

# **Next-Generation Bond Coats in Thermal Barrier Coating Systems Using High Entropy Alloys**

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## School of Graduate Studies

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## **Abstract**

# **Next-Generation Bond Coats in Thermal Barrier Coating Systems Using HighEntropy Alloys**

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**Concordia University, 2025**

TBCs are vital thermal protection systems used in harsh environments, comprising a ceramic top coat and a metallic bond coat. The bond coat enhances adhesion between the top coat and substrate while providing oxidation and corrosion resistance at elevated temperatures. Traditionally, MCrAlX alloys have served as bond coats, where M represents Ni, Co, or NiCo, and X denotes reactive elements such as Y, Hf, Ta, or Si.

As turbine components face increasingly severe operating conditions, conventional bond coats exhibit limitations including phase instability, accelerated oxidation, and reduced durability under thermal cycling. To overcome these issues, high-entropy alloys (HEAs) have emerged as promising alternatives due to their superior thermal and chemical stability. Their multi-principal-element composition improves oxidation and corrosion resistance, optimizes diffusion behavior, and mitigates degradation mechanisms commonly observed in MCrAlX coatings.

HEAs promote the formation of a dense, continuous, and adherent thermally grown oxide (TGO) layer, minimizing spallation and enhancing coating durability. Their low oxygen permeability, stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> formation, and resistance to phase segregation further extend service life in high-temperature applications.

This study investigates the influence of HEA compositions, with and without reactive elements—and the effect of low-temperature spray techniques such as HVOF and HVAF (M3 and i7 guns). It also examines the impact of vacuum heat treatment on bond coat behavior. Comparative analyses with conventional MCrAlX coatings highlight the advantages, challenges, and potential of HEAs as next-generation bond coats in advanced TBC systems.

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I am also deeply grateful to Dr. Rogerio Lima for his support, mentorship, and valuable discussions throughout my research. His expertise in thermal spray technologies and coatings greatly contributed to the technical depth of this work.

Furthermore, I extend my heartfelt appreciation to my friends and family, who have been a constant source of encouragement throughout this journey. A special note of gratitude goes to my fellow lab mates for the stimulating discussions and shared moments of laughter, which helped ease the pressures of rigorous research. I also thank my family for their unwavering belief in me and for expecting nothing less than success during my Ph.D. program.

This work was conducted as part of the project entitled “Engineering the Next Generation of Thermal Barrier Coatings (TBCs) Via Thermal Spraying,” supported by the National Research Council of Canada (NRC) Surftec Industrial R&D Group and NRC’s National Program Office. I sincerely appreciate the support of NRC and the Surftec Industrial R&D Group members, whose contributions were instrumental in this investigation and study. I also acknowledge the financial support provided by the Consortium de recherche et d’innovation en transformation métallique (CRITM) through its Support Program for Research and Innovation Organizations (PSO). Lastly, I extend my gratitude to NRC’s academic collaborator, Concordia University, for its support in this project.

## **Dedication**

*To my incredible family, whose unwavering support, boundless love, and endless encouragement have been the foundation of my journey. Your belief in me has been my greatest strength, and for that, I am forever grateful.*

## **Contribution of the authors**

This thesis follows a manuscript-based format, with Chapter 1 as the introduction, incorporating the first published review paper, and Chapter 7 as the conclusion. The remaining chapters include published or submitted manuscripts. Mr. Shahbazi, as the primary author, conducted the experiments, analyzed the results, and examined the findings. Manuscript details, including publication information and co-author contributions, are provided below.

Chapter 3, entitled “Characterization of HVOF-Sprayed FeCoNiCrAl HEA Bond Coats: A Comparative Study with MCrAlX,” is currently under review in the Journal of Thermal Spray and Technology. This work has been co-authored by Dr. Rogerio S. Lima, with Prof. Pantcho Stoyanov and Prof. Christian Moreau serving as the supervisors of the project.

Chapter 4, entitled “Optimization of HVOF Process Parameters for Enhancing FeCoNiCrAl HEA Bond Coatings in Thermal Barrier Systems” is a published paper in the Journal of Thermal Spray technology. This work has been co-authored by Dr. Rogerio S. Lima, with Prof. Pantcho Stoyanov and Prof. Christian Moreau serving as the supervisors of the project.

Chapter 5, entitled “Effect of Microstructure on Oxidation Resistance and TGO Formation in FeCoNiCrAl HEA Coatings Deposited by Low-Temperature HVOF Spraying” is a published paper in the Journal of Materials. This work has been co-authored by Dr. Rogerio S. Lima, with Prof. Pantcho Stoyanov and Prof. Christian Moreau serving as the project supervisors.

Chapter 6, entitled “Comparative Study of High-Entropy Alloy Bond Coats with and without Reactive Elements for Improved Oxidation Resistance in Thermal Barrier Coating Systems” is a published paper in the Journal of Surface and Coatings Technology. This work has been co-authored by Dr. Rogerio S. Lima, with Prof. Pantcho Stoyanov and Prof. Christian Moreau serving as the project supervisors.

H. Shahbazi conducted the literature review, designed the experiments (DOE) and methodology, performed all experiments, analyzed and examined the results, and collected the data. He carried out all characterization analyses, interpreted the results, and led the discussion. Additionally, he wrote the original draft and was responsible for reviewing and

editing the manuscript. C. Moreau, P. Stoyanov, and R. Lima supervised the research and revised the manuscript. All authors reviewed the final manuscript and approved its contents.

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## List of Abbreviations

|       |                                             |
|-------|---------------------------------------------|
| HVOF  | High-Velocity Oxygen Fuel                   |
| HVAF  | High-Velocity Air Fuel                      |
| CS    | Cold Spray                                  |
| APS   | Air Plasma Spraying                         |
| VHT   | Vacuum Heat Treatment                       |
| DE    | Deposit Efficiency                          |
| EDX   | Energy-Dispersive X-ray Spectroscopy        |
| FESEM | Field Emission Scanning Electron microscopy |
| XRD   | X-ray Diffraction                           |
| DBTT  | Ductile-to-Brittle Transition Temperature   |
| CTE   | Coefficient of Thermal Expansion            |
| IFO   | In-Flight Oxidation                         |

# **1 Chapter One: Introduction & Literature Review**

Thermal barrier coatings (TBCs) conventionally consist of a ceramic top coat and a metallic bond coat, serving as a vital protective layer for turbine components to mitigate the detrimental effects of severe thermo-mechanical conditions and operating environments [1]. The ceramic top coat, predominantly composed of yttria-stabilized zirconia (YSZ), serves the dual purpose of safeguarding against degradation at elevated temperatures and shielding the underlying layers from thermal cycling-induced stresses experienced by engine components [2,3]. In contrast, the primary role of the metallic bond coat is to provide protection to the superalloy substrate components against extensive oxidation and corrosion, while simultaneously enhancing the adhesive strength between the ceramic top layer and the substrate components [4]. The most commonly used materials for bond coats are MCrAlYs ( $M = \text{Ni, Co, or Ni+Co}$ ), since they exhibit excellent mechanical properties and are highly resistant to oxidation and corrosion [5]. In addition, MCrAlYs exhibit a relatively low ductile-to-brittle transition temperature (DBTT) combined with a high chromium content, which helps inhibit cracking during thermal cycling [6]. The incorporation of yttrium within MCrAlY coatings effectively impedes the outward diffusion of aluminum, consequently leading to an enhancement in the adhesion of the thermally grown oxide (TGO) scale [7]. The oxide scale of MCrAlY in TBCs, primarily composed of aluminum oxide ( $\text{Al}_2\text{O}_3$ ), is an integral part of the functioning mechanism of bond coat systems as it provides insulation, prevents oxidation, and contributes to the overall TBC durability before it reaches a critical thickness [8]. While MCrAlY is well established as a TBC bond coat material, its performance and efficiency at elevated temperatures ( $>1100\text{ }^\circ\text{C}$ ) are deteriorated [9,10]. Since the efficiency of gas turbine engines is directly correlated to their operating temperature, turbine industries are focusing on new TBC systems that would allow them to operate at higher temperatures, thus being more fuel-efficient and sustainable [9]. Due to their stable microstructure and promising mechanical properties at elevated temperatures, high entropy alloys (HEAs) are an emerging class of advanced materials that can be a quality choice for TBC bond coats and replace traditional MCrAlY bond coat systems [3]. HEAs are characterized by equimolar or close to equimolar concentrations of five or more principal elements, with each of the constituent elements ranging between 5 at% and 35 at%. Since they have inherently high configurational entropy ( $>1.5 R$ , where  $R$  is the gas constant), the solid-solution phases of HEAs are stabilized, resulting in oxidation resistance at elevated temperatures [11]. Additionally, other core effects such as lattice distortion, sluggish diffusion, and the cocktail effect contribute to bond coat's enhanced properties, including improved bonding and mechanical strength, fracture toughness, corrosion, oxidation, and

creep resistance at high temperatures [12]. Since the demand for HEAs is increasing, the potential benefits of HEAs coupled with thermal spraying technologies can help address numerous challenges associated with TBC systems [13]. Although thermally sprayed HEAs have been studied for several applications, the exploration of thermal sprayed HEAs as TBC bond coats has not been fully explored [14]. Furthermore, although high-velocity oxy-fuel (HVOF) is acknowledged for its capability to generate high-quality bond coats, alternative lower-temperature techniques such as high-velocity air-fuel (HVAF) and cold spraying (CS) present viable means for fabricating HEA coatings. In this way, the powders would not undergo the melting process, hence, reducing in-flight oxidation and improving bond coat properties [15]. The application of CS, HVOF, and HVAF techniques for depositing HEA coatings has attracted attention in bond coat applications, thereby potentially introducing a novel research avenue for TBCs [14,16,17]. Therefore, the primary objective of this review is to undertake a comprehensive evaluation and analysis of the material selection process for HEA bond coats, the microstructure characteristics of thermally sprayed HEA bond coats, and the physical properties exhibited by thermally sprayed HEA coatings. A brief explanation of oxidation resistance, coefficient of thermal expansion (CTE), and TGO is presented in this chapter, as well as a comparison to conventional bond coats in TBC systems.

## **1.1 Historical composition of bond coats and selecting HEA elements for bond coat applications**

### **1.1.1 Historical bond coat composition**

**Figure 1-1** briefly summarizes significant milestones in the development of bond coats. Since the 1950s, diffusion aluminum alloys have been used to protect the hot regions of gas turbine engines due to their low cost and wide availability[18]. During the initial years of the 1970s, the introduction of NiCrAlY overlay coatings marked a significant advancement in mitigating corrosion and oxidation within the high-temperature regions of industrial equipment, with particular emphasis on gas turbine blades [19]. The predominant challenges faced by coated components subjected to elevated temperatures in oxidizing environments were the occurrence of oxide scale spallation and cracking. In the mid-1970s, additional investigations were conducted to enhance the stability and adhesion of the  $\text{Al}_2\text{O}_3$  oxide scale formed on coatings subjected to elevated temperatures. This was achieved by alloying the  $\text{Al}_2\text{O}_3$  oxide scale with Yttrium (Y), Hafnium (Hf), Platinum (Pt), and Silicon (Si) [20].

During the 1980s, researchers dedicated their efforts to examining the mechanical properties and compatibility of NiCrAlY coatings when applied to superalloy substrates. Within this timeframe, scientific investigations focused on enhancing the mechanical characteristics of NiCrAlY coatings and establishing compatibility between the coating layer and the superalloy substrate. These objectives were successfully accomplished through the addition of tantalum (Ta) as an alloying element to the NiCrAlY coatings. A variety of NiCrAlY coatings with different chromium (Cr) and aluminum (Al) contents have been developed to meet the diverse environmental and technological conditions found in various gas turbines [21]. It should be noted that most of the coatings discussed above contain an overall Al content of between 10 and 14 wt.%. Therefore, these coatings were classified as  $\text{Al}_2\text{O}_3$  formers. Notably, in 1984, the initial iteration of NiCoCrAlY coatings emerged, offering enhanced ductility attributed to the inclusion of cobalt (Co). Moreover, the phase structure of a bond coat plays a significant role in determining its microstructure and composition. MCrAlX coatings typically consist of two primary phases:  $\gamma$  and  $\beta$ . The  $\gamma$ -phase represents a solid solution rich in (Ni, Co) with a face-centred cubic (FCC) structure, while the  $\beta$ -phase is an intermetallic NiAl (or CoAl) phase characterized by a body-centred cubic (BCC) structure. Depending on the specific composition, additional phases such as Cr-rich  $\alpha$  and  $\text{Ni}_3\text{Al}$   $\gamma'$  may also be present. The  $\gamma$ -phase has the ability to dissolve various metallic elements, including Fe, Cr, Al, as well as certain refractory metals like Mo, Nb, and Re [22]. By acting as an aluminum reservoir, the  $\beta$ -phase enables the formation of a protective  $\text{Al}_2\text{O}_3$  scale that effectively shields the coating against high-temperature oxidation. The proportion of the  $\beta$ -phase within the coating structure significantly influences its stability and resistance to oxidation at elevated temperatures [23]. Co has been identified as a key element for enhancing hot corrosion resistance by controlling the fraction of  $\gamma'/\gamma$  eutectic phases ( $\gamma$ -Ni and  $\gamma'$ - $\text{Ni}_3\text{Al}$ ) within the coating structure [24]. Increasing the cobalt content from 24 to 30 at% reduces the fraction of  $\gamma'$ - $\text{Ni}_3\text{Al}$  while increasing the amounts of  $\gamma$ -Ni and  $\beta$ -NiAl, which is attributed to the expansion of the  $\gamma + \beta$  region to lower temperatures. The presence of the  $\gamma$  phase (Ni) in the eutectic mixture with  $\gamma'$ - $\text{Ni}_3\text{Al}$  improves the thermodynamic stability of the coating system. The specific microstructure exhibited by the eutectic phases provides resistance to corrosion attacks [25]. At elevated temperatures, the presence of Co within the Ni-Co-Cr-Al system modifies the phase equilibrium, thereby impeding undesirable phase transitions within the MCrAlX (where X represents reactive elements such as Y, Hf, Ta, Re, Zr, etc.) coating structure [26]. Moreover, the incorporation of Co in the coating structure can augment the solubility of Cr within the  $\gamma$ -phase and eliminate the formation of  $\alpha$ -Cr in the microstructure. Consequently, the

introduction of Co in NiCoCrAlY coatings has been demonstrated to bolster their mechanical stability [24]. In the years following 2000, because of its performance at high temperatures, modifications of MCrAlX were performed, specifically through work on reactive elements. Due to the increase in TBC lifetime requirement at elevated temperatures, these have been studied extensively [23,27]. A recent study of MCrAlX coatings has looked at the effects of doping, multilayered/graded design, and surface conditions on the thermal properties of the coatings [23]. After the discovery of HEAs in 2004 by Cantor [28] and its application to coatings in 2014, potential performance improvement was expected for BCs operating at higher temperatures [29].

