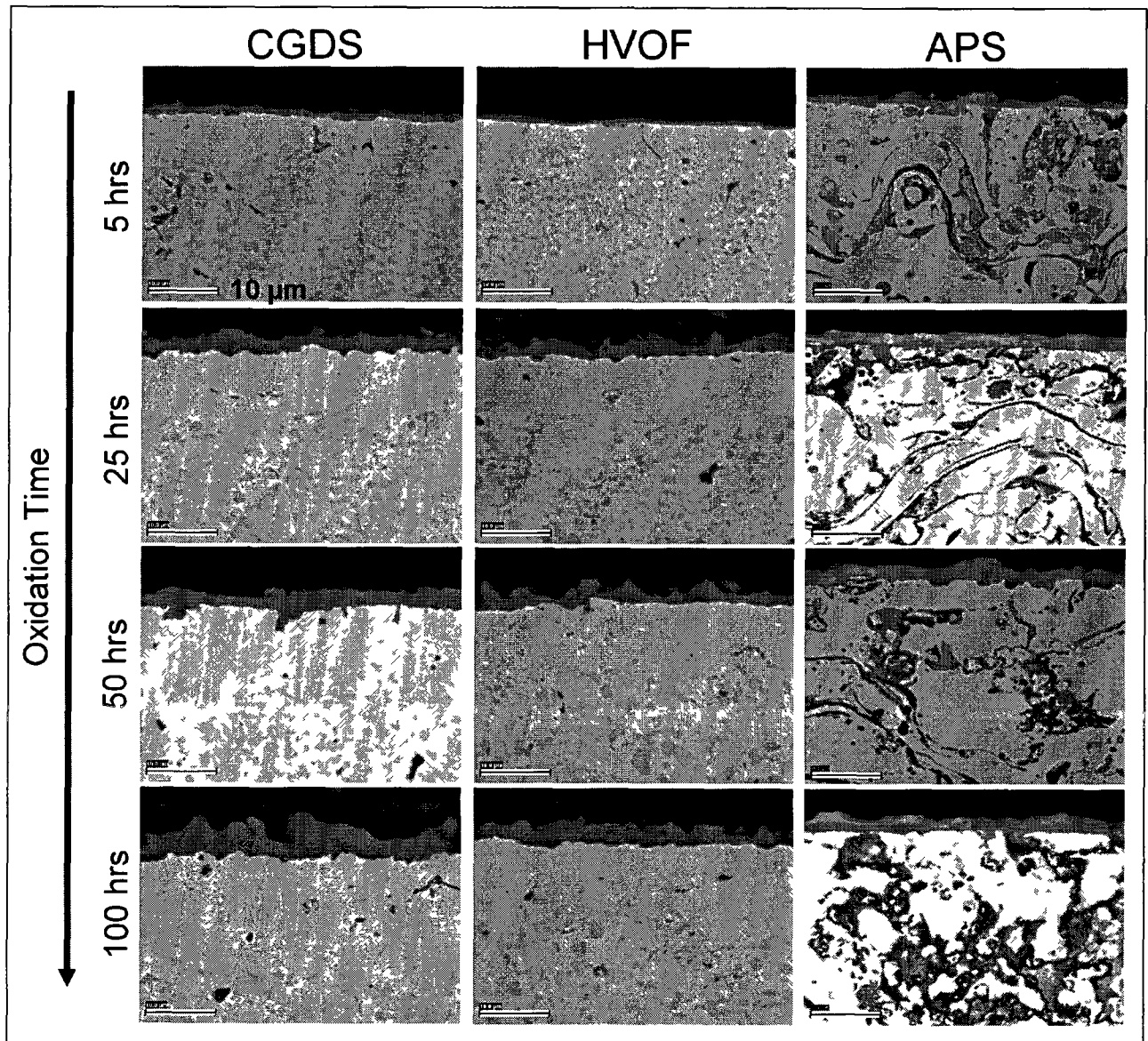


Figure 8.4: Evolution of the oxide scale and depletion zone as a function of oxidation time at 1000°C for CoNiCrAlY coatings manufactured by CGDS, HVOF and APS. All images were taken at the same magnification (2500X)

After 5 hours of oxidation, both coatings exhibit a thin continuous oxide scale on their surface with a similar average thickness ($0.8\mu\text{m}$ and $1.0\mu\text{m}$ for the HVOF and CGDS coatings respectively). Also, the typical two-phase γ/β microstructure originally found in the powder is now clearly visible in both coatings. This is attributed to the fact that the isothermal oxidation test acts as a heat treatment which alleviates the stresses that were initially responsible for the dissolution of the β -phase upon coating deposition. As the heat treatments are carried out, the density of line and point defects in the material is reduced, thus causing a decrease in the solubility of Al in the γ -matrix. This in turn leads to the precipitation of the β -phase which once again becomes visible in the material microstructure. Depletion of the β -phase near the coating surface is also seen, demonstrating the selective oxidation of Al to form the oxide scale. As oxidation time increases, it can be observed that both coatings experience a similar oxide scale growth and β -phase depletion zone evolution. The remaining β -phase precipitates are also seen to slightly coarsen with extended exposure time as a result of enhanced diffusion at high temperature, thereby allowing the migration of Al to the β -phase precipitates and causing them to grow in size. The rate of change in thickness of the oxide scales for these two coatings correlates well with the mass gain measurements reported in Figure 8.1. The thickness of the oxide scales for both the CGDS and HVOF coatings appear to grow at a parabolic rate which is in accordance with Equation 2.13. Analysis of the oxide scale thickness evolution reveals parabolic rate constants of $1.9 \times 10^{-5} \mu\text{m}^2 \cdot \text{s}^{-1}$ and $1.3 \times 10^{-5} \mu\text{m}^2 \cdot \text{s}^{-1}$ for the CGDS and HVOF coatings respectively. These results show that the oxidation dynamics for both the CGDS and HVOF coatings are very similar.

Conversely, the APS coatings feature very different properties. It can be seen that the β -phase remains entirely absent from the coating microstructure for the full duration of the oxidation test. This is further indication that not only has the β -phase not had the opportunity to precipitate out due to the rapid cooling rates involved throughout the APS deposition process, but also that the remaining Al concentration is insufficient to form Al-rich β -precipitates in the coating during heat treatment as was observed for both the CGDS and HVOF coatings. This is further proof of the significant quantity of Al having been consumed by in-spray oxidation of particles during the APS deposition process. The important oxide content in the

as-sprayed condition as well as the large amount of internal oxides that are visible in the APS coating images from Figure 8.4 also support these findings. In addition to the growth of the oxide scale on the coating surface, the apparent increasing quantity of internal oxides resulting from large porosity networks may explain the large mass gain observed for APS coatings during oxidation testing.

8.1.2 Oxide scale composition

Throughout the oxidation trials, the composition of the oxide scale developing on the surface of each sample was investigated by means of XRD, SEM and EDS. Results of the XRD analyses performed on the conventional CGDS coating after the various oxidation times are shown in Figure 8.5, thus allowing for a better understanding of the coating's oxidation dynamics and evolution of its oxide scale.

As discussed previously, the XRD spectra for the as-sprayed coating reveals that only the γ -matrix phase is present as a result of the β -phase having dissolved during the CGDS deposition process. The γ -matrix peaks also show evidence of peak broadening, which was previously shown to be caused by grain refinement of the γ -matrix resulting from severe plastic deformation. It can also be seen that the as-sprayed coating does not exhibit any detectable amounts of oxides, which was expected given the low oxide content measurements previously reported in this study. After 5 hours of oxidation, the formation of an oxide scale composed of α -Al₂O₃ as well as other metastable alumina phases such as γ -Al₂O₃ and θ -Al₂O₃ is observed. The presence of such metastable phases during oxidation testing of the present CoNiCrAlY alloy is not uncommon and has been reported elsewhere [67, 75, 92]. At this stage of the oxidation process, small peaks associated to the β -phase are also visible, thus further confirming that the oxidation process has acted as a heat treatment allowing the β -phase to precipitate out, as evidenced in Figure 8.4. After 25 hours of oxidation however, the β -phase peaks are no longer discernable from the XRD analysis. Although the β -precipitates are clearly visible in the coating cross-section after 25 hours of oxidation (see Figure 8.4), the β -depletion zone has now reached a thickness that is greater than the penetration depth of the incoming analytical X-rays, thereby not registering β -phase peaks in the XRD spectrum.