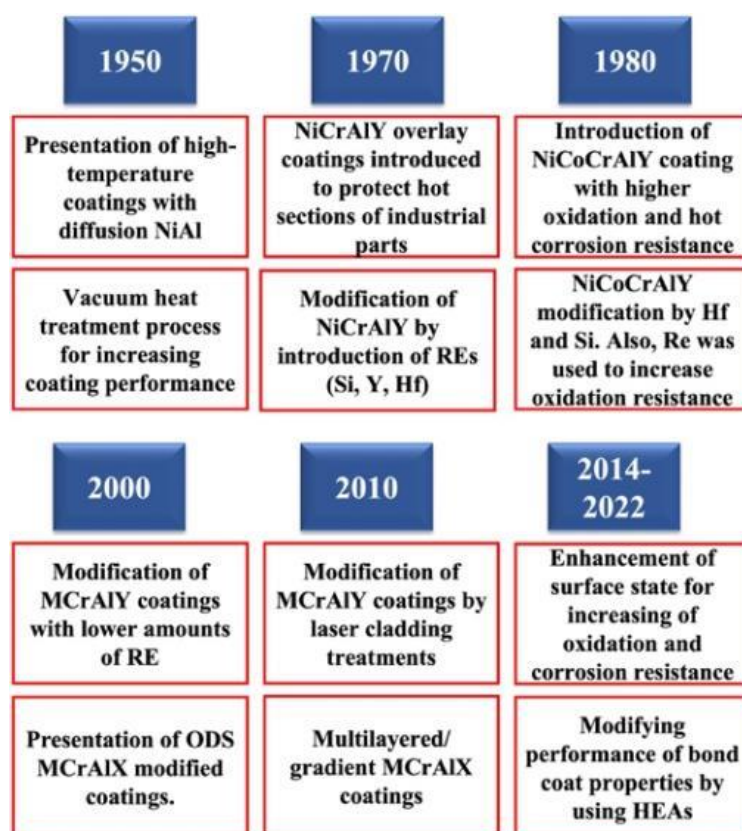


Figure 1-1. Evolution and Enhancements of MCrAlX Coatings from 1950 to 2022, (ODS: oxide dispersion strengthened).

### 1.1.2 HEA composition selection for bond coats

Selecting suitable HEA feedstocks for thermal spray applications is challenging. The microstructure and properties of the resulting coatings depend on the process, synthesis

routes, and HEA composition. Interestingly, identical alloy compositions can yield coatings with diverse characteristics by adjusting feedstock synthesis techniques and thermal spray parameters. This flexibility enables the customization of coatings for specific applications, including oxidation resistance, corrosion resistance, wear resistance, and enhanced plasticity. To explore different compositions and predict their phase composition and properties, high-throughput experiments and computational techniques are valuable tools [30]. The range of thermal spray processes provides opportunities to manipulate HEA coating characteristics and tailor them to meet specific application requirements [31]. HEAs, with their unique and promising properties, exhibit the potential to serve as viable alternatives to commercial MCrAlX materials. When searching for ways to enhance HEA compositions, several key properties of bond coats should be taken into account: **(a)High oxidation resistance**: The formation of a protective TGO primarily comprising  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, the most favorable oxide scale, is essential. During the initial oxidation stage, non-protective oxides such as Cr<sub>2</sub>O<sub>3</sub> and NiO are formed due to the sluggish diffusion of Al from the bond coat to the surface. Although Al exhibits higher reactivity towards oxygen compared to Cr and Ni, its diffusion rate is insufficient to sustain the exclusive formation of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> scale [32]. TGO spinel types (AB<sub>2</sub>O<sub>4</sub>), such as spinel Ni (Cr, Al)<sub>2</sub>O<sub>4</sub>, are considered less desirable due to their brittleness and lower adhesion compared to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The presence of such spinel phases may have an impact on the microstructure of the HEA bond coat [33]. The presence of titanium and silicon in HEAs promotes the formation of Al<sub>2</sub>O<sub>3</sub>, contributing to improved oxidation resistance. However, it should be noted that the addition of Ti and Si may lead to reduced mechanical properties and the occurrence of rumpling phenomena within the HEAs [34]. **(b)Compatibility, Ductility, Integrity**: HEAs used in bond coat applications require compatibility with nickel-based alloys as substrates. This is achieved by incorporating Ni or other alloying elements, including Co, Cr, Cu, Fe, Mn, Pd, and Pt, which maintain a stable solid solution structure at high temperatures without undergoing phase transitions with nickel. In addition to compatibility, HEA compositions must exhibit ductility to achieve the desired strength-ductility trade-off necessary for bond coat applications. This allows for accommodating higher fracture toughness. Incorporating multiple phases, such as FCC and BCC structures, effectively fulfills this requirement. To preserve the structural integrity of TBC systems during thermal cycling, it is essential to establish a gradual CTE transition between the top coat, bond coat, and substrate. This gradual transition minimizes the risk of separation or detachment of the top coat from the substrate, ensuring the overall structural integrity of the TBC system [35,36]. **(c)High thermal stability**: it is crucial that no first-order phase

transformations take place within the specified temperature range of application [36]. In conclusion, developing a HEA for a bond coat application requires a careful selection of desirable candidates with specific characteristics. These candidates should demonstrate high oxidation resistance. This can be achieved by prioritizing forming a protective  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> scale and minimizing the presence of less desirable TGO spinel phases. Compatibility with nickel-based alloys is another crucial aspect, requiring alloying elements that maintain a stable solid solution structure and contribute to ductility, enabling a desired balance between strength and ductility. Moreover, establishing a gradual CTE transition within the TBC system is vital to ensure structural integrity during thermal cycling. Finally, it is essential to prioritize high thermal stability by avoiding first-order phase transformations within the designated temperature range. By considering these factors, researchers can effectively identify and develop HEA candidates suitable for bond coat applications.

Presently, endeavors have been undertaken to optimize the phase and composition of this alloy category, specifically targeting TBC bond coats, utilizing artificial intelligence and software tools such as PANDAT, FactSage, MTDATA, MatCalc, JMatPro, and Thermo-Calc [11]. However, the modelling of multi-element systems comprising more than four elements is currently constrained by the scarcity of initial data sources, which heavily rely on experimental data [3]. In the realm of thermal spraying, it is envisaged that the amalgamation of prior alloying expertise with artificial intelligence holds the potential to yield improved outcomes. The realm of HEAs presents notable complexities due to the intricate interplay of multiple elements and diverse processing methods. The thermal spray process, characterized by high temperatures and rapid solidification, further complicates the understanding of HEA behavior.

## **1.2 Microstructural characteristics of thermally sprayed HEA bond coats**

A coating displaying a fine-grained structure generally demonstrates a strong balance between strength and ductility. Consequently, as-sprayed HEA coatings may manifest distinct phase compositions in contrast to their as-cast counterparts [37,38]. The phase constituents in HEAs are influenced by both the synthesis techniques of the feedstock and the thermal spraying processes. Through mechanical alloying, powders can undergo nanoscale mixing, resulting in improved solid solubility and the formation of solid solution phases prior to thermal processing [39]. Powders subjected to air plasma spray (APS) or HVOF processes experience additional phase transformations as a result of melting or partial melting. In

contrast, materials processed through cold spraying retain their composition due to low processing temperatures. In the case of the Al-Co-Cr-Fe-Ni system, the mechanical alloying process predominantly yields a BCC phase, as the aluminum acts as a stabilizer for the BCC structure during the alloying process [40].

The microstructure of HEA bond coats can be affected by several factors, such as the presence of oxides and pores, the HEA powder structure (BCC, FCC and/or (BCC + FCC)), the coating parameters (spray distance, substrate roughness, and coating thickness), as well as particle characteristics (dimension and morphology) [41,42]. Recent research has indicated that the sluggish diffusion, which is a fundamental characteristic of HEAs, can lead to the formation of nanocrystalline structures and hinder the growth of oxide scales at elevated temperatures [43]. This results in an increase in the bond coat oxidation resistance at high temperatures, which will ultimately result in an increase in the TBC lifetime. In most thermally sprayed HEA bond coats, solid solution strengthening mechanisms also contribute to enhancing hardness [44]. In HEAs, the strengthening mechanism primarily involves solid solution strengthening, which arises from significant lattice distortion caused by disparities in atomic sizes among various constituent elements [45].

The presence of oxides during the spraying process significantly influences the microstructure of HEA bond coat, thereby impacting the spallation of the bond coat layer. Oxidation is a prominent defect observed in thermally sprayed HEA coatings [46]. The rigid nature of randomly distributed oxides, in contrast to the relatively soft HEA matrix, disrupts the chemical uniformity of the coating.

Therefore, the role of oxides becomes crucial, especially in bond coat applications within TBC systems [47,48]. It is important to note that oxides exhibiting high porosity can compromise corrosion resistance and lead to accelerated failure of components [49–51]. The formation of oxide precipitates is a prominent concern when HEAs consist of elements that are susceptible to oxidation [52]. In contrast, coatings deposited by cold spraying [15,17,36], HVAF [16], and HVOF [14,46] showed minimal oxidation. As an illustration, in the context of CS, the operation temperature is relatively lower (typically at least 500 °C) than the metals' melting point, leading to a diminished amount of particle oxidation. To conclude, through the meticulous selection of thermal spray techniques, elements, and powder feed rate, it is possible to effectively reduce oxide pore formation, thereby mitigating corrosion and minimizing the possibility of component failure.

In a recent study by Ossiansson *et al.* [16], two HEA compositions (CrFeCoNi and AlCrFeCoNi) were used and compared to conventional bond coat types (AMDRY-386 and AMPERIT-410.860). The study examined the microstructure of the HVOF-sprayed coating, which displayed a densely packed structure with minimal oxide inclusions. Comparisons were made between the CrFeCoNi coatings, specifically the microstructures of short nozzle (4L4C) and long nozzle (5L4C), revealing greater oxidation and thicker oxide stringers in the former [53,54]. The length of the spraying nozzle influenced the coating's density and the thickness of oxide stringers, with longer nozzles resulting in denser coatings and thinner oxide stringers. In-flight oxidation (IFO) potentially occurred in both coatings due to factors like material chemistry and particle size distribution. The presence of 20 at% of Al in the CrFeCoNi coatings did not significantly contribute to the formation of oxide scales. In contrast, the AlCrFeCoNi coatings exhibited a two-phase microstructure, benefiting from the presence of Al, which enhanced their resistance to oxidation [55]. The AF-386 (NiCoCrAlYSiHf) microstructure demonstrated an even distribution of distinct phases, indicating minimal alteration of the feedstock material during the HVOF-spray process. The APS-coating exhibited lamellar splats with occasional unmolten particles, likely attributed to incomplete melting. APS-410 (NiCoCrAlY) displayed a more porous microstructure characterized by larger interlamellar splat regions, oxide stringers, and globular pores compared to the other coatings [56].

In the study conducted by Hsu *et al.* [46], the researchers investigated the microstructure and chemical composition of thermal-sprayed coatings produced from HEAC1 ( $\text{NiCo}_{0.6}\text{Fe}_{0.2}\text{Cr}_{1.5}\text{SiAlTi}_{0.2}$ ) and HEAC2 ( $\text{NiCo}_{0.6}\text{Fe}_{0.2}\text{Cr}_{1.3}\text{SiAl}$ ) using three different techniques: APS, HVOF, and Warm Spraying (WS), as illustrated in **Figure1-2**. The APS coatings were characterized by a lamellar structure consisting of a substantial phase along with dispersed oxide stringers, which could be attributed to the elevated temperature during the spraying process. On the other hand, the HVOF technique is characterized by a relatively low spraying temperature and high particle velocity. In the case of warm-sprayed HEA coatings, researchers observed minimal oxide content, which can be attributed to the precise control of particle temperature during the process. Significantly, HVOF processed HEA coatings exhibit a denser microstructure with minimal oxide formation, in contrast to HEA coatings produced via HVOF methods [34,57]. The presence of dense coatings is highly advantageous for bond coat applications as they effectively protect the substrate against oxidative deterioration and preserve its structural integrity by preventing the formation and

growth of detrimental oxides in and around any existing pores. This effectively inhibits any subsequent detrimental oxidation and ensures the preservation of the intended material composition within the deposited coatings [58].

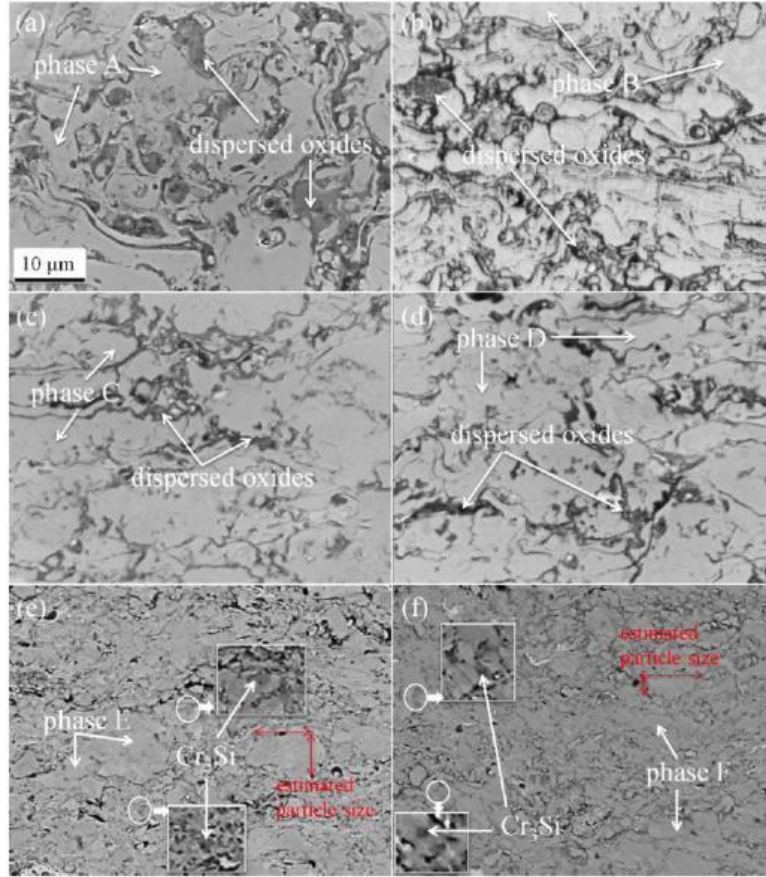


Figure 1-2 Cross-sectional examinations were performed on the as-sprayed HEA coatings, (a) APS-HEAC1, (b) APS-HEAC2, (c) HVOF-HEAC1, (d) HVOF-HEAC2, (e) WS-HEAC1, and (f) WS-HEAC2 (Ref 46).

Ma *et al.* [36] conducted thermal cycle testing on TBC specimens with an HVOF-deposited HEA bond coat in a controlled laboratory setting. The specimens were exposed to a temperature of 1150 °C ( $\pm 10$  °C) in air. Each thermal cycle involved a 60-minute hold at 1150 °C, followed by forced air cooling for 15 minutes. Visual inspections were carried out after each cycle, and the weight of the specimens was measured every 10 cycles. After 100 cycles, the researchers performed microstructural analysis on the TBC samples before and after the cyclic oxidation test at 1150 °C. They also examined the top views of the test samples. No signs of spallation or damage to the TBC were observed in the top view. However, the microstructure of the tested TBC indicated a tendency for cracking and

separation of the topcoat near the interface with the HEA bond coat. The weight gain chart demonstrated that there was no further increase in weight after the initial transient oxidation stage, which resulted in a gain of approximately  $0.2 \text{ mg/cm}^2$  [36].

Finally, in a study carried out by Löbel *et al.* [59], a comprehensive investigation was undertaken to examine the microstructures of the coatings. The AlCrFeCoNi coating, fabricated using the HVOF process, exhibited a well-defined lamellar structure with visible oxide and partially formed pores between the spray particles. The coating exhibited a porosity level of approximately  $0.6 \pm 0.2\%$ . Although the individual spray particles displayed a dendritic structure, there was no significant variation in material composition. In contrast, the coatings produced via the HVAF process did not display prominent oxide lamellae due to the decreased thermal input during the coating process, leading to the suppression of oxygen absorption. Additionally, the HVAF coatings exhibited significantly lower porosity than the HVOF coatings, with values of approximately  $0.3 \pm 0.1\%$ . This meticulous examination of the microstructures provides valuable insights into the distinct characteristics and properties of HVOF and HVAF coatings, thereby enhancing our understanding of their potential applications in various industries.

**Table 1-1** provides a concise compilation of the key properties exhibited by thermally sprayed HEAs tailored for use in bond coat applications. HVAF and HVOF have emerged as the predominant methods employed thus far. Their utilization has proven advantageous due to the relatively low operating temperatures involved, which enable the formation of denser microstructures compared to alternative techniques such as APS or flame spraying. These denser structures are highly desirable for BC applications within TBC systems.

### **1.3 Effect of heat treatments on the microstructure and properties of HEA bond coats**

Heat treatments will generally modify the bond coat microstructure. This can improve its mechanical properties, such as toughness and corrosion resistance. Heat treatments can also be used to modify the phase stability of the bond coat, which improves thermal stability and oxidation resistance [60,61]. Additionally, heat treatments influence the microstructure and phase stability of HEA bond coats and has been extensively investigated [62]. Moreover, heat treatment can be used to tailor the bond coat properties to the specific application and to reduce the risk of bond coat corrosion and oxidation [61,63].

Smith *et al.* [64] studied a CoCrFeMnNi HEA bond coat, observing that a heat treatment at 1000 °C for 1 hr brought about a fine-grained microstructure. This treatment led to improved mechanical properties, including enhanced strength and ductility, contributing to the bond coat's superior performance. The fine-grained microstructure allowed for better stress distribution throughout the component, increasing strength and ductility. Furthermore, the heat treatment also resulted in a reduction in porosity, which further improved the material's mechanical properties.

In another study by Wu *et al.* [65], an AlHfNbTiZr HEA bond coat was examined. A heat treatment at 800 °C induced a transformation from a single-phase solid solution to a dual-phase microstructure. This phase transformation improved the bond coat's thermal stability and resistance to oxidation, making it more capable of withstanding high-temperature environments. Wang *et al.* [66] explored a FeCoCrNiCu HEA bond coat using tailored heat treatment processes involving rapid solidification and subsequent annealing. This approach induces the precipitation of coherent nanoscale precipitates within the bond coat's microstructure, enhancing strength and resistance to creep deformation. The study found that the rapid solidification process resulted in a gradient microstructure, with homogeneous, nanometer-sized, coherent precipitates within the matrix. This produced a very strong material with high creep resistance. Furthermore, Chen *et al.* [67] investigated an AlCrFeNiTi HEA bond coat. They discovered that a heat treatment at 900 °C for 2 hrs induced secondary phase precipitation, enhancing its corrosion resistance and elevated-temperature stability.

Collectively, these studies demonstrate the significant influence of heat treatment on HEA bond coat microstructure and phase stability. By precisely controlling heat treatment parameters, researchers can manipulate the microstructure, induce favorable phase transformations, and enhance the mechanical properties, thermal stability, oxidation resistance, and creep resistance of HEA bond coats within TBC systems. This means that with careful control of heat treatment, researchers can create bond coats with optimized properties for TBC systems. These bond coats are highly resistant to thermal cycling, oxidation, and creep, while also having improved mechanical properties.

#### **1.4 Coefficient of thermal expansion of HEAs**

The extensive utilization of metallic bond coatings in TBCs can be attributed to two key factors. Firstly, it is crucial to consider the disparity in CTE between the YSZ ceramic topcoats ( $\sim 10\text{--}11 \times 10^{-6}/\text{K}$ ) and the metallic Ni-based substrates ( $\sim 13 \times 10^{-6}/\text{K}$ ) [68,69]. On the

contrary, BC materials possess an intermediate CTE, enabling them to serve as an intermediary layer capable of accommodating thermal stresses within the TBC system. Secondly, the presence of bond coats is essential for TBC systems, for which the porous top coat is typically produced through APS, as they provide protection against substrate corrosion and oxidation. In a TBC system, having a high CTE for the topcoat is generally advantageous. The topcoat's high CTE allows it to expand and contract more closely with the underlying substrate and bond coat as they heat and cool during thermal cycling. This close match in CTE helps to reduce the build-up of thermal stresses and strains within the TBC system. By minimizing the thermal mismatch between layers, a high CTE topcoat promotes improved coating adhesion, reduced spallation, and enhanced durability. Therefore, a higher CTE is typically considered beneficial for the topcoat in a TBC system [70]. During cooling, a martensitic phase transformation in substrate superalloys occurs from  $\beta$  to  $\gamma$  phases, which could build up tensile stress in the top coat, which is linearly proportional to  $E_{TC} \cdot \Delta\alpha_{TC-BC} \Delta T$ , where  $E_{TC}$  is the Young's modulus of the top coat,  $\Delta\alpha_{TC-BC}$  is the difference in thermal expansion between top coat and bond coat, and  $\Delta T$  is the applied temperature difference [71].

There is a distinct absence of published studies that specifically investigate the CTE of thermally sprayed HEA bond coats. This prominent research gap underscores a significant void in the current literature, emphasizing the urgent need to address this aspect through further research and comprehensive investigation. Despite the crucial role of the CTE in designing TBC systems, the CTE values of potential HEA bond coats remain unexplored. Limited research exists on the characterization of the CTE of HEAs at elevated temperatures, with only two studies comparing it to MCrAlY materials. These studies highlight the potential of HEAs as alternative materials to conventional MCrAlY, warranting further investigation in the context of TBC systems[34,60]. The corresponding data can be found in **Table 1-1**, and a detailed description of the results is provided in the subsequent paragraph.

Furthermore, it is important to note that the CTEs of the HEA bond coat and YSZ topcoat are closer than the CTEs of MCrAlY bond coat and YSZ. Hsu *et al.* [60] conducted a characterization study on a heat-resistant coating composed of a HEA with the composition of  $NiCo_{0.6}Fe_{0.2}Cr_{1.5}SiAlTi_{0.2}$ , specifically designed for high-temperature applications. The research conducted by the authors involved the fabrication of the HEA through spark plasma sintering. The study revealed that the HEA exhibited remarkable thermal stability, high hot hardness, low thermal conductivity, and a reduced coefficient of thermal expansion (CTE) compared to its MCrAlY counterparts. The CTE of the HEA was then investigated at various

temperatures and compared to that of MCrAlY and Ni-based substrates (CMSX4 and Inconel 718). The results demonstrated that the CTE of the HEA increased from  $10$  to  $15 \times 10^{-6}/\text{K}$  within the temperature range of  $200\text{ }^{\circ}\text{C}$  to  $800\text{ }^{\circ}\text{C}$ , while the MCrAlY exhibited a relatively higher CTE range of  $14$  to  $19 \times 10^{-6}/\text{K}$  at similar temperatures.

Due to its single-phase FCC structure, the MCrAlY showed a higher CTE ( $\sim 16.8 \times 10^{-6}/\text{K}$ ) value compared to that of  $\text{NiCo}_{0.6}\text{Fe}_{0.2}\text{Cr}_{1.5}\text{SiAlTi}_{0.2}$  HEA (BCC structure) ( $\sim 13.9 \times 10^{-6}/\text{K}$ )[72].

Table 1-1 Properties of HEAs as promising bond coat materials for TBCs.

| HEA BCs                                                                                                                | Coating method | Phases observed                           | CTE (x 10 <sup>-6</sup> /K) | TGO (Thickness $\mu$ m)        | TGO type                                                                                           | Oxidation behaviour                                                |
|------------------------------------------------------------------------------------------------------------------------|----------------|-------------------------------------------|-----------------------------|--------------------------------|----------------------------------------------------------------------------------------------------|--------------------------------------------------------------------|
| AlCrFeCoNi (Ref 16)                                                                                                    | HVAF           | BCC                                       | -                           | At 1000 °C = 3.1 and 4.3       | Cr <sub>2</sub> O <sub>3</sub> & Al <sub>2</sub> O <sub>3</sub>                                    | No visible spallation was observed (low oxidation rate)            |
| NiCo <sub>0.6</sub> Fe <sub>0.2</sub> Cr <sub>1.5</sub> SiAlTi <sub>0.2</sub> (Ref 46, 60)                             | HVOF & WS      | FCC + BCC                                 | ~13.9                       | -                              | -                                                                                                  | Very good oxidation resistance (at 1100 °C up to 336 cycles)       |
| AlCoCrNiSi <sub>2</sub> (ref 36)                                                                                       | HVOF & APS     | B2+BCC                                    | -                           | -                              | -                                                                                                  | Good oxidation resistance up to 1000 °C                            |
| Ni <sub>0.2</sub> Co <sub>0.6</sub> Fe <sub>0.2</sub> CrSi <sub>0.2</sub> AlTi <sub>0.2</sub> (Ref 50)                 | HVOF           | BCC                                       | -                           | -                              | -                                                                                                  | Specific weight gain = 3.8 mg cm <sup>-3</sup> (at 1100 °C & 100h) |
| Al <sub>1.4</sub> Co <sub>2.1</sub> Cr <sub>0.7</sub> Ni <sub>2.45</sub> Si <sub>0.2</sub> Ti <sub>0.14</sub> (Ref 14) | HVOF           | FCC + BCC                                 | -                           | At 1050 °C= 3.7 for 100 cycles | Al <sub>2</sub> O <sub>3</sub> & NiAl <sub>2</sub> O <sub>4</sub>                                  | Excellent oxidation resistance (up to 336 cycles at 1100 °C)       |
| MCrAlY (ref 14)                                                                                                        | HVOF           | BCC to FCC (With the consumption of NiAl) | -                           | At 1050 °C= ~4 for 100 cycles  | Al <sub>2</sub> O <sub>3</sub> & NiAl <sub>2</sub> O <sub>4</sub> & Cr <sub>2</sub> O <sub>3</sub> | Good oxidation resistance up to 1000 °C                            |

\*FCC: face center cubic

\*BCC: body center cubic

\*B2: an order body center cubic

\*WS: Warm Spray: Modified HVOF technique

\*MCrAlY: AMDRY 365-4

Another study by Jadhav *et al.*[34] investigated FeCoCrNi<sub>2</sub>Al, FeCoCrNiAl<sub>0.3</sub>, NiCoCrAlSi, and FeCoNiAlTi<sub>0.4B</sub> HEA compositions by means of spark plasma sintering.

The evolution of the CTE of several HEA coatings as a function of temperature (200-1200 °C) is presented in **Figure1-3**, alongside the evolution of the CTE for the Ni-based superalloy (substrate), the standard MCrAlY bond coat, and a generic Al<sub>2</sub>O<sub>3</sub> top coat. As can be observed in **Figure1-3**, the CTE of the materials tends to increase with increasing temperatures. In general, the CTE of 6-8 wt.% YSZ is around 10-11. It is desirable for the bond coat CTE to be close to this value. However, there are no studies on the CTE of HEAs used as bond coats. Therefore, using HEAs may offer a promising approach to achieving the desired CTE matching between the bond coat and topcoat [73–75]. Of notable interest, beyond 800 °C, the CTE of the MCrAlY bond coat visibly increases from the range of 12-16×10<sup>-6</sup>/K to 25×10<sup>-6</sup>/K, which shows a certain limitation of this material with increasing temperature. On the other hand, the HEAs retain a CTE that is close to that of the substrate. By tailoring the choice of HEA, such as FeCoNiAlTi<sub>0.4</sub>, it seems possible to choose a HEA that would have an intermediate CTE between the top coat Al<sub>2</sub>O<sub>3</sub> and the substrate, further defending the use of HEAs as bond coats.

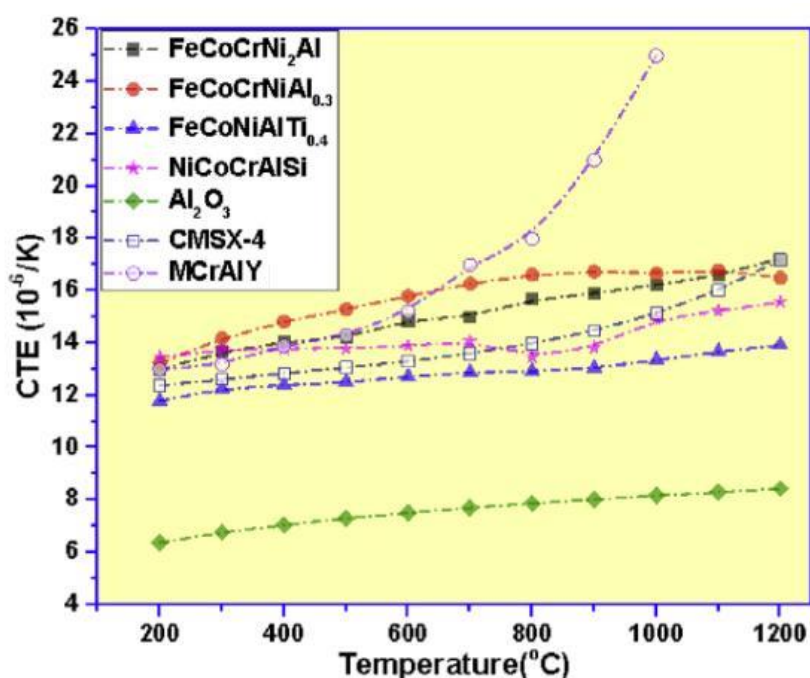


Figure 1-3 Behaviour of the CTE of several HEAs as compared to that of the Ni-based superalloy (CMSX-4), MCrAlY, and Al<sub>2</sub>O<sub>3</sub> (Ref 34).