Increasing oxidation time up to 100 hours shows the emergence of α - Al_2O_3 as the dominating oxide, with lesser amounts of γ - Al_2O_3 and θ - Al_2O_3 . Once again, the presence of these metastable phases is not uncommon and it has been suggested that they eventually transform into α - Al_2O_3 upon increased oxidation time [67, 92]. This is further validated in Figure 8.6 which shows the surface oxide morphology and EDS elemental mapping of the CGDS coating after 100 hours of oxidation at 1000°C .

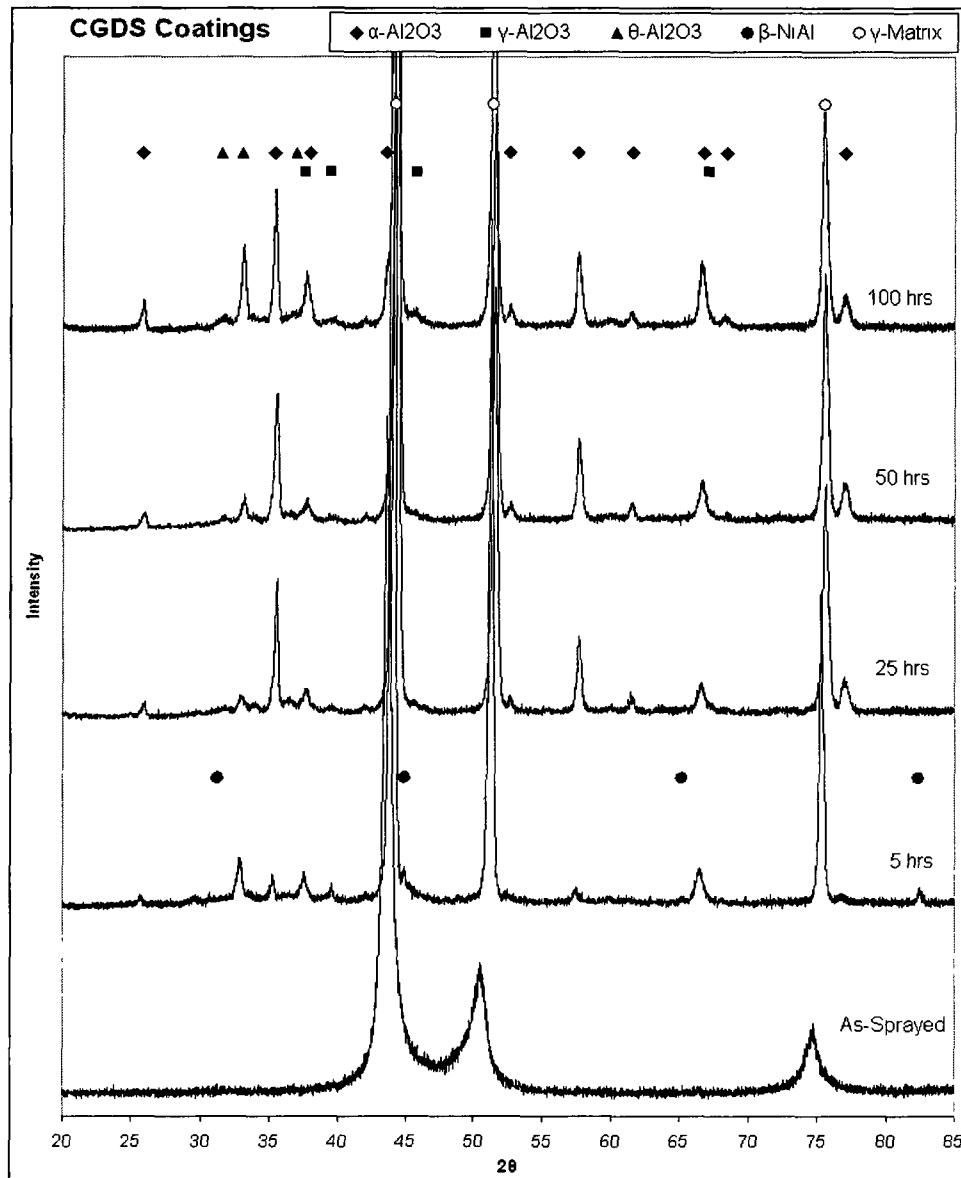


Figure 8.5: XRD spectra of the CGDS CoNiCrAlY coatings after various oxidation times at 1000°C

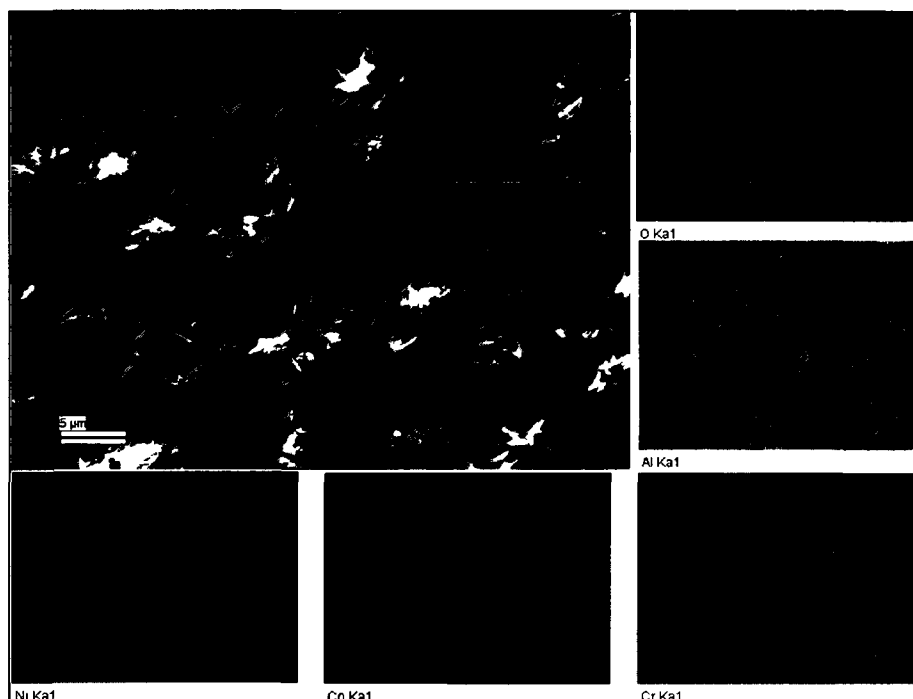


Figure 8.6: SEM image and EDS elemental mapping showing the surface oxide morphology of a CoNiCrAlY CGDS coating following 100 hours of oxidation at 1000°C

It can be seen from this figure that the surface is well covered with a continuous oxide scale composed of alumina. The acicular (or whisker-like) morphology of the oxides observed in Figure 8.6 is characteristic of the θ - Al_2O_3 phase [67, 92]. However, it should be noted that when this phase transforms into α - Al_2O_3 , it retains its acicular morphology and subsequent growth of α - Al_2O_3 appears to be unaffected by this phase transformation [67]. As such, although it would appear that θ - Al_2O_3 is the dominant oxide on the CGDS coating surface based on the oxide morphology, the XRD analysis reveals that α - Al_2O_3 is dominant based on peak intensity. This demonstrates that some of the θ - Al_2O_3 has already begun to transform into α - Al_2O_3 after 100 hours of oxidation. Most importantly, the XRD analysis shows that even after 100 hours of oxidation there are no detectable peaks to suggest the presence of significant amounts of NiO or spinel-type mixed oxides which are known to be detrimental to TBC performance. These results demonstrate that the CGDS deposition technique was successful at producing high quality CoNiCrAlY coatings that form alumina in preference to other detrimental mixed oxides when subjected to isothermal oxidation testing. This favourable oxidation behaviour is believed to be partly caused by the low oxide content in the as-sprayed CGDS coating. As mentioned previously, Tang et al. [87] had observed that in-

process particle surface oxidation was detrimental to the TGO growth mechanism as it promoted the formation of undesirable fast-growing non-alumina oxides. The low oxide content observed in the CGDS is thus expected to assist in delaying the onset of these undesirable oxides. Additionally, it is believed that a grain refinement mechanism observed in the deposited material as a result of severe plastic deformation (as detailed in the previous chapter) also plays a part in the oxidation dynamics. Ajdelsztajn et al. [86] investigated the oxidation behaviour of a nanocrystalline NiCrAlY alloy deposited by HVOF and observed that the refined grain structure promoted the formation of a continuous and stable alumina oxide scale. This was suggested to be caused by enhanced diffusion of aluminum at the grain boundaries, thereby increasing the amount of alumina nucleation sites. The plastic deformation driven grain refinement mechanism observed in the CGDS coating may therefore have had a similar effect on the oxidation dynamics observed here.