## 1.5 Oxidation resistance of HEAs bond coat

HEA coatings exhibit favorable resistance to oxidation when compared to conventional materials, indicating promising performance [76–78]. In the context of TBC bond coats, investigations on oxidation behavior are essential, and the manipulation of material design

can be influential in regulating oxidation rates. Oxidation resistance is needed when materials are exposed to elevated temperatures in extreme environments [79]. Extensive research efforts have been dedicated to investigating the oxidation behavior of a variety of HEA coatings to gain a comprehensive understanding of their performance in this regard [31].

Cai *et al.* [80] analyzed laser clad  $\text{Al}_x\text{CrFeCoNi}$  HEA coatings, specifically investigating their oxidation behavior. The study revealed that increasing the Al content in the coatings led to reduced oxidation rates. This decrease was attributed to the concurrent formation of  $(\text{Al}, \text{Cr})_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ . Notably, the presence of an  $\text{Al}_2\text{O}_3$  TGO layer played a significant role in enhancing the high-temperature oxidation resistance of the coatings. In one study by Huang *et al.* [81],  $\text{AlSiTiCrFeCoNiMo}_{0.5}$  and  $\text{AlSiTiCrFeNiMo}_{0.5}$  coatings were subjected to oxidation at different temperatures. The coatings demonstrated favorable oxidation resistance up to 1000 °C for 100 hrs due to the formation of protective  $\text{TiO}_2$  and  $\text{Cr}_2\text{O}_3$  layers, which resulted from their slow diffusion.

Bhattacharya *et al.* [82] focused on HVOF  $\text{Al}_{30}\text{Si}_2\text{Cr}_{23}\text{Co}_{22}\text{Ni}_{23}$  (at. %) HEA coatings and examined their oxidation at 1050 °C for varying durations. The microstructure of the oxidized coatings consisting of BCC/B2 + FCC +  $\text{Al}_2\text{O}_3$ , with alumina, contributes to their oxidation resistance. The initial weight gain after 100 cycles was significantly lower, measuring 0.2 mg/cm<sup>2</sup>, compared to MCrAlX BCs, which typically exhibit a weight gain of 1 mg/cm<sup>2</sup>. This lower weight gain can be attributed to the desirable lower thickness and growth rate of the coating. Consequently, HVOF  $\text{Al}_{30}\text{Si}_2\text{Cr}_{23}\text{Co}_{22}\text{Ni}_{23}$  coatings demonstrated excellent oxidation resistance, making them well-suited for aerospace applications.

A recent study by Ossiansson *et al.* [16], investigated HEA CrFeCoNi and AlCoCrFeNi coatings sprayed via HVOF for TBC bond coats, to understand the influence of Al in the HEA composition. These coatings were tested in isothermal oxidation, and they were compared to commercially available NiCoCrAlYSiHf and NiCoCrAlY bond coats. These coatings displayed strong adherence of oxide scales without any visible spallation, indicating their effectiveness in resisting oxidation. When compared to conventional MCrAlY coatings, all the tested coatings exhibited a reduced rate of oxidation. The rate of oxidation was evaluated based on the increase in mass per sample area, enabling relative comparisons between the samples rather than absolute values [83]. **Figure 1-4**[16] illustrates the oxidation behavior of various coatings, including APS-410 (NiCoCrAlY), AF-386 (NiCoCrAlYSiHf), H2 (HEA: AlCrFeCoNi), and H1 (HEA: CrFeCoNi). APS-410 demonstrated the highest increase in mass per surface area after 1 hr of oxidation, attributed to its lower density and

enhanced oxygen diffusion. Conversely, AF-386 exhibited the lowest oxidation rate due to its dense microstructure and distinguished chemistry. H2 coatings, with their higher aluminum content, displayed superior initial oxidation resistance. Surprisingly, H1 coatings, which had no aluminum content, showed more increase in mass than APS-410 [56]. This suggests the influence of other elements, such as yttrium, in APS-410. Throughout the test, AF-386 consistently maintained a low oxidation rate due to its refined chemistry. After 20 hrs, all samples exhibited a decrease in oxidation rate, attributed to forming a thicker and continuous oxide layer. The study provides valuable insights into the oxidation behavior of coatings. It emphasizes the importance of spraying technique, composition, and material selection in determining performance [31]. The conventional bond coat, as a result, exhibits a lower mass gain, indicating higher oxidation resistance. Furthermore, the HEA with Al content shows a slightly higher mass gain (approximately  $0.2 \text{ mg/cm}^2$  after 50 hours) compared to MCrAlY+HfSi. This suggests that the composition of the HEA should be optimized and include reactive elements [16].

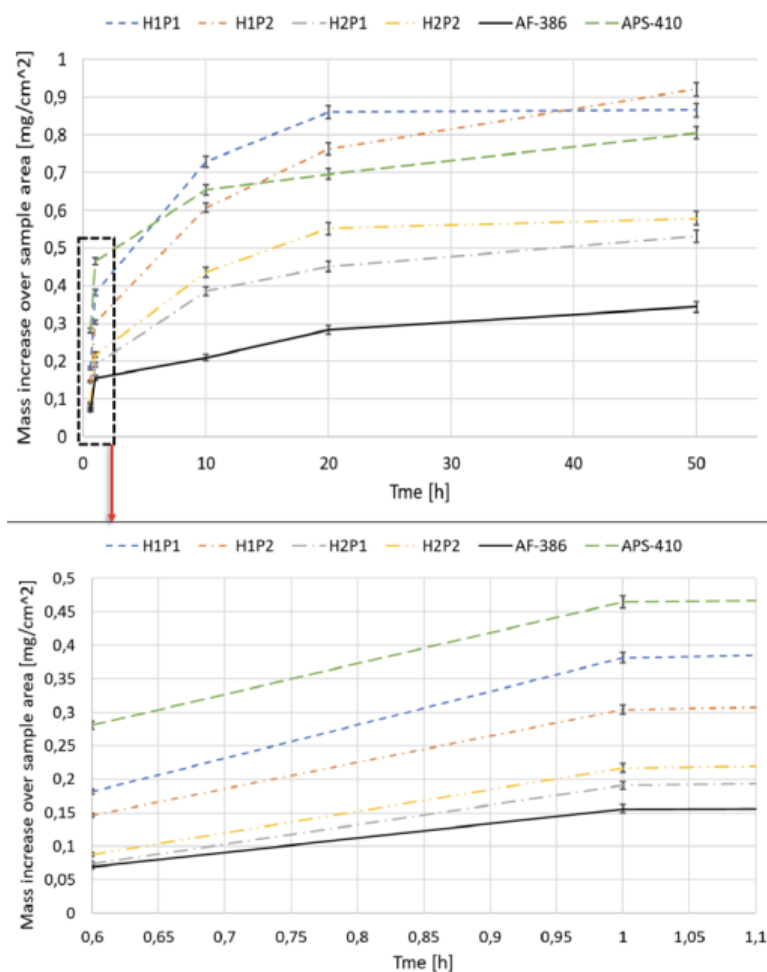


Figure 1-4 The results obtained from the isothermal oxidation test were depicted graphically, with error bars included to indicate the standard deviation (Ref 16).

HEAs have the potential to play a direct role in the attainment of a uniform TGO layer, thereby offering enhanced oxidation resistance owing to their participation in the multi-component composition. Accordingly, the controlled consumption of Al and Cr can effectively regulate the formation and growth rates of the TGO layer [14].

Weight gain in the BCs TBCs system is primarily caused by the formation of oxide scales during oxidation, indicating the degradation of the coating's protective properties, and monitoring weight gain serves as a reliable method for assessing the oxidation behavior and performance of these coatings [84]. In a study by Hsu *et al.* [46], thermal-sprayed HEA coatings were subjected to isothermal oxidation tests at 1100 °C. The results, presented in **Figure1-5**, revealed that the HEAC1 ( $\text{NiCo}_{0.6}\text{Fe}_{0.2}\text{Cr}_{1.5}\text{SiAlTi}_{0.2}$ ), exhibited rapid weight gain, while the HEAC2 ( $\text{NiCo}_{0.6}\text{Fe}_{0.2}\text{Cr}_{1.3}\text{SiAl}$ ), showed a slower and more consistent weight gain during initial oxidation (50-100 h). After 250 hrs, all coating specimens displayed minimal additional weight gain. The APS-HEA coatings showed a weight gain increase of 3.1-3.6%, while HVOF and WS-HEA coatings had a weight gain increase of less than 1%. The WS-MCrAlY coating exhibited a weight gain increase of 1.2%. Notably, the HEA coatings demonstrated comparable oxidation resistance to conventional MCrAlY coatings at 1100 °C, indicating their potential as alternative materials for high-temperature applications. Therefore, based on the results of **Fig. 1-5**, for the respective HEA bond coats to surpass the oxidation performance of the conventional MCrAlY, a further R&D on the HEA feedstock composition and spray parameter optimization is necessary.

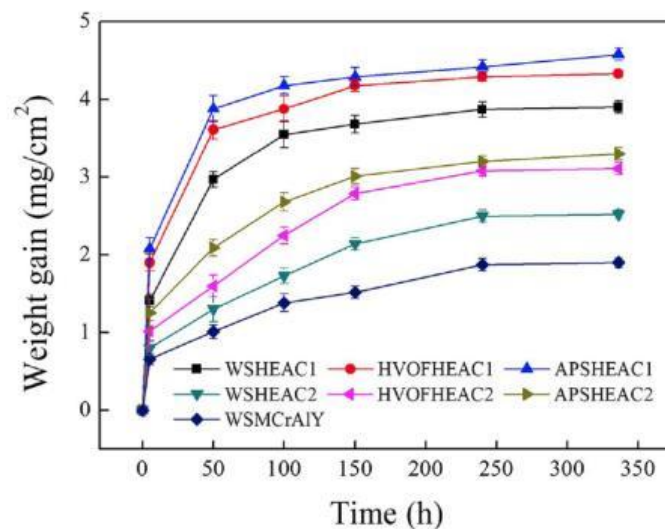


Figure 1-5 Isothermal oxidation weight gain tests were conducted at 1100 °C to evaluate the weight gain of the thermally sprayed HEAC1 and HEAC2 coatings (Ref 46).

In the recent work, Lu *et al.* [76] have performed Y-Hf doping of AlCoCrFeNi<sub>2.1</sub> by using arc-melting under a Ti-gettered high-purity argon atmosphere, resulting in the formation of a eutectic high-entropy alloy (EHEA). EHEAs, an emerging subgroup within the HEAs category, were introduced with the aim of enhancing liquidity and castability through the incorporation of eutectic principles. To balance high fracture strength and good ductility, eutectic alloys with a mixture of soft FCC and dense BCC phases were proposed. Eutectic alloys, known for their near-equilibrium microstructures, low-energy phase boundaries, and controllable microstructures, have advantageous mechanical properties and castability, making them promising for technological applications in high-temperature alloys. Furthermore, the composite FCC/BCC structure of eutectic HEAs is expected to provide improved mechanical properties and overcome castability obstacles [85]. The alloy has a close symmetrical balance between strength and ductility and is highly resilient against oxidation and spallation under thermal cycling conditions at 1100 °C and 1200 °C after 1008 hrs. Finally, they considered the role of reactive elements doped on the oxidation resistance of bond coat. Remarkably, they discovered that the EHEA illustrated significantly lower oxidation rates at temperatures of 1100 °C and 1200 °C compared to commercial bond coats such as NiCoCrAlYHf. Additionally, after subjecting the samples to 504 hrs of oxidation at 1200 °C, the scale thickness reached  $8.8 \pm 0.7 \mu\text{m}$  for NiCoCrAlYHf, causing severe scale spallation. In contrast, the EHEA exhibited a scale thickness of  $10.2 \pm 0.5 \mu\text{m}$  in the same oxidation test, yet the scale remained well-bonded to the alloy [76].

Another study by Xu *et al.* [7] investigated the oxidation characteristics of HEA CuAlNiCrFe compared with a NiCoCrAlY bond coat deposited by a high-speed cladding process. The HEA powders contained a BCC phase, whereas the sprayed coatings contained both FCC and BCC phases. During post-treatment, the bond coat is treated using a diffusion process in a furnace filled with Ar. The low partial pressure of oxygen ensures that only a dense alumina layer is generated [86]. Through the use of high-speed laser cladding, the CuAlNiCrFe high-entropy alloy bond coat can efficiently complete the pre-oxidation and form the  $\alpha\text{-Al}_2\text{O}_3$  TGO, which shortens the initial oxidation stage and prevents the formation of other oxides and spinel structures. The spinel structures are very brittle and have a lower adherence compared to  $\alpha\text{-Al}_2\text{O}_3$  and can lead to TBC failure through the combined effects of

stress and adherence [87]. Due to the diffusion of aluminum from the bond coat to the top coat, the thickness of the pure alumina-TGO layer increased from 0.89  $\mu\text{m}$  to 3.2  $\mu\text{m}$ , after 4 hrs to 100 hrs of oxidation. The novel CuAlNiCrFe HEA BC compared to the commercial bond coat, demonstrated outstanding oxidation and diffusion resistance by regulating the diffusion between the bonding layer and the substrate [7].

Jadhav *et al.* [34] believed that FeCoCrNi<sub>2</sub>Al exhibits excellent oxidation resistance by creating the TGO layer rich in  $\alpha\text{-Al}_2\text{O}_3$ . The TGO layer reaches a thickness of  $3 \pm 1 \mu\text{m}$  following 100 hrs of oxidation at 1050 °C. To mitigate the occurrence of localized separations at the interface between the TGO layer and the TBC, the TGO layer must retain its elasticity under high operating temperatures. This elasticity is essential for safeguarding against detrimental effects such as "rumpling" or cavitation that may arise during thermal cycling.

Ma *et al.* [36] used an Al<sub>30</sub>Co<sub>22</sub>Cr<sub>23</sub>Ni<sub>23</sub>Si<sub>2</sub> HEA as a bond coat deposited by HVOF to characterize the TGO formation. **Figure 1-6** depicts the XRD pattern obtained from a sample subjected to a 100 hrs. oxidation test at 1050 °C. Following oxidation, the predominant phase observed is the BCC/B2 phase, accompanied by minor peaks representing FCC and Al<sub>2</sub>O<sub>3</sub>. These findings suggest the thermal stability of the HEA coating, with the oxidation test primarily resulting in the formation of  $\alpha\text{-Al}_2\text{O}_3$  TGO on the coating's surface. This outcome is favorable for bond coats as it imparts high oxidation resistance at elevated temperatures.

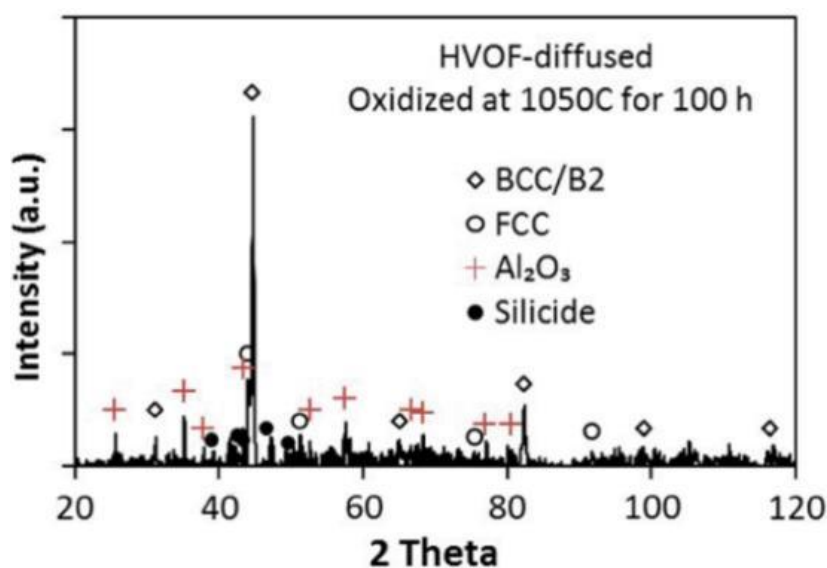


Figure 1-6 XRD spectrum of an  $\text{Al}_{30}\text{Co}_{22}\text{Cr}_{23}\text{Ni}_{23}\text{Si}_2$  coating following isothermal oxidation at 1050 °C for 100 hrs. in the air (Ref 36).

In a recent study conducted by Srivastava *et al.* [14], HEA-based and MCrAlY-based TBC coatings with YSZ topcoats were subjected to cyclic oxidation at 1050 °C for 100 cycles. The presence of NiAl-rich phases in the bond coat facilitated the formation of  $\text{Al}_2\text{O}_3$  at high temperatures. The application of YSZ as a topcoat effectively mitigated accelerated oxidation in both types of coatings. Notably, the HEA coating exhibited reduced waviness in the TGO scale when compared to the MCrAlY coating. The average thickness of the TGO layer, as shown in **Table 1-2** [14], was found to be similar for both coatings, approximately 3.7  $\mu\text{m}$  and 3.8  $\mu\text{m}$ , respectively, after 100 cycles of oxidation. A study has reported a TGO thickness of approximately 4 mm for a NiCrAlY-based TBC subjected to oxidation at 1050°C for 100 cycles [88]. These findings contribute valuable insights into the behavior of TBC coatings under cyclic oxidation conditions [89].

Table 1-2 The TBC system exhibited variation in the average thickness of the TGO layer as the number of cycles increased (Ref 14).

| Cyclic oxidation duration<br>(Hrs./Cycle) | Oxide layer thickness ( $\mu\text{m}$ ) |        |
|-------------------------------------------|-----------------------------------------|--------|
|                                           | HEA                                     | MCrAlY |
| 25 h                                      | 2.1                                     | 2.1    |
| 50 h                                      | 2.2                                     | 2.2    |
| 100 h                                     | 3.7                                     | 3.8    |

Currently, only two studies have specifically examined TGO parameters in HEA bond coats. However, these studies have not observed any noteworthy variations in TGO properties (thickness, uniformity, and slowing of growth rate), when compared to conventional commercial bond coat materials. As shown in **Table 1-1**, it is clear that there is a need for greater emphasis on improving the thickness control and uniformity of the TGO layer in HEAs, especially at elevated temperatures. HEA composition and spray parameters can be optimized in order to achieve this goal. Commonly, the thickness of the TGO layer is regarded as an essential factor in determining the remaining lifetime of a TBC system, particularly when thermal cycles and associated thermal stresses are present. As a result, TGO thickness increases, and it could cause top coat failure by producing stresses and cracking.

Moreover, according to **Table 1-1**, some TGO types ( $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{NiAl}_2\text{O}_4$ ) are related to a certain portion of the composition elements. In order to achieve the desired TGO layer composed of  $\alpha\text{-Al}_2\text{O}_3$ , the presence of Al is typically required. Collectively, HEA coatings exhibit better oxidation resistance than conventional bond coat materials (MCrAlX). Material design manipulations, such as increasing aluminum content or incorporating reactive elements, can enhance performance. Based on these findings, HEA coatings can be used for high-temperature applications, emphasizing the importance of the coating's oxidation behavior when developing advanced protective coatings.

## 1.6 Objective of the Thesis

The overarching goal of this research is to develop a fundamental understanding of the relationships between processing, microstructure, and properties in FeCoNiCrAl-based HEA bond coats, with and without reactive elements (Y, Hf), for application in advanced TBC systems. This work aims to assess their suitability as a next-generation alternative to the conventional NiCoCrAlYHfSi (MCrAlX) benchmark by combining systematic experimental evaluation with process optimization using industrially relevant thermal spray techniques.

This overarching goal is motivated by three critical gaps in the current state of the art:

1. Performance limitations of current MCrAlX coatings: Conventional NiCoCrAlYHfSi bond coats typically perform reliably up to  $\sim 1100^\circ\text{C}$  in service. Above this temperature, accelerated Al depletion,  $\beta$ -phase instability, and mixed-oxide (spinel) formation reduce their oxidation resistance and shorten component lifetime.
2. Process limitations: The high spraying temperatures of most thermal spray processes accelerate oxidation and phase decomposition during deposition, compromising coating performance.
3. Material design challenges: While HEAs offer unique thermodynamic stability via sluggish diffusion and high configurational entropy, their phase stability under realistic spraying and service conditions remains poorly understood.
4. Insufficient comparative studies: Few systematic studies directly compare HEA bond coats with and without reactive elements, using identical processing routes, against the industry benchmark MCrAlX.

To address these gaps, the following specific objectives are pursued:

1. Process selection and optimization: Select and justify HVOF and HVAF as the most suitable processes for HEA deposition due to their relatively low particle in-flight temperatures, high particle velocities, and ability to minimize oxidation during spraying. Optimize spraying parameters to produce dense coatings with minimal porosity and controlled phase retention.
2. Material selection and compositional rationale: Investigate FeCoNiCrAl HEAs as the base material for bond coats due to their excellent high-temperature stability, alumina scale formation capability, and reduced reliance on expensive elements such as Co. Examine the effect of adding reactive elements (Y, Hf) in small concentrations (~0.6 at.%) on oxidation resistance, TGO adhesion, and phase stability.
3. Powder characterization and justification: Characterize the as-received feedstock powders (morphology, size distribution, composition, and phase constitution) to understand their suitability for the chosen spraying techniques. Establish the link between powder characteristics and as-sprayed coating microstructure.
4. Microstructural and phase evolution analysis: Using advanced characterization techniques (FE-SEM, EDS, XRD), examine the influence of process type and spray parameters on grain size, phase distribution, porosity, and oxide content. Identify ordered and disordered BCC phases, detect secondary phases if present, and assess their stability post-deposition.
5. Oxidation resistance and TGO formation: Evaluate isothermal oxidation behavior at 1150 °C over extended durations. Quantify TGO growth kinetics, identify oxide phases, and compare oxidation mechanisms between HEA, HEA\_RE, and MCrAlX coatings.
6. Post-processing effect (Vacuum Heat Treatment – VHT): Assess the influence of VHT on coating densification, porosity reduction, oxide healing, and microstructural refinement. Determine how post-processing modifies oxidation resistance and TGO morphology.
7. Comparative performance assessment: Benchmark the performance of HEA and HEA\_RE bond coats against the NiCoCrAlYHfSi benchmark coating in terms of oxidation kinetics, TGO adherence, microstructural integrity, and suitability for next-generation TBC applications.

By addressing these objectives in a systematic and comprehensive manner, the research seeks to provide both fundamental insight and practical guidelines for the industrial adoption of HEA-based bond coats in high-temperature aerospace and energy applications.

## **1.7 Structure of Thesis**

This thesis follows a manuscript-based format, with Chapter 1 serving as the introduction and incorporating the first published review paper, while Chapter 7 presents the conclusion. The remaining chapters consist of published or submitted manuscripts focusing on HEA bond coats and their performance in TBC systems.

The research investigates the development, characterization, and optimization of HEA-based bond coats deposited using HVOF and HVOF thermal spray techniques. It examines the influence of spray parameters, microstructural evolution, oxidation resistance, and the effect of reactive elements on coating performance. The findings contribute to the advancement of next-generation bond coats for high-temperature applications.

### **Chapter 1: Introduction & Literature Review**

Chapter 1 provides an overview of HEAs and their potential as bond coats in TBC systems. The chapter introduces thermal spray processes (HVOF, HVOF), oxidation mechanisms, and the role of reactive elements in enhancing TGO stability and coating performance. The chapter also presents a comprehensive literature review on the advantages of HEAs over conventional MCrAlX bond coats and discusses key challenges in their implementation.

### **Chapter 2: Methodology**

### **Chapter 3: Characterization of HVOF-Sprayed FeCoNiCrAl HEA Bond Coats: A Comparative Study with MCrAlX**

This chapter presents a comparative study on HVOF-sprayed FeCoNiCrAl HEA bond coats and conventional MCrAlX coatings to evaluate the influence of HEAs and the potential benefits of replacing commercial bond coats with HEA-based alternatives. Furthermore, as a first step, it is essential to optimize the parameters and utilize commercially viable methods applicable in the industry, such as HVOF. The work, currently under review in the Journal of

Alloys and Compounds, examines the deposition efficiency, porosity, and microstructural characteristics of the coatings.

#### Chapter 4: Optimization of HVAF Process Parameters for Enhancing FeCoNiCrAl HEA Bond Coatings in Thermal Barrier Systems

This chapter explores the influence of HVAF process parameters (M3 gun) in lowering the spray temperature to investigate its effect on the microstructure of FeCoNiCrAl HEA coatings. By reducing the spray temperature, the study aims to enhance phase stability, minimize oxidation, and improve overall coating integrity, making the process more viable for industrial applications. The study, published in the Journal of Thermal Spray Technology, focuses on particle velocity, phase retention, and oxidation kinetics in HVAF-sprayed bond coats. The findings provide key insights into optimizing the deposition process for improved coating performance and long-term durability in high-temperature environments.

#### Chapter 5: Effect of Microstructure on Oxidation Resistance and TGO Formation in FeCoNiCrAl HEA Coatings Deposited by Low-Temperature HVAF Spraying

This chapter investigates the microstructural evolution, oxidation resistance, and TGO formation in FeCoNiCrAl HEA coatings fabricated using HVAF-i7. The study examines the correlation between coating porosity, mass gain, and TGO growth kinetics to enhance coating longevity under high-temperature conditions. This is the first study to produce an HEA bond coat using the HVAF-i7 process. The manuscript is prepared for submission to the Journal of Materials.

#### Chapter 6: Comparative Study of High-Entropy Alloy Bond Coats with and without Reactive Elements for Improved Oxidation Resistance in Thermal Barrier Coating Systems

This chapter explores the role of reactive elements (Y, Hf) in improving the oxidation resistance and phase stability of HEA bond coats. The study evaluates the formation of alumina TGO layers, interdiffusion behavior, and high-temperature durability. The findings demonstrate how reactive elements enhance the performance of HEAs compared to conventional bond coats. Moreover, this study examines the influence of vacuum heat treatment (VHT) on the microstructure of HEA bond coats and its effect on TGO layer formation. The manuscript is prepared for submission to the Journal of Surface and Coatings Technology.

## **2 Chapter Two: Methodology**

## 2.1 Materials

### 2.1.1 Powder Selection and Compositions

The experimental program was designed to decouple the effects of alloy composition from those of the thermal spray process on the oxidation resistance of next-generation bond coats. Two high-entropy alloy (HEA) compositions were investigated: FeCoNiCrAl (hereafter HEA) and FeCoNiCrAlYHf (hereafter HEA-RE). Both were gas-atomized by Heeger Co. (USA) and supplied in two particle size distributions:  $-5 + 30\ \mu\text{m}$  for HVAF spraying and  $-15 + 45\ \mu\text{m}$  for HVOF spraying.

The baseline FeCoNiCrAl was chosen for its proven high-temperature oxidation resistance, ability to form a continuous  $\alpha\text{-Al}_2\text{O}_3$  thermally grown oxide (TGO), and stable microstructure under prolonged exposure. It was also readily available and cost-effective, making it a practical starting point for industrial evaluation. The FeCoNiCrAlYHf variant was developed to explore the influence of reactive elements (REs) on oxidation performance. Yttrium and hafnium were selected because of their known ability to improve oxide adherence, delay void nucleation, and promote uniform scale growth. Their combined addition ( $\sim 0.6\ \text{at.}\%$ ) was kept low to prevent phase instability while enabling detectable effects.

For benchmarking, a commercial NiCoCrAlYHfSi MCrAlX powder (Amdry 386-2, Oerlikon Metco) was included. This alloy remains the industry standard for gas turbine bond coats and has well-documented oxidation behavior. Its particle size distribution ( $-88 + 16\ \mu\text{m}$ ,  $d_{50} \approx 36\ \mu\text{m}$ ) closely matched the  $-15 + 45\ \mu\text{m}$  HEA powders, ensuring similar in-flight heating and melting behavior.

The particle size distribution (PSD) for each powder was matched to the spray process based on prior optimization studies. Finer powders ( $-5 + 30\ \mu\text{m}$ ) heat and accelerate efficiently in HVAF's lower temperature environment, ensuring full melting with minimal oxidation. Coarser powders ( $-15 + 45\ \mu\text{m}$ ) are better suited to HVOF, where higher flame temperatures could overheat or oxidize finer particles. This matching was critical for producing dense, well-bonded coatings with low oxide content. **Figure 2.1** shows the overall experimental design, including powder types, PSD, and process routes.