The XRD spectra for the HVOF coatings shown in Figure 8.7 reveal various interesting features as well as an oxidation behaviour very similar to that of the CGDS coating. Firstly, the XRD scan of the as-sprayed HVOF coating exhibits a single-phase microstructure composed only of the γ -phase Co-Ni-Cr solid solution, as was the case for the CGDS coating. These results would suggest that the HVOF deposition process has also caused dissolution of the β -phase due to severe plastic deformation of the particles upon impact on the substrate. Furthermore, as observed for the CGDS coating, peak broadening of the γ -phase is also visible, once again suggesting a refinement of the grain structure. This is quite surprising for a thermal spray deposition process that is typically associated to thermally induced grain growth. However, it is important to recall that HVOF is a deposition process that uses a combination of thermal energy to soften and/or partially melt the sprayed material as well as kinetic energy to promote plastic deformation upon impact of the particles on the substrate. Based on these findings, it would appear that the HVOF coatings considered in this study were manufactured using spraying parameters that favoured the contribution of plastic deformation as opposed to thermal softening for successful coating deposition. After 5 hours of oxidation, the oxide scale is seen to be composed of α -Al₂O₃ as well as γ -Al₂O₃ and θ -Al₂O₃. Similarly to the CGDS coating, peaks associated to the β -phase are visible after 5 hours of oxidation and disappear after 25 hours for reasons mentioned previously. Following

100 hours of oxidation, the oxide scale is shown to be composed predominantly of α - Al_2O_3 with lesser amounts of γ - Al_2O_3 and θ - Al_2O_3 , as was the case for the CGDS coating. Conversely to the CGDS coatings however, small amounts of Cr_2O_3 are identified at this stage of the oxidation process. What is most significant is that once again there are no peaks to suggest the presence of NiO or mixed spinel-type oxides even after 100 hours of oxidation time. This is also seen in Figure 8.8 which shows the surface oxide morphology and elemental mapping of the HVOF coating after 100 hours of oxidation time.

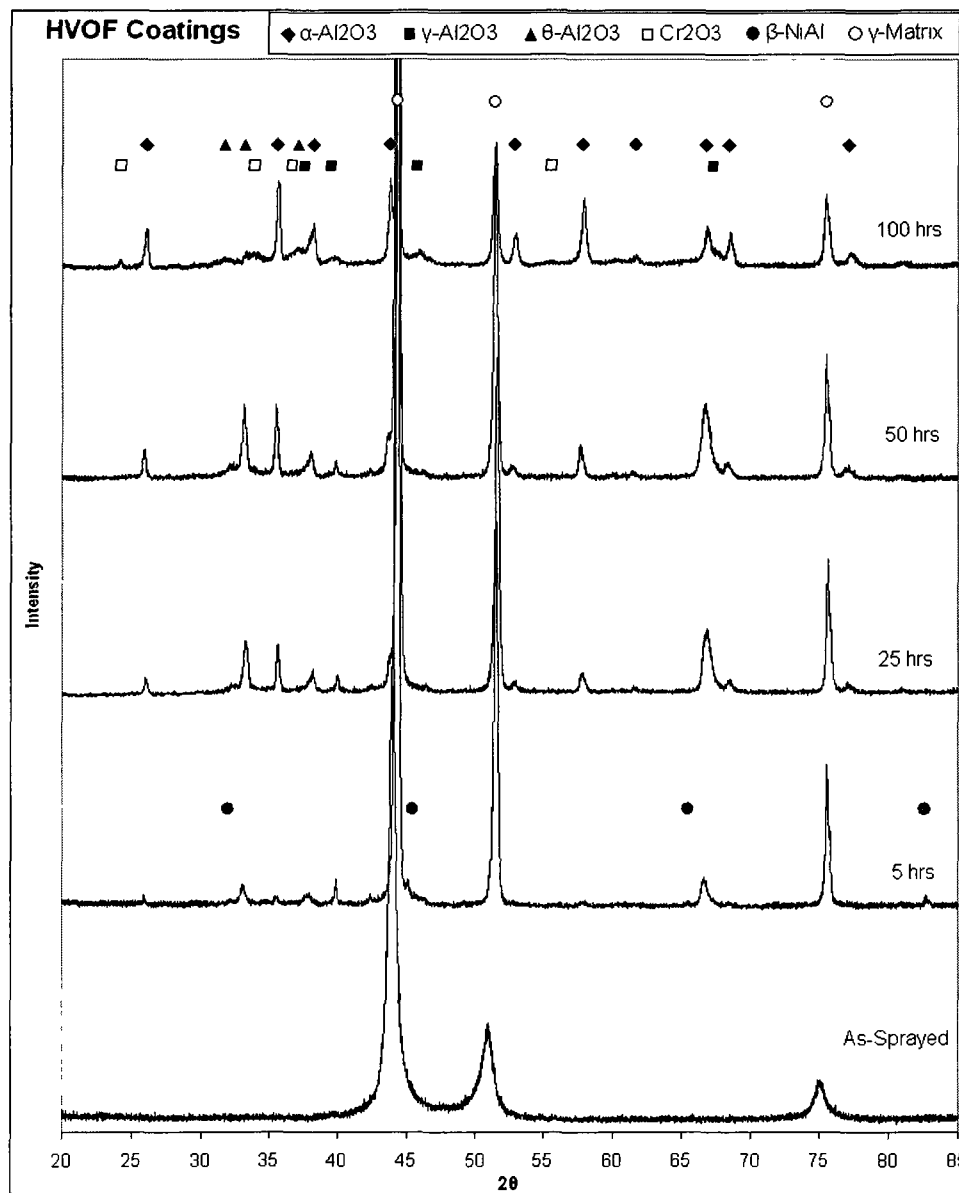


Figure 8.7: XRD spectra of the HVOF CoNiCrAlY coatings after various oxidation times at 1000°C

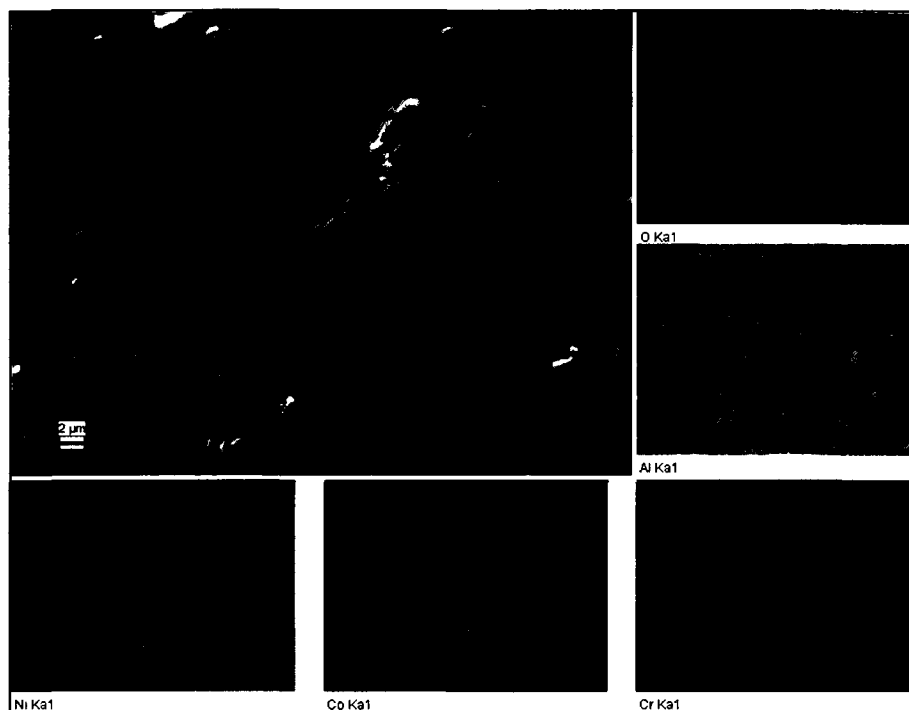


Figure 8.8: SEM image and EDS elemental mapping showing the surface oxide morphology of a CoNiCrAlY HVOF coating following 100 hours of oxidation at 1000°C

Once again, this figure shows that the oxide scale is continuous and predominantly composed of alumina. In agreement to the XRD spectra, elemental mapping also reveals the presence of chrome oxides (Cr_2O_3). The acicular morphology of the alumina oxide is once again present, thus suggesting similar oxidation dynamics to those observed in the CGDS coatings. These findings are particularly interesting, specifically those suggesting the absence of significant amounts of NiO and mixed spinel-type oxides, given that results of oxidation testing carried out on the same CoNiCrAlY alloy and reported by Tang et al. [92] suggest otherwise. In their work, Tang et al. [92] observed the onset of mixed spinel-type oxides on the surface of a conventional HVOF-sprayed CoNiCrAlY coating after only 24 hours of oxidation time at 1000°C. This demonstrates that both the CGDS and HVOF coatings presented in this study out-perform the HVOF coatings from the aforementioned reference by exhibiting a lower porosity and the formation of a stable alumina oxide scale that grows in preference to other non-desirable fast-growing mixed oxides. It has also been argued in this work that the present HVOF coating features a microstructure and properties that resemble more closely those of a CGDS coating than those of other HVOF coatings published in the literature. Perhaps the

only noticeable distinction between the CGDS and HVOF coatings is the appearance of Cr_2O_3 on the HVOF coating surface after 100 hours of oxidation. The onset of Cr_2O_3 on HVOF sprayed CoNiCrAlY coatings has been reported elsewhere [92] and was suggested to be linked to the reduction of Al diffusion activity in the coating, thereby resulting in the selective oxidation of Cr. This could be caused by either of the two following reasons: either diffusion of Al was inhibited due to the increased presence of embedded oxides resulting from the HVOF deposition process (when compared to CGDS), or the low Al diffusion activity is an indication that depletion of Al in the coating was becoming important, thus suggesting that the coating was nearing the end of its Al-rich lifecycle. Prolonged oxidation testing would be required to fully assess this issue. The fact that the CGDS coating did not exhibit the presence of detectable amounts of Cr_2O_3 demonstrates that its Al diffusion activity remains high even after 100 hours of oxidation. These findings seem to support the theory that depositing MCrAlY materials with lower temperature processes such as CGDS, and thereby limiting the coating oxide content, is beneficial to their oxidation behaviour.

Finally, observation of the XRD spectra for the APS coating after various oxidation times, as shown in Figure 8.9, reveals important differences when compared to the CGDS and HVOF coatings. After 5 hours of oxidation, strong peaks associated to undesirable NiO are observed in addition to the detrimental mixed spinel-type oxides previously identified in the as-sprayed condition. Once again, peaks indicated as “spinel” represent either a mixture of some/all of other spinel mixed oxides such as NiCr_2O_4 , NiAl_2O_4 , CoAl_2O_4 , CoCr_2O_4 and NiCo_2O_4 , or a substitutional solid solution of $(\text{Ni},\text{Co})(\text{Al},\text{Cr})_2\text{O}_4$. Weak peaks of $\alpha\text{-Al}_2\text{O}_3$ can also be identified after 5 hours of oxidation. As opposed to the CGDS and HVOF coatings, the β -phase is still not visible after 5 hours of oxidation, further demonstrating that Al was depleted throughout the spray process to an extent that the β -phase can no longer precipitate out. As oxidation time is increased up to 100 hours, it can be seen that the intensity of the peaks associated to NiO and spinel-type oxides also increases, while the intensity of the $\alpha\text{-Al}_2\text{O}_3$ peaks remains relatively low. The presence of Cr_2O_3 is also noticeable in the oxide scale. The presence of these various oxides is evidenced in Figure 8.10 which shows the surface oxide morphology and elemental mapping of the APS coating after 100 hours of oxidation time.

Figure 8.10 also shows that the oxide scale is composed of a sub-layer of α - Al_2O_3 with NiO and mixed spinel-type oxide protrusions. These findings are in accordance with those reported in another study [75] and prove that the important in-spray oxidation and consequent depletion of Al promotes the reaction of oxygen with other metallic constituents in the coating (Ni, Co, Cr), thereby favouring the formation of mixed spinel-type oxides and NiO.

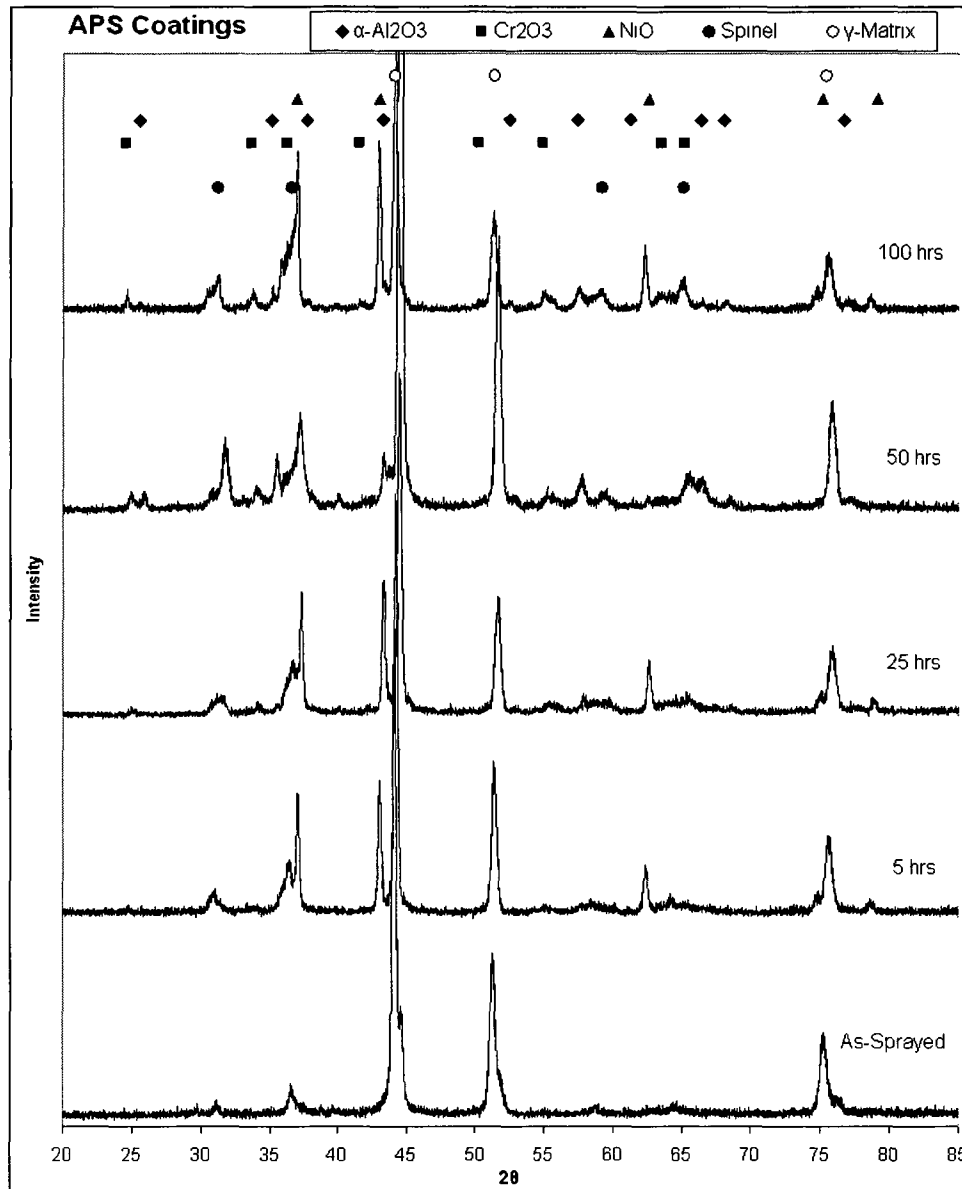


Figure 8.9: XRD spectra of the APS CoNiCrAlY coatings after various oxidation times at 1000°C. As suggested by Tang et al. [92], peaks indicated as “spinel” are believed to be spinel-type oxides and represent either a mixture of some/all of other spinel mixed oxides such as NiCr_2O_4 , NiAl_2O_4 , CoAl_2O_4 , CoCr_2O_4 and NiCo_2O_4 , or a substitutional solid solution of $(\text{Ni,Co})(\text{Al,Cr})_2\text{O}_4$.