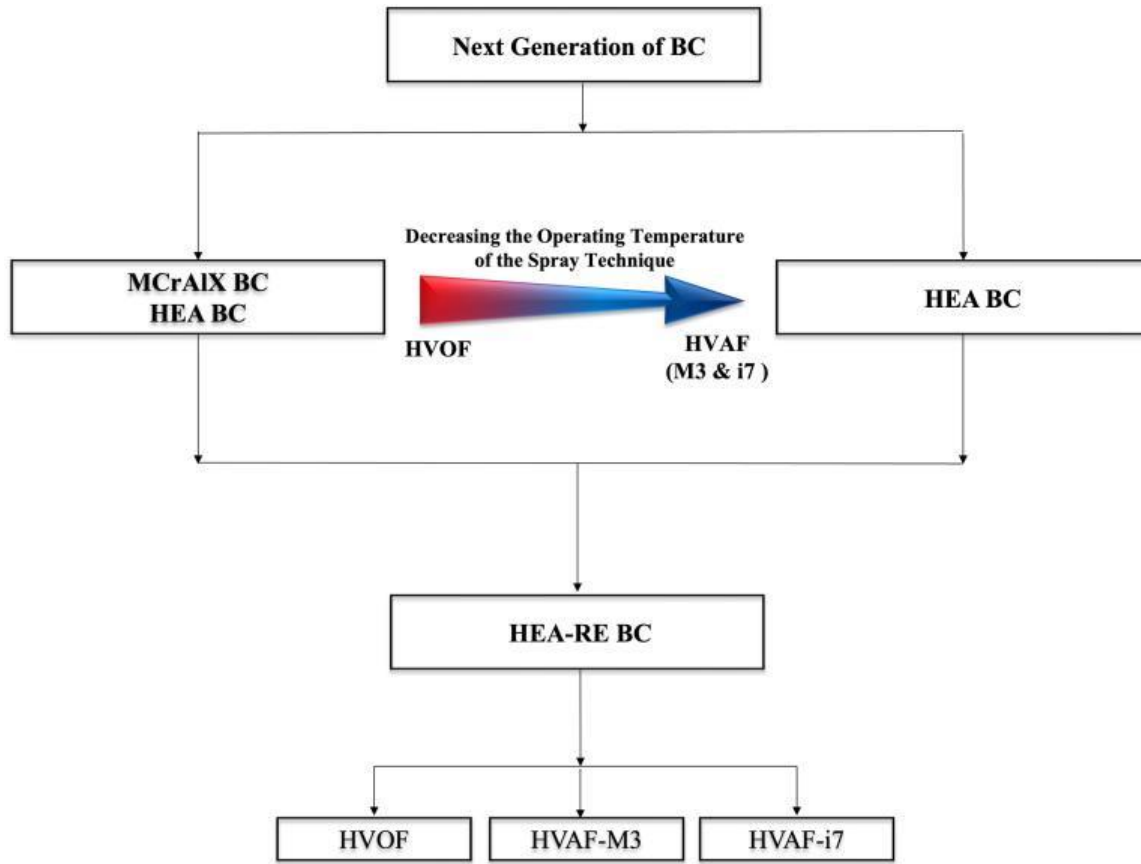


Figure 2-1 Experimental design showing powder types, particle size distributions (PSD), and process routes for HVOF and HVOF spraying.

## 2.2 Thermal Spray Process Selection

The goal was to replicate industrially relevant deposition processes that produce dense, adherent bond coats with low oxidation. Among available processes, Atmospheric Plasma Spray (APS), Vacuum Plasma Spray (VPS), and Cold Spray, this work focused on High Velocity Oxygen Fuel (HVOF) and High Velocity Air Fuel (HVOF). Both processes deliver high particle velocities with lower flame temperatures than plasma-based techniques, minimizing oxidation during deposition and promoting dense splat formation.

The key difference is the oxidizer: HVOF uses oxygen, while HVOF uses compressed air. HVOF's lower combustion temperature ( $\approx 1900\text{--}2000\text{ }^{\circ}\text{C}$  vs.  $\approx 2500\text{--}3000\text{ }^{\circ}\text{C}$  for HVOF) further reduces in-flight oxidation of Al, critical for preserving Al in HEAs and MCrAlX for later  $\alpha\text{-Al}_2\text{O}_3$  scale formation.

### 2.2.1 HVOF Spraying – Diamond Jet™ 2700

In HVOF, oxygen and fuel combust under high pressure to form a supersonic jet. Powder is injected axially, rapidly heated to a semi or fully molten state, and propelled toward the substrate at  $>600$  m/s. On impact, particles flatten into splats, rapidly solidifying into a dense coating.

The Diamond Jet™ 2700 gun was selected for its industrial relevance in MCrAlX deposition. Parameters were optimized to fully melt particles without overheating, preserving Al-rich phases essential for alumina TGO formation and refining microstructure without excessive oxidation.

### 2.2.2 HVAF Spraying – M3 and i7 Guns

HVAF uses compressed air instead of oxygen, reducing flame temperature and further limiting oxidation. This is advantageous for Al-containing alloys, where premature oxide formation during flight depletes the Al reservoir.

Two HVAF systems were used: the M3 for medium PSD powders and the i7 for fine PSD powders. The i7 achieves velocities  $>900$  m/s, enhancing splat flattening, density, and bonding. HVAF-i7 was therefore paired with  $-5 + 30$   $\mu\text{m}$  powders to maximize deposition efficiency and minimize oxide content.

The configurations and nozzle geometries of the HVAF-M3 and HVAF-i7 systems are illustrated in **Figure 4-3** and **Figure 4-4** in Chapter 4, respectively. These schematics visually clarify the distinct hardware setups used for each HVAF configuration.

## 2.3 Substrate Selection and Preparation

Initial trials used Inconel 718, but oxidation tests above  $1100$   $^{\circ}\text{C}$  caused partial melting due to its lower melting point ( $\sim 1260$   $^{\circ}\text{C}$  solidus). Inconel 625 was selected for final experiments, offering higher oxidation resistance and being widely used in turbine hot-section components.

Substrates were grit-blasted with #80 alumina at 4.13 bar to achieve  $R_a \approx 3.6$   $\mu\text{m}$ , optimizing mechanical interlocking while avoiding excessive roughness that can induce cracks.

## **2.4 Particle Size Distribution (PSD) Measurement**

PSD was measured by Malvern Spraytec laser diffraction. Particles scatter laser light at angles inversely proportional to size, large particles at small angles, fine particles at larger angles. The system uses Mie theory to compute PSD.

PSD affects melting, oxidation, and coating density. Fine particles risk overheating or vaporization; coarse particles risk incomplete melting, leading to porosity. Matching PSD to the process ensures optimal melting and minimal oxidation.

## **2.5 Microstructural and Elemental Analysis (FESEM + EDS)**

A Field Emission Scanning Electron Microscope (FE-SEM, Hitachi Regulus 8230) was employed to obtain high-resolution imaging of the coating microstructure. In FE-SEM, a focused electron beam is emitted from a field emission gun, which provides a much smaller probe size and higher brightness compared to conventional thermionic sources. This enables imaging with nanometer-scale resolution, essential for resolving fine splat boundaries, oxide stringers, and sub-micron precipitates within the bond coat.

Two main detection modes were utilized. Secondary electron (SE) imaging detects low-energy electrons emitted from the sample surface, providing high sensitivity to surface topography. This mode was used to examine splat morphology, inter-splat boundaries, and the surface roughness of the thermally grown oxide (TGO). Backscattered electron (BSE) imaging detects high-energy electrons scattered back from the specimen, with the BSE yield increasing with atomic number. This provides compositional contrast, which is particularly valuable for visualizing phase segregation in HEAs and MCrAlX coatings, such as Al-rich  $\beta$ -NiAl versus Cr-rich phases, as well as identifying oxide inclusions.

Chemical and elemental analyses were carried out using Energy-Dispersive X-ray Spectroscopy (EDS) in conjunction with both SE and BSE imaging. When the primary electron beam interacts with atoms in the specimen, it can eject inner-shell electrons, and the subsequent filling of these vacancies by outer-shell electrons releases characteristic X-ray photons whose energies are element-specific. By measuring these energies and intensities, EDS provides both qualitative and quantitative elemental information.

EDS measurements were performed in two modes: point analysis to determine the local chemical composition of specific phases or oxide particles, and elemental mapping to visualize the spatial distribution of elements across the TGO/bond coat interface. This

combined approach was critical for detecting elemental segregation within the sprayed coatings, such as the enrichment of reactive elements (Y and Hf) at splat boundaries in HEA-RE compositions, identifying diffusion profiles after oxidation or heat treatment (e.g., inward oxygen diffusion and outward aluminum diffusion), and mapping oxide distributions at the TGO/bond coat interface to differentiate  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> from mixed oxides.

By correlating SE/BSE imaging with EDS elemental mapping, oxidation mechanisms could be interpreted, the uniformity of alumina scale formation assessed, and the influence of reactive elements on oxide adherence and growth morphology evaluated.

### 2.5.1 Phase Identification by X-ray Diffraction (XRD)

X-ray Diffraction (XRD) analysis was performed using a Bruker D8 Advance DaVinci diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). In XRD, a monochromatic X-ray beam interacts with the periodic arrangement of atoms in the crystal lattice. Constructive interference occurs when the path-length difference between reflected beams from adjacent lattice planes satisfies Bragg's law:

$$n\lambda = 2d\sin\theta$$

where  $n$  is the diffraction order,  $\lambda$  is the X-ray wavelength,  $d$  is the interplanar spacing, and  $\theta$  is the diffraction angle. Each crystalline phase has a unique set of  $d$ -spacings, producing a characteristic diffraction pattern.

The peak positions provide information about the crystal structure and lattice parameters, while peak intensities reflect the relative abundance and preferred orientation of phases. Peak widths (FWHM) can indicate crystallite size or residual strain according to the Scherrer equation.

In the present work, X-ray diffraction (XRD) was employed for multiple purposes. First, phase verification after spraying was conducted to confirm the retention of the expected HEA phase structures—namely FCC, BCC, and B2 ordered phases—despite the rapid solidification inherent to thermal spraying. This verification was essential for correlating microstructural stability with oxidation behavior. Second, XRD was used for oxide phase identification in oxidized samples, allowing the detection and distinction of thermodynamically stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> from transient oxides such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, spinels, or mixed oxides (e.g., NiAl<sub>2</sub>O<sub>4</sub>, (Co,Ni)(Cr,Fe)<sub>2</sub>O<sub>4</sub>) that may form during the early stages of oxidation.

Third, phase decomposition monitoring was carried out to identify any decomposition or transformation of the HEA matrix or  $\beta$ -NiAl phase during spraying, vacuum heat treatment, or prolonged oxidation. Finally, semi-quantitative phase analysis was performed to estimate the relative fraction of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> compared to other oxide phases under different compositions and processing conditions.

By applying XRD to both as-sprayed and oxidized coatings, it was possible to directly link spray-process effects (HVOF vs. HVAF) and reactive-element additions (Y, Hf) to the stability of protective  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> scales. This information was critical for validating whether the designed HEA compositions could outperform the benchmark MCrAlX in forming adherent, slow-growing alumina TGOs.

## **2.6 In-flight Particle Diagnostics**

Real-time measurement of in-flight particle temperature and velocity is critical to ensure optimal thermal spray deposition, particularly when comparing different spraying processes and alloy compositions. Both parameters strongly influence splat morphology, coating density, oxide content, and ultimately the oxidation resistance of the bond coat. In this work, two complementary diagnostic systems were used, DPV-2000 and Accuraspray, selected according to the spray process and particle emission characteristics.

### **2.6.1 DPV-2000**

The DPV-2000 (Tecnar Automation) is a dual-mode, laser-assisted diagnostic system capable of measuring both particle velocity and temperature with high precision. Its operation is based on two optical principles:

#### **2.6.1.1 Laser Scattering for Velocity Measurement**

In this measurement approach, a pulsed laser beam is directed to illuminate particles while they are in flight. The light scattered from these particles is collected by two photodetectors positioned at a precisely known spatial separation along the particle trajectory. By performing phase correlation analysis on the scattered light signals from the two detectors, the time-of-flight (TOF) of the particles between the detection points is accurately determined. Using the measured TOF and the fixed detector spacing, the mean particle velocity can then be calculated with high precision.

### **2.6.1.2 Multi-wavelength Pyrometry for Temperature Measurement**

For sufficiently hot particles, the system records their self-emitted thermal radiation over multiple wavelengths. By fitting the measured spectral intensity distribution to Planck's law, the surface temperature of the particles can be accurately determined.

### **2.6.1.3 Operating Modes**

The DPV-2000 system can operate in two distinct modes depending on the thermal emission characteristics of the particles. In cold mode, the particle emission is too weak for reliable pyrometric measurement, as occurs in HVOF-i7 spraying of fine powders ( $-5 + 30\text{ }\mu\text{m}$ ) at temperatures of approximately 1900–2000 °C. Under these conditions, particle velocity is determined exclusively from laser scattering measurements. This mode is particularly well suited for low-emission, high-velocity spraying conditions, where accurate velocity determination is required without relying on thermal emission analysis. In laser mode, used when particle emission is sufficient for pyrometric analysis—as in HVOF or HVOF-M3—velocity is measured from laser scattering while temperature is simultaneously determined using multi-wavelength pyrometry. This enables accurate and concurrent measurement of both key parameters, providing comprehensive characterization of the in-flight particle state. In this study, HVOF-i7 was measured in cold mode due to its inherently low particle emission, whereas both HVOF and HVOF-M3 were measured in laser mode, benefiting from their strong emission signals and enabling full temperature–velocity mapping.

## **2.6.2 Accuraspray**

The Accuraspray (Tecnar Automation) is a non-intrusive optical diagnostic system designed to measure particle velocity and temperature based solely on their self-emitted thermal radiation. This technique is particularly effective in high-temperature, high-emission spray processes. Particle velocity is determined through optical cross-correlation, in which the thermal emission from hot particles is collected at two detection points separated by a precisely known distance within the spray plume. Cross-correlation analysis of the temporal intensity fluctuations at these two points yields the particle transit time, from which the velocity is calculated. Particle temperature is measured using two-color pyrometry, where the emission intensity is recorded at two discrete wavelengths. The ratio of these intensities is

then applied to Planck's law to determine the particle temperature, a method that largely compensates for variations in particle emissivity.

#### **2.6.2.1 Advantages**

This method does not require laser illumination, making it particularly suitable for bright spray plumes such as those produced by HVOF processes ( $>2400\text{ }^{\circ}\text{C}$ ) and HVOF-M3. It also enables continuous process monitoring, which is highly beneficial for verifying spray stability and ensuring repeatability during extended production runs.

#### **2.6.3 Application in This Study**

The HVOF-i7 process was characterized using the DPV-2000 in cold mode, selected due to the use of fine powders, the low thermal emission of the particles, and the requirement for accurate velocity control ( $>900\text{ m/s}$ ). For the HVOF-M3 process, measurements were performed using either the DPV-2000 in laser mode or the Accuraspray system to simultaneously capture both particle temperature ( $\sim 1900\text{--}2000\text{ }^{\circ}\text{C}$ ) and velocity ( $>750\text{ m/s}$ ). The HVOF process was assessed using the Accuraspray, with results cross-validated by the DPV-2000 in laser mode. These measurements confirmed optimal particle melting at approximately  $2300\text{--}2400\text{ }^{\circ}\text{C}$  with velocities around  $600\text{ m/s}$ . Selecting the appropriate diagnostic tool for each spray process ensured accurate characterization of in-flight particle conditions, thereby enabling precise process parameter optimization for producing dense, low-oxide coatings—a prerequisite for maximizing oxidation resistance in service.

### **2.7 Isothermal Oxidation Testing**

Isothermal oxidation tests were performed to evaluate the high-temperature oxidation resistance of the sprayed bond coats under controlled, fatigue-free conditions. The coatings were exposed at  $1150\text{ }^{\circ}\text{C}$  in static laboratory air for up to  $150\text{ h}$  using a Barnstead F21135 high-temperature box furnace. Coated specimens were placed in high-purity alumina crucibles to avoid contamination or spallation from reactions with support materials. Mass gain was measured at predetermined intervals with a Mettler Toledo ME204E analytical balance ( $0.1\text{ mg}$  resolution). Between measurements, the samples were cooled to room temperature to ensure gravimetric accuracy and allow inspection of surface condition.