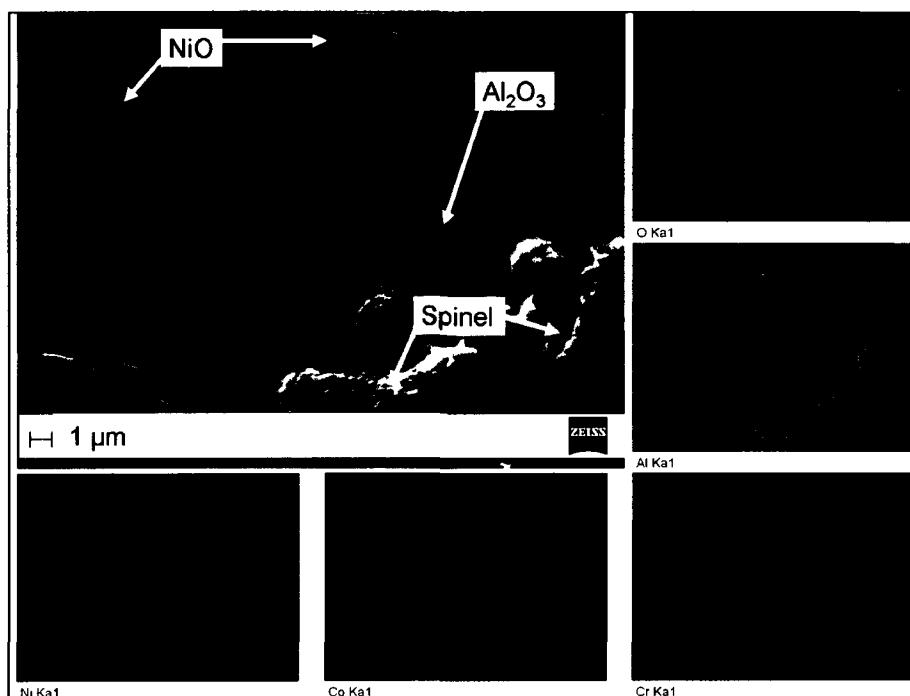


Figure 8.10: SEM image and EDS elemental mapping showing the surface oxide morphology of a CoNiCrAlY APS coating following 100 hours of oxidation at 1000°C

In summary, it appears that both the CGDS and HVOF coatings were successful in forming an alumina layer in preference to other mixed oxides upon oxidation testing. The formation of this protective alumina layer, which is characterized with a low diffusivity across its thickness, then reduces the rate of oxidation upon prolonged exposure to the high temperature gases. This explains why both the CGDS and HVOF coatings exhibit very low oxide growth rates after 100 hours of oxidation. Conversely, APS coatings showed the presence of significant amounts of spinel and other undesirable fast growing mixed oxides. The APS coating's inability to form a protective alumina layer as well as the large porosity networks observed in the coating structure explain the much larger oxide growth rate. These results demonstrate that the deposition technique and more specifically the resulting porosity and oxide content of the as-sprayed coating microstructure play an important role on the oxidation behaviour.

8.2 Nanocrystalline CoNiCrAlY Coatings Oxidation Behaviour

This section of the report presents the experimental results of the oxidation tests carried out on the nanocrystalline CGDS CoNiCrAlY coatings. Results obtained from these trials have been compared to those of the conventional CGDS coatings in order to verify the influence of a coating's grain structure on its oxidation behaviour.

8.2.1 Oxide Growth Rates

As for the conventional coating samples, the overall oxide growth rate for the nanocrystalline coating samples was determined by means of mass gain measurements. Results of this analysis are presented in Figure 8.11 as the average mass gain normalized per unit surface area for five coating samples. Once again, error bars have been included to illustrate the mass gain standard deviation obtained from this analysis.

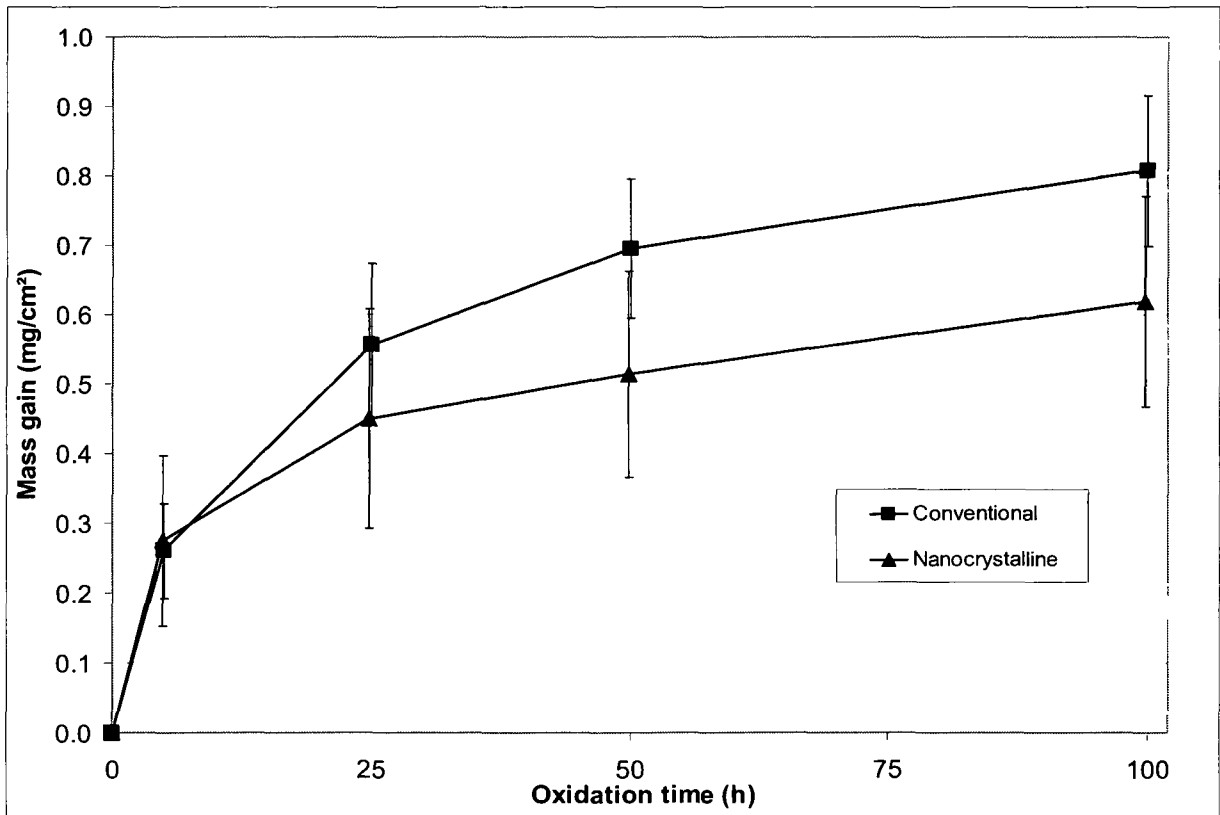


Figure 8.11: Normalized mass gain measurements of conventional and nanocrystalline coating samples as a function of oxidation time at 1000°C.

As can be seen from this figure, the mass gain analysis demonstrates that the nanocrystalline coatings generally experience a slower overall oxide growth rate when compared to the conventional coatings. It is also apparent that the nanocrystalline coatings experience a slightly increased mass gain in the early stages of oxidation (less than 5 hours). This suggests that the nanocrystalline microstructure promotes the formation of a protective alumina oxide scale in the early stages of oxidation which in turn helps inhibit additional oxidation of the coating upon further exposure. This is in accordance with findings reported by Ajdelsztajn *et al.* [86] who observed the oxidation behaviour of conventional and nanocrystalline NiCrAlY coatings manufactured by HVOF spraying. This study demonstrated that slower overall oxide growth rates were achieved with the nanocrystalline coatings as a result of their ability to rapidly form of a protective alumina oxide layer in the early stages of oxidation. It was explained that enhanced diffusion of aluminum at the grain boundaries, which are present in greater proportion in nanocrystalline microstructures, promotes the rapid formation of a dense, continuous and homogeneous alumina oxide layer in the early stages of oxidation. This stable alumina scale was then said to act as a diffusion barrier, thereby reducing the oxide growth rate upon prolonged exposure when compared to the conventional coating. This explanation of the oxidation behaviour of nanocrystalline coatings appears to agree with the overall oxide growth rate trends observed in this work. However, a more detailed investigation of the oxidation behaviour in the early stages of oxidation would be required to further validate this hypothesis.

Another important consideration is the influence of the different coating porosity on the recorded mass gain measurements. It has been previously discussed and demonstrated that increased porosity in a coating sample results in higher mass gain measurements during isothermal oxidation testing. This was explained by the fact that pores within a coating microstructure effectively increase the available surface area for the oxidation reaction to take place, thereby resulting in an increase of the measured mass gain. As such, direct comparison of the mass gain measurements for the nanocrystalline and conventional coatings considered in this work may not be entirely accurate given their different porosity levels. Based on previous findings, it is believed that nanocrystalline CoNiCrAlY coatings with a lower porosity level would lead to further reduction of the oxide growth rate, thereby revealing an

even greater improvement of the oxidation behaviour when compared to the conventional coatings. The fact that the nanocrystalline coatings considered in this study exhibit a slower oxide growth rate than the conventional coatings despite having a porosity level nearly three times larger is a clear indication of the potential benefits that fully dense nanocrystalline bond coats could offer.

Figure 8.12 shows the evolution of the oxide scale and depletion zone in the conventional and nanocrystalline CoNiCrAlY coatings as a function of oxidation time. After 5 hours of oxidation, both coatings exhibit a thin continuous oxide scale with a similar average thickness ($0.8\mu\text{m}$ and $1.2\mu\text{m}$ for the conventional and nanocrystalline coatings respectively). The slightly thicker oxide scale observed on the nanocrystalline coating is consistent with results from the mass gain measurements and supports the theory of the rapid initial growth of the alumina scale. Also, the typical two-phase γ/β microstructure is now visible in both coatings. The β -phase precipitates in the conventional coating are observed to have an equiaxed morphology whereas those in the nanocrystalline coating appear in the form of thin elongated strips. Once again, the reappearance of the β -phase is attributed to the fact that the oxidation test acts as a heat treatment and manifests itself as a decrease in the density of point and line defects, thereby decreasing the solubility of Al in the γ -matrix and causing the β -phase to once again become visible in the form of precipitates. Depletion of the β -phase near the coating surface is also observed in both coatings. As oxidation time increases, both coatings experience similar oxide scale growth rates. The rate of change in thickness of the oxide scales for these two coatings appears to be parabolic and agrees well with the mass gain measurements reported in Figure 8.11.

An interesting distinction between both coatings is that the oxide scale on the nanocrystalline coating appears to be generally more uniform in thickness when compared to that on the conventional coating. This is most obvious after 100 hours of oxidation and is typically desirable for improved TBC performance [67]. The differences in oxide scale morphologies will be discussed further in section 8.2.3.

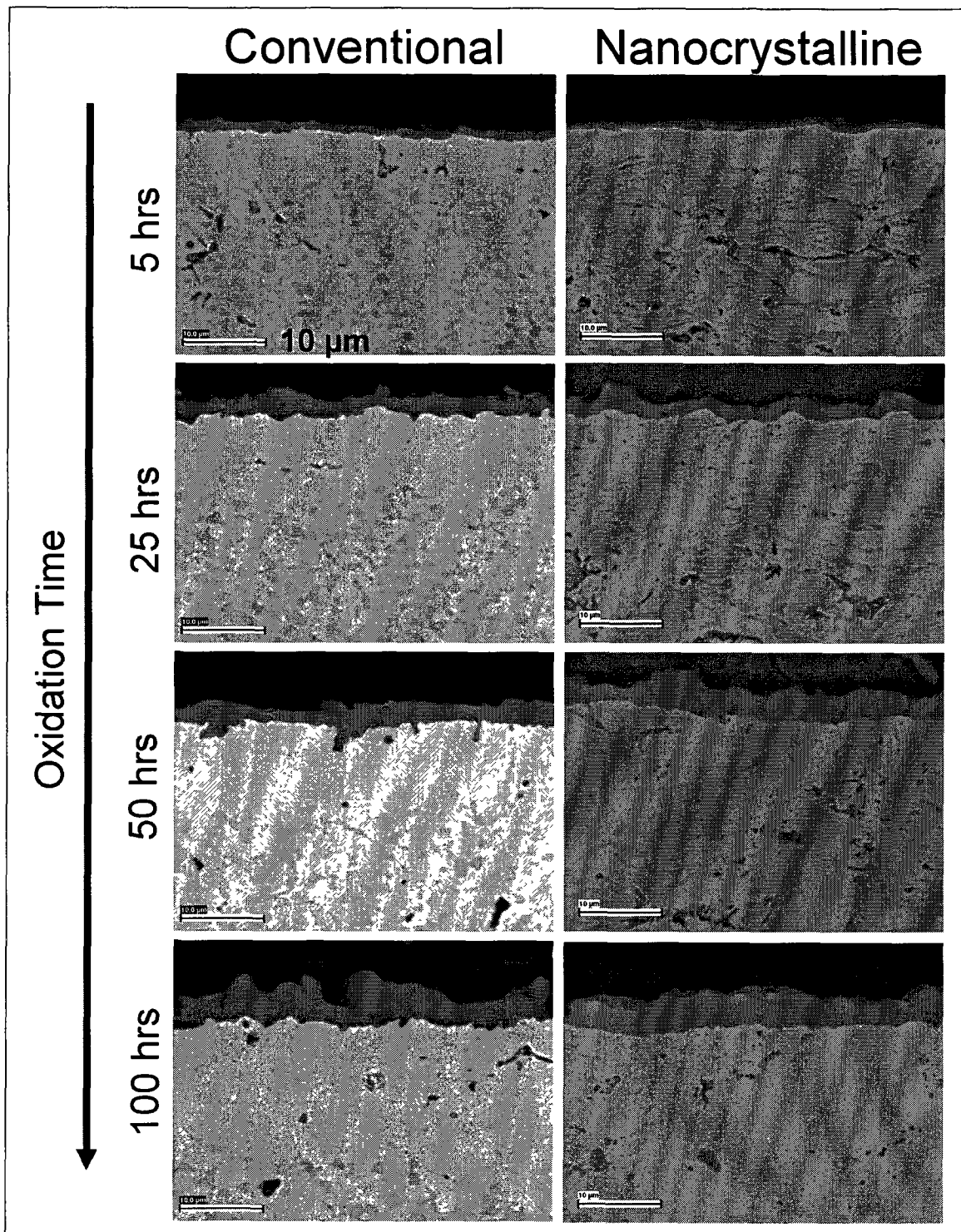


Figure 8.12: SEM images of conventional and nanocrystalline coating cross-sections showing the evolution of the oxide scale and β -phase depletion zone with increasing oxidation time

8.2.2 Oxide Scale Composition

As for the conventional CGDS coating samples, an XRD analysis was carried out on the nanocrystalline coating samples after each different oxidation period in order to identify the composition of the oxide scale that formed on its surface. The XRD spectra obtained from this analysis are presented in Figure 8.13. When compared to the XRD spectra of the conventional CGDS coatings (Figure 8.5), it can be seen that both coatings exhibit very similar oxide compositions after each oxidation period. After 5 hours of oxidation, both coatings are observed to form an oxide scale composed of α -Al₂O₃ as well as other metastable alumina phases such as γ -Al₂O₃ and θ -Al₂O₃. As mentioned previously, the appearance of such metastable alumina phases upon oxidation of CoNiCrAlY alloys is not uncommon [67, 75, 92] and is believed to be attributed to rapid heating rates of the coating samples at the onset of each oxidation test. At this stage of the oxidation process, small β -phase peaks also become visible, thus further confirming that the oxidation test has acted as a heat treatment allowing the β -phase to precipitate out, as evidenced in Figure 8.12. After 25 hours of oxidation, peaks associated to the β -phase are still just barely visible, whereas they had disappeared in the case of the conventional CGDS coatings due to increasing depletion zone thickness. The presence of the β -phase after 25 hours suggests that the growth of the depletion zone in the nanocrystalline coating is slower, thereby also indicating a slower oxidation rate. Although the thickness of the depletion zone is difficult to identify precisely on Figure 8.12, the presence of weak β -phase peaks in the XRD spectra would agree with the previously reported mass gain measurements.