The change in mass during these tests is directly related to the growth of the thermally grown oxide (TGO) layer, predominantly  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in Al-rich alloys such as HEAs and MCrAlX. Conducting the tests in static air eliminates mechanical effects such as thermal cycling fatigue or erosion, isolating the intrinsic oxidation kinetics governed by oxygen diffusion through the oxide scale and aluminum diffusion from the bond coat to the surface. The choice of 1150 °C—above the typical turbine service temperature (~1050 °C) yet below the melting onset of the Inconel 625 substrates—accelerates oxide growth while ensuring substrate integrity and promotes rapid transformation of transient alumina phases to the stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> form.

By tracking the parabolic growth constant ( $k_p$ ) from mass-gain data, the oxidation kinetics can be compared among HEA, HEA-RE, and the benchmark MCrAlX. Lower  $k_p$  values indicate slower oxide growth and superior long-term protective capability. These gravimetric results are directly correlated with subsequent microstructural analysis to assess the stability of the bond coat, the effectiveness of reactive element additions in improving oxide adherence, and the retention of aluminum necessary for sustained  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> formation.

## 2.8 Vacuum Heat Treatment (VHT)

The treatment was performed under high vacuum ( $\sim 6.8 \times 10^{-4}$  mbar) rather than in an inert gas such as argon or nitrogen. While inert gases can limit oxidation, they still contain trace levels of oxygen and moisture, which can promote undesirable oxidation of reactive elements such as Al, Y, and Hf during high-temperature exposure. In contrast, a high-vacuum environment significantly lowers the oxygen partial pressure ( $p_{O_2}$ ), often to below the threshold required for bulk oxidation of aluminum at this temperature, thereby almost completely suppressing internal oxidation and oxide contamination during heat treatment.

Moreover, in vacuum, the low  $p_{O_2}$  promotes selective oxidation kinetics at the very surface, favoring the thermodynamically most stable oxide ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) rather than transient polymorphs ( $\gamma$ ,  $\theta$ ) that typically form in inert gas atmospheres containing residual oxygen. This selective formation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> provides a uniform, adherent template that improves TGO adhesion during subsequent oxidation exposure. Additionally, vacuum conditions enhance degassing of entrapped volatiles from splat boundaries and pores, further reducing internal

defect content and improving coating density—an effect not as pronounced in inert gas heat treatments.

Finally, vacuum heat treatment offers superior control over contamination: in inert gas systems, trace impurities ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , hydrocarbons) from gas supply lines or furnace internals can adsorb on the coating surface, potentially affecting oxide nucleation and adhesion. Under high vacuum, these contamination pathways are largely eliminated, ensuring a chemically clean interface between the bond coat and the developing  $\alpha\text{-Al}_2\text{O}_3$  layer.

### **3 Chapter Three: Characterization of HVOF-Sprayed FeCoNiCrAl HEA Bond Coats: A Comparative Study with MCrAlX**

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- Hossein Shahbazi designed and conducted the experiments, analyzed the results, and wrote the manuscript.
- Dr. Rogerio S. Lima, Dr. Pantcho Stoyanov, and Prof. Christian Moreau supervised the research, contributed to the interpretation of results, and reviewed the manuscript.

### 3.1 Introduction

Thermal barrier coatings (TBCs) consist of a ceramic top coat for thermal insulation and a bond coat that serves as an intermediary between the ceramic and the Ni-based superalloy substrate. The bond coat primarily mitigates thermal strain between the ceramic and metallic layers while enhancing the oxidation resistance of the substrate[4,82,90–92]. Typically, bond coats are produced through thermal spraying, where a powder feedstock with a tailored chemical composition is applied to the substrate, or through diffusional aluminization, where the bond coat forms via diffusion and reaction between nickel (Ni) and aluminum (Al)[90,93,94]. This layer is essential for oxidation and corrosion resistance and for balancing thermal expansion differences between the ceramic top coat and metallic substrate. MCrAlX (where M represents Ni, Co, or both, and X includes reactive elements such as Y, Si, and Hf) is widely used as a conventional bond coat material in TBC systems due to its excellent oxidation and corrosion resistance[9,23,88,95]. These coatings protect the substrate from high-temperature degradation while accommodating thermal expansion mismatches. Conventional MCrAlX coatings primarily consist of  $\gamma$  (Ni, Co-rich FCC) and  $\beta$  (NiAl-rich BCC) phases. The  $\gamma$ -phase contributes to corrosion resistance and provides structural stability, while the  $\beta$ -phase serves as a critical source of aluminum for the formation of protective  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> thermally grown oxide (TGO) layers. However,  $\beta$ -NiAl is inherently brittle and susceptible to cracking below its ductile-to-brittle transition temperature (DBTT), which typically ranges from 600 to 700 °C. This brittleness can lead to premature crack initiation and propagation during thermal cycling, ultimately reducing coating durability. Although the addition of Co in MCrAlX stabilizes the  $\gamma$ -phase and helps suppress the formation of brittle  $\alpha$ -Cr phases, these coatings still face limitations in high-temperature performance and long-term oxidation resistance[22]. These drawbacks underscore the need to investigate alternative bond coat materials with improved thermal stability and oxidation behavior, such as high-entropy alloys (HEAs)[25,26].

However, recent interest has arisen in HEAs as alternative bond coat materials. HEAs, composed of multiple principal elements in nearly equal proportions, exhibit superior mechanical properties, thermal stability, and oxidation resistance [28,45,96]. These characteristics make them promising candidates for advanced TBCs. HEAs benefit from the ‘four core effects’: high entropy, sluggish diffusion, severe lattice distortion, and the cocktail effect which collectively contribute to their enhanced performance under extreme thermal environments [11,28,45,59,90,96,97]. A key advantage of carefully designed HEA bond coats, such as FeCoNiCrAl, is their ability to suppress the formation of brittle  $\beta$ -phase microstructures particularly when processed under optimized conditions using rapid solidification thermal spray techniques like HVOF [90]. Moreover, HEAs exhibit sluggish diffusion, contributing to a stable microstructure at high temperatures and enhancing oxidation resistance [98].

Several thermal spray techniques can be employed to deposit bond coats; among them, high-velocity oxy-fuel (HVOF) spraying has proven particularly effective for producing high-quality bond coats due to its ability to generate dense, well-adhered coatings with minimal oxidation. For example, MCrAlY and Ni-based alloy coatings deposited by HVOF have shown superior microstructural integrity and oxidation resistance in various studies [1,9,99]. This method propels powdered feedstock at high velocities, resulting in coatings with low porosity and minimal oxidation, attributes that are critical for bond coat performance. Compared to air plasma spraying, HVOF offers a lower flame temperature and higher particle velocity, making it especially suitable for depositing HEA coatings with preserved microstructure and enhanced oxidation resistance. [8,51,100]. Although lower-temperature processes such as high-velocity air-fuel (HVOF) and cold spray (CS) have also shown promise for HEA bond coats by further reducing in-flight oxidation, particularly in our previous works [101,102]. This study focuses on HVOF as a practical and industrially viable technique. It builds upon our earlier findings by exploring the use of HVOF for optimizing HEA bond coats, aiming to balance coating quality, oxidation resistance, and scalability for thermal barrier coating systems [15,103–105].

Another essential aspect of the TBC system is the thermally grown oxide (TGO) layer, which forms at the bond coat surface during high-temperature exposure. TGO growth is a key factor in TBC durability, as its thickness and formation kinetics significantly impact system performance[93]. The oxidation rate depends on the interface temperature between the

ceramic top coat and bond coat, which is influenced by the top coat's insulating properties[8,32,106–108]. This temperature, in turn, is influenced by the thickness and insulating properties of the ceramic top layer.

While extensive research has explored the use of HEAs in high-temperature applications, including some studies on HEA bond coats via thermal spray techniques, there remains limited comparative work on their oxidation-driven TGO formation and evolution in direct contrast to conventional MCrAlX systems. This study addresses that gap by investigating FeCoNiCrAl HEA bond coats sprayed via HVOF and comparing their oxidation performance and TGO behavior with a commercial MCrAlX coating under identical conditions. Listyawan *et al.* [109] investigated the oxidation resistance of AlCoCrFeNi HEA at 900–1100 °C. Below 1000 °C, oxidation occurred through unstable mixed oxides, whereas above 1000 °C, stable Al<sub>2</sub>O<sub>3</sub> or Cr<sub>2</sub>O<sub>3</sub> phases dominated. Adjusting the Al and Co content optimized oxidation resistance by stabilizing the phases and promoting the formation of protective oxide layers. Ossiansson *et al.* [16] examined HVAF-sprayed HEA bond coats for TBC applications. Their findings showed that AlCrFeCoNi HEA formed a protective alumina (Al<sub>2</sub>O<sub>3</sub>) TGO layer, improving oxidation resistance compared to CrFeCoNi HEA. However, its oxide growth rate was higher than that of conventional MCrAlY bond coats, likely due to the absence of reactive elements such as Y, Hf, or Si. In their study, Lobel *et al.* [59] analyzed AlCrFeCoNi HEA coatings deposited by HVAF and HVOF. Their study revealed that HVAF produced coatings with fewer defects and higher hardness. The rapid cooling of the sprayed powder preserved the metastable single-phase structure, enhancing corrosion resistance, particularly in NaCl and H<sub>2</sub>SO<sub>4</sub> electrolytes.

Therefore, this study aims to investigate the potential of FeCoNiCrAl HEA as a next-generation bond coat material in TBC systems, in direct comparison with a conventional MCrAlX coating, both deposited via HVOF to ensure consistent processing conditions and enable a fair evaluation of their respective oxidation behaviors. The use of HVOF for both coatings was selected not only for methodological consistency but also due to its well-established benefits, including lower in-flight oxidation, reduced porosity, and improved adhesion strength compared to APS. These advantages are particularly important for complex compositions such as HEAs, where phase stability and compositional integrity must be preserved during spraying. Emphasis is placed on the oxidation behavior, TGO formation, and microstructural evolution under prolonged high-temperature exposure. The findings are

intended to provide new insights into the suitability of HEA coatings for high-performance, high-temperature applications in aerospace and power generation industries.

## 3.2 Materials and methods

### 3.2.1 As-received Powders

The selected FeCoNiCrAl HEA powder (gas-atomized, Heeger Co., USA) has a particle size range of -15+45  $\mu\text{m}$  ( $d_{10} = 21 \mu\text{m}$ ,  $d_{50} = 34 \mu\text{m}$ ,  $d_{90} = 53 \mu\text{m}$ ). The MCrAlX powder, a commercial Amdry 386-2 (Oerlikon Metco), has the nominal composition Ni (bal.), Co 22 wt%, Cr 17 wt%, Al 12 wt%, Hf 0.5 wt%, Y 0.5 wt%, Si 0.4 wt%, and a particle size range of -88+16  $\mu\text{m}$  ( $d_{10} = 23 \mu\text{m}$ ,  $d_{50} = 36 \mu\text{m}$ ,  $d_{90} = 60 \mu\text{m}$ ). The conventional MCrAlX (NiCoCrAlYHfSi) powder used in this study can be classified as a medium entropy alloy (MEA), as it contains multiple principal elements but with lower configurational entropy compared to high entropy alloys (HEAs) like FeCoNiCrAl. This intermediate level of entropy influences its phase stability and microstructural evolution during thermal spraying and high-temperature exposure. The distinction between MEAs and HEAs is important in this work, as it helps frame the observed differences in oxidation behavior and coating characteristics. The FeCoNiCrAl HEA was selected based on literature reports highlighting its excellent high-temperature oxidation resistance, phase stability, and ability to form dense  $\alpha\text{-Al}_2\text{O}_3$  scales, which are essential for enhancing TBC longevity [110]. In contrast, MCrAlX alloys, such as NiCoCrAlYHfSi, are conventionally used for their proven high-temperature corrosion and oxidation resistance in turbine applications[111].

The powders were characterized in terms of particle size distribution, morphology, and phase composition. A wet laser diffraction particle size analyzer (Spraytec, Malvern Panalytical, UK) was used to measure size distribution. Cross-sectional powder morphology was examined via Field Emission Scanning Electron Microscopy (FESEM, Hitachi Regulus 8230, Japan), equipped with a photodiode BSE detector. Chemical compositions were analyzed using Energy Dispersive X-ray Spectroscopy (EDS), while X-ray Diffraction (XRD) (D8 Advance DaVinci Bruker, Germany) with Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ,  $2\theta = 10^\circ\text{--}120^\circ$ ) was employed for phase analysis of both powders and coatings, as shown in **Figure 3-2**.

### 3.2.2 Coating Preparation

Inconel 718 substrates were grit-blasted with #80 Al<sub>2</sub>O<sub>3</sub> at 4.13 bar (60 psi) to enhance surface roughness and improve coating adhesion. This yielded an average roughness (Ra) of  $3.5 \pm 0.4 \mu\text{m}$ , measured using a Mitutoyo SJ-210 profilometer (Japan). The FeCoNiCrAl HEA and MCrAlX powders were deposited using the Oerlikon-Metco Diamond Jet™ 2700 HVOF gun under optimized parameters (Table 1). The HVOF process, with high particle velocities and lower deposition temperatures, minimizes porosity and oxidation, preserving phase stability and microstructural integrity, which are crucial for bond coat performance in TBC systems[112].

Table 3-1 Spray parameters for bond coat production using the HVOF of HEA and MCrAlX compositions.

| Gun utilized                                            | Diamond Jet™ 2700 |
|---------------------------------------------------------|-------------------|
| Feed rate                                               | 50g/min           |
| Oxygen                                                  | 216 LPM           |
| Propylene                                               | 394 LPM           |
| Air                                                     | 424 LPM           |
| Transverse Speed                                        | 1 m/s             |
| No. of passes                                           | 10                |
| Spraying distance                                       | 225 mm            |
| Substrate Temperature (with IR camera)                  | 320 °C            |
| In-flight particles temperature/ HEA (with DPV 2000)    | 2390 °C           |
| Velocity (with DPV 2000)/ HEA                           | 600 m/s           |
| In-flight particles temperature/ MCrAlX (with DPV 2000) | 2400 °C           |
| Velocity (with DPV 2000)/ MCrAlX                        | 530 m/s           |

Microstructural characterization followed standard metallographic preparation, including grinding, polishing, and FESEM analysis. Porosity was quantified using ImageJ software based on ten FESEM images captured at 1K magnification, covering the top surface, interface, and mid-layer regions. The 1K magnification was selected to provide a broader field of view, allowing for a more representative evaluation of the overall coating structure, consistent with previous studies.

### 3.2.3 Oxidation Tests and TGO Layer Characterization

The isothermal oxidation test was conducted at 1150 °C for 150 hours using a tubular furnace (Barnstead, USA). Samples were placed in alumina crucibles to avoid contamination. At specific time intervals, they were briefly removed from the furnace and cooled to room temperature before being weighed using a high-precision analytical balance ( $\pm 0.0001$  g accuracy) to monitor mass gain. The mass gain was normalized to surface area and recorded with the samples placed in alumina crucibles to retain any spalled oxide, ensuring accurate assessment of TGO growth. The exposure interruptions were kept as short as possible to minimize thermal cycling effects. After the final oxidation period, the samples were fully removed for cross-sectional analysis of the thermally grown oxide (TGO) layer. FESEM, EDS, and XRD were used to examine oxide layer composition and microstructural evolution.