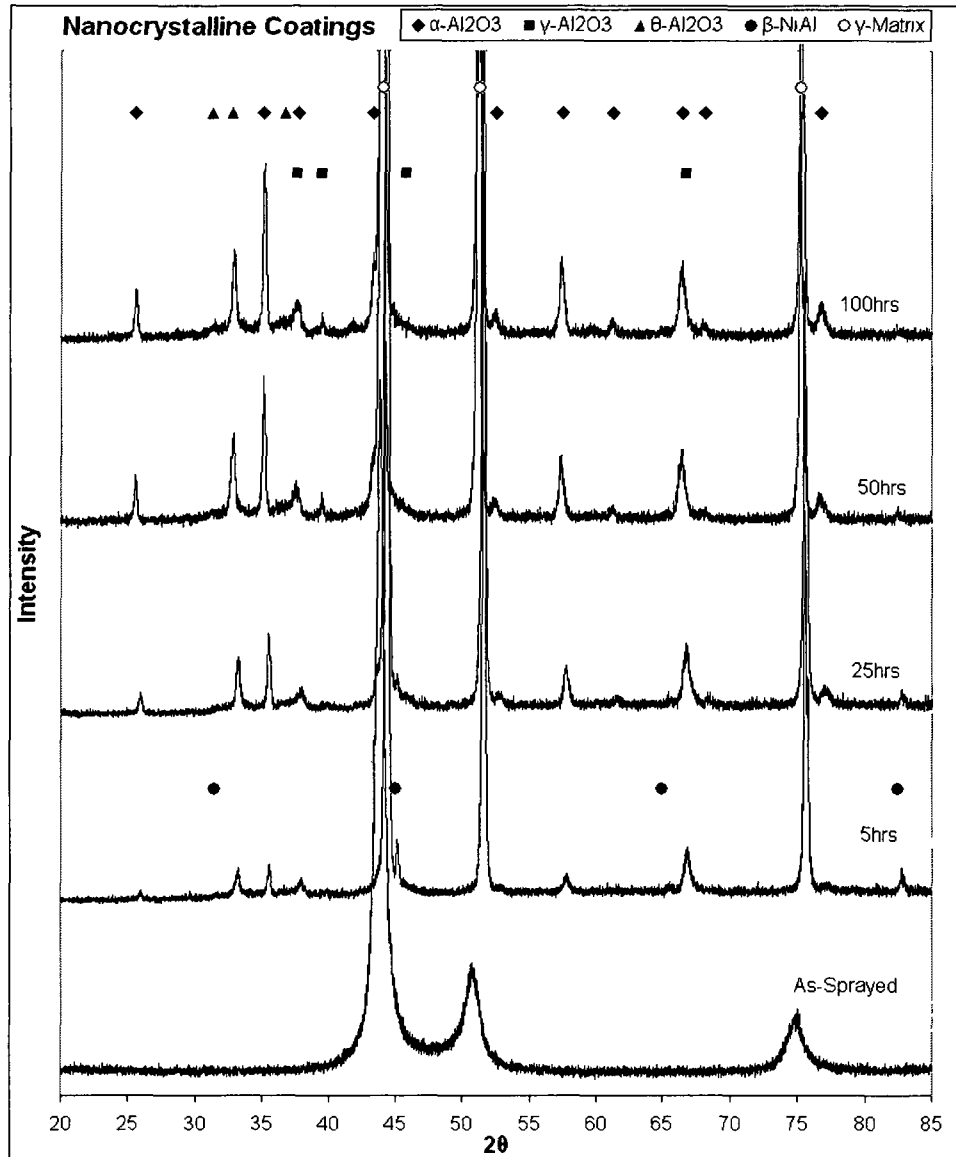


Figure 8.13: XRD spectra of a CS nanocrystalline CoNiCrAlY coating after various oxidation times at 1000°C

Increasing the oxidation time to 100 hours shows the emergence of $\alpha\text{-Al}_2\text{O}_3$ as the dominant oxide for the nanocrystalline coating, with lesser amounts of $\gamma\text{-Al}_2\text{O}_3$ and $\theta\text{-Al}_2\text{O}_3$. Most importantly, as was the case for the conventional coating, the XRD analysis shows that even after 100 hours of oxidation, the nanocrystalline coating exhibits no detectable peaks to suggest the presence of significant amounts of detrimental NiO or spinel-type mixed oxides. These findings demonstrate that the grain structure of the bond coat, whether conventional or nanocrystalline, does not have a significant influence on the composition of the oxide scale.

On the other hand, the fine grain structure of the nanocrystalline coating does accelerate the initial oxidation process, which leads to a more rapid formation of the protective alumina layer when compared to the conventional coating and ultimately decreases the oxidation rate upon prolonged exposure to high temperature gases. In summary, the ability of the CGDS process to minimize in-spray oxidation as well as to preserve the nanocrystalline microstructure of the cryomilled feedstock throughout deposition significantly improves the coatings oxidation behaviour.

8.2.3 Surface Oxide Morphology

The general morphology of the oxide scale for the nanocrystalline coating was also investigated and compared to that of the conventional coating by means of SEM imaging and EDS elemental mapping. Figure 8.14 shows the surface oxide morphology of a nanocrystalline coating after 100 hours of oxidation. When compared to results obtained with the conventional coating, it can be seen that the nanocrystalline coating also exhibits a continuous oxide scale composed of alumina having an acicular morphology. Also, as was observed in the conventional coating, partial transformation of the metastable θ -Al₂O₃ phase into α -Al₂O₃ appears to have occurred: the acicular oxide morphology typical of θ -Al₂O₃ is still visible after 100 hours of oxidation, however the XRD analysis clearly reveals α -Al₂O₃ as the dominant oxide. These similarities in oxide scale morphology are in accordance with findings from the XRD analysis and were predictable given the very similar oxide scale compositions discussed previously.

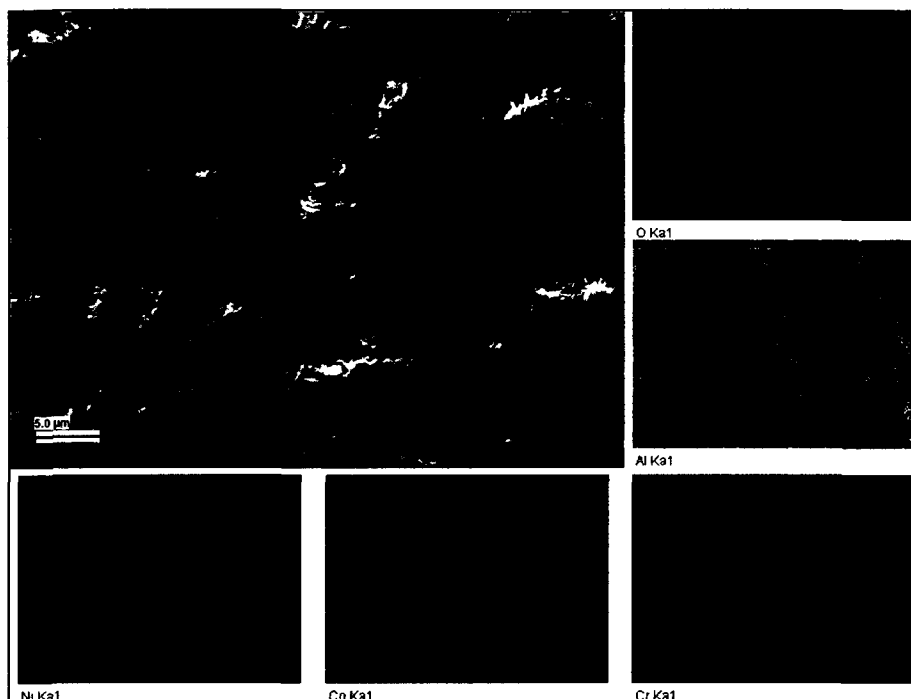


Figure 8.14: SEM image and elemental mapping of the oxidized surface of a CS nanocrystalline CoNiCrAlY coating after 100 hours of oxidation at 1000°C

The only significant difference between both coatings with respect to the oxide morphology pertains to oxide scale uniformity. This was also observed upon investigation of the coating cross-sections after various oxidation times (Figure 8.12). Closer inspection of the elemental mapping results for the surface oxides of the conventional CGDS coating (shown in Figure 8.6) reveals the detection of some regions with greater concentrations of Co, Ni and Cr in addition to Al. This is believed to be attributed to the detection of metallic constituents in the underlying bond coat material, thereby identifying regions on the surface where the alumina oxide scale is relatively thin. These results suggest that the oxide scale formed on the conventional coatings is not uniform in thickness. It is important to mention here that quantitative analysis of elemental maps collected on rough surfaces can lead to misinterpreted results due to the occurrence of shadowing effects (regions hidden behind an obstruction will not be detected and appear as dark areas on the maps). As such, the results presented here are intended for use as a qualitative description of the general uniformity of the oxide scale. Thin regions in the oxide scale are believed to act as weaker diffusion barriers, thereby offering less protection and possibly representing areas that would be more vulnerable to the formation of mixed oxide protrusions upon prolonged oxidation testing beyond 100 hours. The non-

uniform oxide scale thickness may be related to the bimodal grain size distribution observed in the conventional CS coating. Regions of the coating with a small grain size would tend to promote the formation of a dense and homogenous alumina layer due to the enhanced diffusion of Al along the grain boundaries, whereas regions composed of coarse grains would promote the formation of a thinner alumina layer. Contrarily to the conventional coating, the elemental mapping from the nanocrystalline coating surface reveals no detection of metallic constituents from the underlying bond coat, thereby suggesting a more homogeneous and uniformly distributed oxide scale. This is once again believed to be attributed to the enhanced diffusion of aluminum at the grain boundaries. The greater proportion of grain boundary area in the nanocrystalline coating promotes diffusion of aluminum and therefore encourages the nucleation of alumina [86, 92]. As such, the alumina nucleation sites on a nanocrystalline coating are well dispersed, thereby promoting the rapid formation of a homogeneous and uniform alumina oxide scale.

8.3 Summary

Based on the findings presented in this chapter, the following conclusions can be made. For the conventional CoNiCrAlY coatings, overall oxide growth rates were found to be minimal for the HVOF coatings, followed closely by the CGDS coatings. Although oxidation is often considered as a surface phenomenon, it was shown that porosity plays an important role on the mass gain measurements during oxidation testing, and as such the full three-dimensional structure of the coating must be taken into account. Coatings with low porosity and low oxide content were shown to have the lowest oxide growth rates. The oxide scale for the CGDS and HVOF coatings was predominantly composed of alumina, without the presence of NiO or spinel-type mixed oxides. Conversely, the APS coating featured the onset of significant amounts of undesirable NiO and mixed spinel-type oxides in the early stages of oxidation testing. Given that the HVOF coating considered in this study featured characteristics more similar to CGDS coatings than to other HVOF coatings in the literature, results from this work demonstrate that low-temperature processing of CoNiCrAlY materials is highly beneficial to their oxidation behaviour, and therefore CGDS represents an interesting and promising alternative for their manufacturing.

The nanocrystalline CGDS coatings exhibited a slower overall oxide growth rate when compared to the conventional CGDS coatings despite their larger porosity level. These nanocrystalline coatings were shown to rapidly form a protective alumina scale in the early stages of oxidation as a result of enhanced diffusion of Al at the grain boundaries. The fine grain structure of these coatings was not found to influence the oxide scale composition, however it was shown to lead to a more uniform and homogeneous oxide scale morphology due to the more evenly dispersed alumina nucleation sites at the grain boundaries. It is believed that significant improvements to the bond coat oxidation behaviour could be achieved by manufacturing nanocrystalline bond coats using the CGDS deposition technique.

Conclusions

The general purpose of this research work was to study CoNiCrAlY coatings manufactured by CGDS and to explore their potential for the advancement of bond coats and thermal barrier coatings technology. Intended as the launching point of a broader ongoing research project, the work addressed in this thesis was designed to focus solely on the properties and behaviour of the CoNiCrAlY bond coatings without interactions from the ceramic top coat. This was achieved by establishing a number of specific research objectives that were then investigated by means of numerous experimental trials. The work emphasized the influence of various coating microstructures by considering both conventional and nanocrystalline CGDS coatings and comparing their properties and behaviour with coatings prepared by other thermal spraying techniques.

The feasibility of depositing CoNiCrAlY bond coatings using the CGDS technique was first verified. Both conventional and nanocrystalline coatings were successfully deposited using this technique with a pre-existing nozzle and non-optimized spraying conditions taken from a previous study. However, as expected, the resulting coatings featured high levels of visible defects and improvement of the spraying conditions was required. Optimization of the CGDS spray parameters was thus carried out using a combination of numerical and experimental trials. The influence of various spraying parameters was investigated and optimal spraying conditions were determined. While these conditions were said to be optimal in this work, it is important to note that they are only optimal for the specific nozzle considered and that they are also bounded by physical limitations pertaining to the experimental apparatus. With this in mind, it is believed that further improvement to coating quality could likely be achieved by means of more complex nozzle designs. Coatings manufactured with the optimized spraying parameters were shown to exhibit good build-up thickness, minimal oxide contents and low levels of porosity (1.0% and 2.9% for the conventional and nanocrystalline coatings respectively).

A detailed microstructural investigation of the initial as-received and as-cryomilled CoNiCrAlY feedstock powders as well as the resulting optimized conventional and

nanocrystalline CGDS coatings was then performed. This was carried out in order to verify whether any microstructural changes occurred in the deposited material throughout the CGDS coating process. This was motivated by the fact that findings from other studies in the literature have shown that thermally induced microstructural transformations (grain growth and in-spray oxidation) in thermal sprayed coatings have a detrimental influence on the bond coat oxidation behaviour. Results obtained in the present work demonstrate that microstructural changes do occur in the CoNiCrAlY material during CGDS deposition. For the conventional CGDS coatings, grain refinement of the γ -phase matrix and dissolution of the β -phase precipitates were observed. These changes were attributed to the severe plastic deformation involved upon particle impact during deposition. Conversely, the nanocrystalline CGDS coatings were not observed to exhibit such microstructural changes simply because they had already taken place during the cryomilling process. These findings are of significant interest as they disagree with the generally accepted claim that CGDS has the ability to preserve a material's microstructure throughout the spraying process.

The oxidation behaviour of the conventional and nanocrystalline CGDS coatings was then investigated. This was achieved by a series of isothermal oxidation tests involving mass gain measurements to determine oxide growth rates as well as SEM and XRD analyses to verify the oxide scale compositions. For comparison purposes, identical oxidation tests were carried out using coatings prepared by APS and HVOF spraying. Results from these experiments demonstrated that low porosity and low coating oxide contents reduced the oxide growth rate and promoted the formation of a stable alumina oxide scale in preference to other detrimental mixed oxides. While the HVOF coatings were shown to feature a slightly lower oxide growth rate than the conventional CGDS coatings, it was also demonstrated that these HVOF coatings had a microstructure more similar to that of CGDS coatings than to that of other HVOF coatings in the literature. This finding further reinforces the idea that low temperature processing of CoNiCrAlY coatings is beneficial to their oxidation behaviour. Oxidation tests carried out on the nanocrystalline CGDS coatings also revealed that a fine grain structure promotes the rapid growth of a uniform alumina oxide scale in the early stages of oxidation, thereby forming an effective diffusion barrier and reducing the oxide growth rate by inhibiting subsequent oxidation.

The work carried out in this thesis has demonstrated that manufacturing CoNiCrAlY coatings by means of CGDS deposition is not only possible, but that its lower processing temperatures may also offer interesting advantages with respect to coating oxidation behaviour in comparison to other thermal spray techniques. Furthermore, with its ability to produce coatings characterized with fine grain structures (either by means of a grain refinement process of the conventional material or by preserving the fine grain structure of the nanocrystalline material), the CGDS deposition technique represents a promising opportunity for the production of high performance CoNiCrAlY bond coats.

Future Work

The following is a list of various topics that could be of interest in subsequent studies for the advancement of the work carried out in the present thesis.

1. Throughout this work, the CGDS CoNiCrAlY coatings were said to be manufactured using optimized spraying parameters. However, it is important to note that these parameters were determined for a specific nozzle geometry, which was relatively simple. Future work should be carried out to develop new nozzle geometries having greater particle acceleration capabilities. It is believed that improved coating quality could be achieved using this approach. Further improvement of the CGDS equipment to ensure better stability at elevated gas pressures and temperatures could also lead to improvements of coating quality. Finally, it would be very interesting to see whether such improvements of the CGDS system could allow CoNiCrAlY coatings to be manufactured using nitrogen as the main propellant gas, thereby making the process much more economical and industrially attractive.
2. A more detailed investigation of the oxidation behaviour of CGDS CoNiCrAlY coatings should be carried out in the early stages of oxidation. Specifically, a comparison of the oxidation behaviour for both conventional and nanocrystalline coatings in the first five hours of oxidation would be interesting. Measurements of the real-time oxide growth rates and characterization of the oxide scale composition would reveal further valuable information with respect to the influence of the nanocrystalline grain structure on the initial oxide formation dynamics, which seems to play an important role on the subsequent stability of the oxide scale, as shown in this work.
3. Results obtained in this thesis revealed that the HVOF coating exhibited an excellent oxidation behaviour in comparison to other HVOF coatings in the literature. This was attributed to the fact that the HVOF coating featured more microstructural similarities with the low-temperature CGDS coating than with other HVOF coatings. An in-depth

microstructural analysis of the HVOF coatings considered in this work, involving TEM analysis, would provide further insight with respect to this claim.

4. While this work has focused only on the oxidation behaviour of CoNiCrAlY coatings, this material is also reported to exhibit good hot-corrosion resistant properties. Some work could thus be carried out to investigate the hot-corrosion behaviour of these coatings. The influence of the deposition technique (CGDS vs. thermal spray) and also coating microstructure (conventional vs. nanocrystalline) could be examined.
5. Finally, perhaps one of the more interesting next steps with respect to this work would be the manufacturing of actual TBC system specimens. Larger CGDS coating samples on inconel substrates should first be produced and optimized, followed by the application of a zirconia top coat. Thermal cycling testing could be performed to verify the durability of TBC systems prepared with both conventional and nanocrystalline CGDS bond coats. The performance of these coatings could also be compared with that of TBC systems prepared using HVOF sprayed bond coats. Lastly, it would be interesting to investigate various TBC system heat pre-treatments and their effect on the subsequent development of the TGO.

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