## 3.3 Results and Discussion

### 3.3.1 Feedstock

**Figure 3-1** shows the microstructure and composition of the as-received FeCoNiCrAl HEA and NiCoCrAlYHfSi powders. **Figures 3-1(a)** and **1(a')** show the particle size distributions of the HEA and MCrAlX powders, respectively. Both distributions exhibit a narrow range centered around the target size ( $d_{50} \approx 34\text{--}36\text{ }\mu\text{m}$ ); however, a small population of finer particles ( $<10\text{ }\mu\text{m}$ ) is also visible, likely representing satellite or fractured particles from the gas atomization process. These fines are minimal and were largely removed during sieving. **Figures 3-1(c)** and **1(c')** present the EDS point analysis results for selected areas of the HEA and MCrAlX powders, confirming the expected multi-elemental compositions. In both powders, slight variations among EDS points suggest the presence of microsegregation, consistent with elemental mapping results (**d, d'**). As shown in **Figures 3-1(b)** and **1(b')**, both powders exhibit a spherical morphology typical of gas atomized materials, which improves deposition efficiency and coating uniformity [113]. The elemental mapping in **Figures 3-1(d)** and **1(d')** highlights the segregation of Al and Cr within the powder microstructure, as indicated by the arrows.

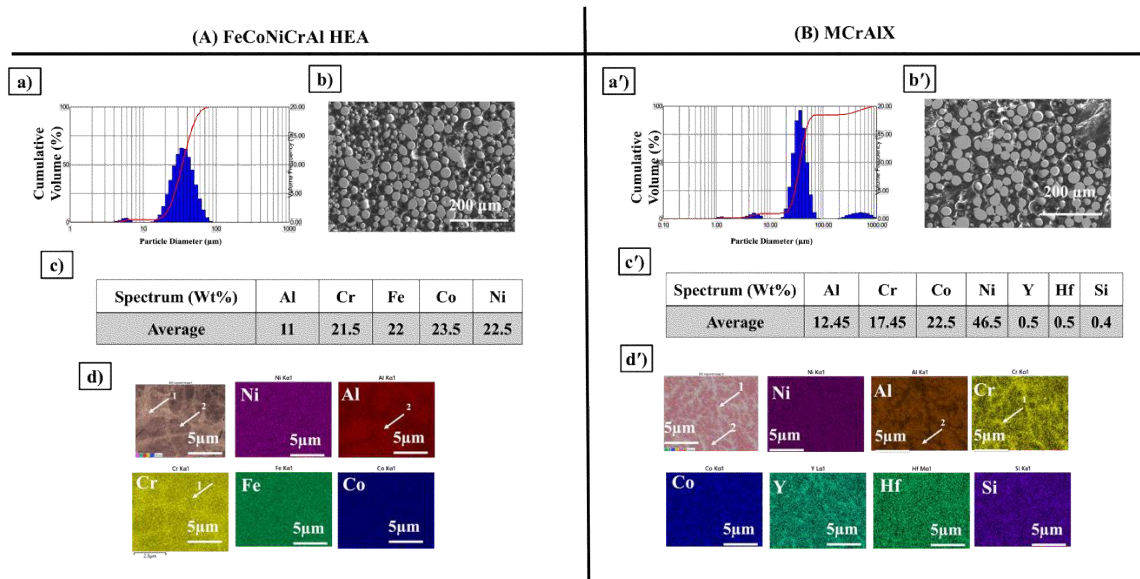


Figure 3-1 SEM morphology of A) FeCoNiCrAl HEA gas-atomized powder: a) Particle size distribution, b) FESEM cross-sectional image, c) EDS point analysis, d) Elemental mapping. B) MCrAlX gas-atomized powder: a') Particle size distribution, b') FESEM cross-sectional image, c') EDS point analysis, d') Elemental mapping. Arrows indicate the microsegregation of gathered elements.

### 3.3.2 Analysis of Coatings and Their Distinctive Attributes

**Figure 3-2** presents the XRD patterns of the as-received powders and as-sprayed coatings for FeCoNiCrAl HEA and NiCoCrAlYHfSi (MCrAlX), with annotations indicating the crystal structures and diffraction planes for each phase. The XRD patterns of FeCoNiCrAl HEA, in both powder and coating states, exhibit distinct BCC (Body-Centered Cubic) diffraction peaks at (110), (200), (211), and (310), indicating the presence of a BCC-based structure. While no separate B2 superlattice peaks were observed, prior literature suggests that FeCoNiCrAl-type HEAs often consist of a dual-phase mixture of disordered BCC (A2) and ordered B2 (NiAl-type) phases. These phases share the same BCC lattice, which can make them indistinguishable by XRD without superlattice reflections. The presence of a NiAl-rich B2 phase contributes to oxidation resistance by supplying Al for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> formation, functionally similar to the  $\beta$ -NiAl phase in MCrAlX. However, due to differences in phase distribution, chemical complexity, and the absence of reactive elements (e.g., Y), the oxidation behavior of FeCoNiCrAl HEA coatings may not entirely replicate that of conventional MCrAlY coatings under prolonged exposure. This stability highlights the influence of high entropy, which promotes the formation of a single-phase structure, resisting phase decomposition or oxide formation even under rapid cooling and high-temperature exposure during spraying [90,98]. In contrast, the XRD patterns of NiCoCrAlYHfSi

(MCrAlX) powders and their corresponding HVOF-sprayed coatings consistently show the presence of both FCC ( $\gamma$ -Ni) and BCC ( $\beta$ -NiAl) phases. The diffraction peaks corresponding to the (111), (110), (200), (220), (211), and (331) planes confirm that the same phase constituents are observed in both the powder and the as-sprayed coating. No new phases were detected, although slight peak broadening and intensity variations may reflect differences in crystallite size, residual stress, or minor oxidation. These findings are in agreement with literature reports, which indicate that the phase structure of MCrAlX powders is largely preserved during HVOF spraying, due to the occurrence of partial melting followed by rapid solidification, which limits extensive phase transformation [114,115]. The intensities of peaks at 32°, 42°, 50°, 61°, and 99° are reduced in the as-sprayed condition, suggesting a decrease in crystallinity due to partial melting and rapid solidification. Additionally, the broadening of the peak at 83° suggests potential oxide formation ( $\text{Y}_2\text{O}_3$ ,  $\text{HfO}_2$ ) or the presence of an amorphous phase, resulting from oxidation during spraying. The observed transformation between  $\gamma$  and  $\beta$  phases further indicates that the HVOF process induces phase changes, potentially influencing the performance and stability of the bond coat. These findings demonstrate the superior phase stability of HEA coatings compared to MCrAlX coatings, highlighting their potential for improved oxidation resistance and thermal stability in high-temperature applications [90,116–118]. The XRD patterns of the MCrAlX (NiCoCrAlYHfSi) powders and coatings reveal a typical dual-phase structure consisting of  $\gamma$  (FCC) and  $\beta$  (B2, NiAl-type) phases. A distinct diffraction peak near 30°  $2\theta$  corresponds to the (100) superlattice reflection of the ordered  $\beta$ -NiAl phase, a characteristic feature of the B2 structure. Other major reflections include  $\gamma$ (111),  $\gamma$ (200) from the FCC matrix, and  $\beta$ (110),  $\beta$ (200) from the intermetallic  $\beta$ -phase. These peaks confirm the coexistence of both  $\gamma$  and  $\beta$  phases within the microstructure.

All major peaks in the XRD pattern are annotated with their corresponding phases ( $\gamma$  or  $\beta$ ) and Miller indices. This annotation facilitates clearer differentiation between overlapping peaks and highlights the dual-phase constitution of the coating. The presence of  $\beta$ -NiAl is particularly noteworthy, as it acts as a crucial aluminum reservoir during high-temperature exposure and plays a key role in TGO formation. These observations are consistent with previous studies on NiCoCrAlY-based bond coats, which also exhibit  $\gamma/\beta$  microstructures after thermal spraying.

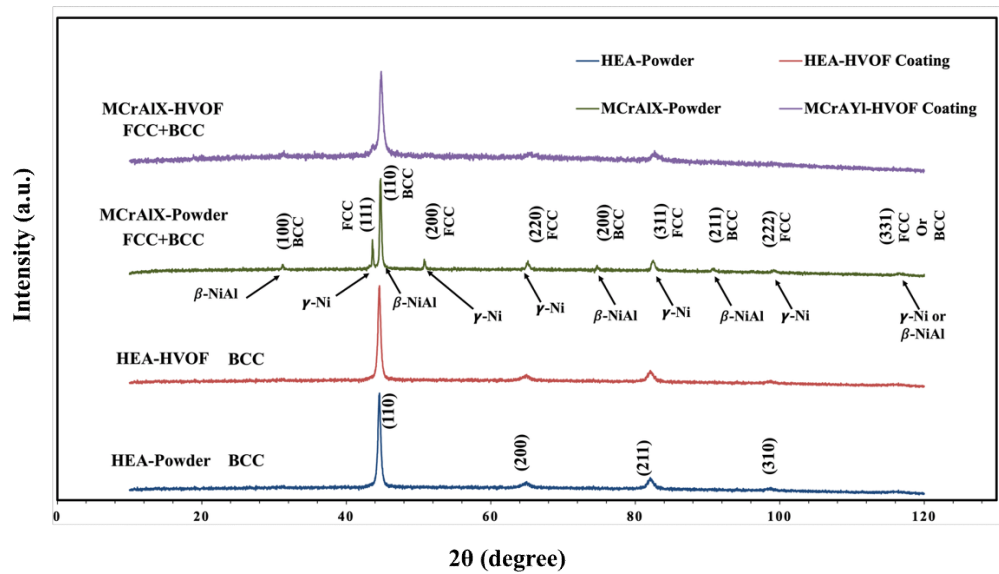


Figure 3-2 XRD patterns of a) FeCoNiCrAl HEA powder, b) As-sprayed HEA bond coat produced by HVOF, c) MCrAlX conventional powder, d) As-sprayed MCrAlX bond coat produced by HVOF.

**Figure 3-3** presents a comparative analysis of the cross-sectional microstructures between the FeCoNiCrAl HEA and the conventional NiCoCrAlYHfSi coatings, focusing on differences in deposition efficiency (DE) and porosity under identical HVOF conditions. The HEA bond coat demonstrates a higher DE of 64% and a lower porosity of 3.4%, whereas the MCrAlX bond coat shows slightly lower values with a DE of 58% and a porosity of 4.2% as depicted in Table 2. The FeCoNiCrAl HEA bond coat demonstrated higher deposition efficiency and lower porosity compared to the MCrAlX coating, as confirmed by multiple measurements with associated standard deviations. Although the differences are quantitatively modest, they are statistically significant and reflect improved coating quality. These characteristics are presented as supporting evidence that may contribute to the enhanced oxidation resistance and microstructural stability of the HEA coating. However, it is acknowledged that such microstructural differences alone may not fully account for performance variation and should be interpreted in conjunction with other factors such as phase composition, elemental distribution, and TGO behavior.

Table 3-2 Deposition efficiency (DE) and porosity of FeCoNiCrAl (HEA) and NiCoCrAlYHfSi (MCrAlX) bond coats sprayed by HVOF. Each value represents the mean  $\pm$  standard deviation (SD) based on multiple measurements ( $n = 6$  for DE and  $n \approx 100$  for porosity).

|  | DE (%) | Porosity (%) |
|--|--------|--------------|
|  |        |              |

|                  |            |             |
|------------------|------------|-------------|
| HEA bond coat    | $64 \pm 1$ | $3 \pm 0.1$ |
| MCrAlX bond coat | $58 \pm 1$ | $4 \pm 0.1$ |

The slight differences in deposition efficiency and porosity between the HEA and MCrAlX coatings can be linked to intrinsic materials properties such as powder morphology, particle size distribution, and the thermophysical behavior of the alloys during HVOF spraying. Firstly, the particle size distribution plays a critical role. HEAs like FeCoNiCrAl typically exhibit a more uniform and finer particle distribution compared to medium entropy alloys such as MCrAlX [119,120]. The finer particle size distribution (+45–15  $\mu\text{m}$ ) of the FeCoNiCrAl HEA powder increases the likelihood of particle softening and partial or full melting during HVOF spraying, which contributes to improved coating quality. However, even in cases where particle sizes are similar, the lower melting point and favorable thermal properties of the HEA material may inherently promote better deposition efficiency and splat formation compared to conventional MCrAlX alloys. This, combined with the HEA's lower melting temperature ( $\sim 1411\text{ }^{\circ}\text{C}$ ) compared to MCrAlX powders ( $\sim 1526\text{ }^{\circ}\text{C}$ ), promotes better melting, spreading, and adhesion upon particle impact during the HVOF spraying process. Consequently, this results in higher DE and reduced porosity in the coatings. Additionally, the elemental composition and atomic interactions within the alloys influence their thermal and mechanical properties. HEAs are known for their high configurational entropy, which promotes solid solution strengthening and impedes dislocation movement [11,28,39,94]. This property enhances the mechanical integrity of the deposited layer and contributes to improved adherence, provided it is preserved after the thermal spraying process. Furthermore, the uniform distribution of elements observed in the mapping analysis (Figs. 4(c and c')) and confirmed by EDS (Figs. 4(b and b')) highlights another advantage of HEAs. The uniform elemental distribution observed in the HEA coating is expected to enhance the homogeneity of oxidation behavior and contribute to the stable formation of alumina scale, as supported by theoretical predictions and prior studies on high-entropy alloys [14,16,121]. In conclusion, the superior performance of FeCoNiCrAl HEA in terms of higher DE and lower porosity, compared to the NiCoCrAlYHfSi, can be attributed to different key factors. Although the differences in deposition efficiency and porosity between the HEA and MCrAlX coatings are modest, the slightly lower porosity observed in the HEA coating may contribute to reduced oxygen ingress during high-temperature exposure, potentially influencing the uniformity and rate of TGO layer growth by limiting internal oxidation pathways. Additionally, the

FeCoNiCrAl HEA feedstock exhibits a melting temperature of approximately 1411 °C, nearly 100 °C lower than that of the MCrAlX powder (~1526 °C), which likely contributes to the enhanced deposition efficiency and reduced porosity. Examination of the as-sprayed coatings revealed that the microsegregation observed in the powders—particularly Al and Cr-rich regions in the HEA and Hf/Cr-rich regions in the MCrAlX—persisted to some extent within the coatings. However, the HEA coating displayed a more uniform elemental distribution with finer microstructural features, while the MCrAlX coating showed localized enrichment zones. These differences may influence diffusion behavior and the stability of the TGO during prolonged oxidation, as discussed in later sections.

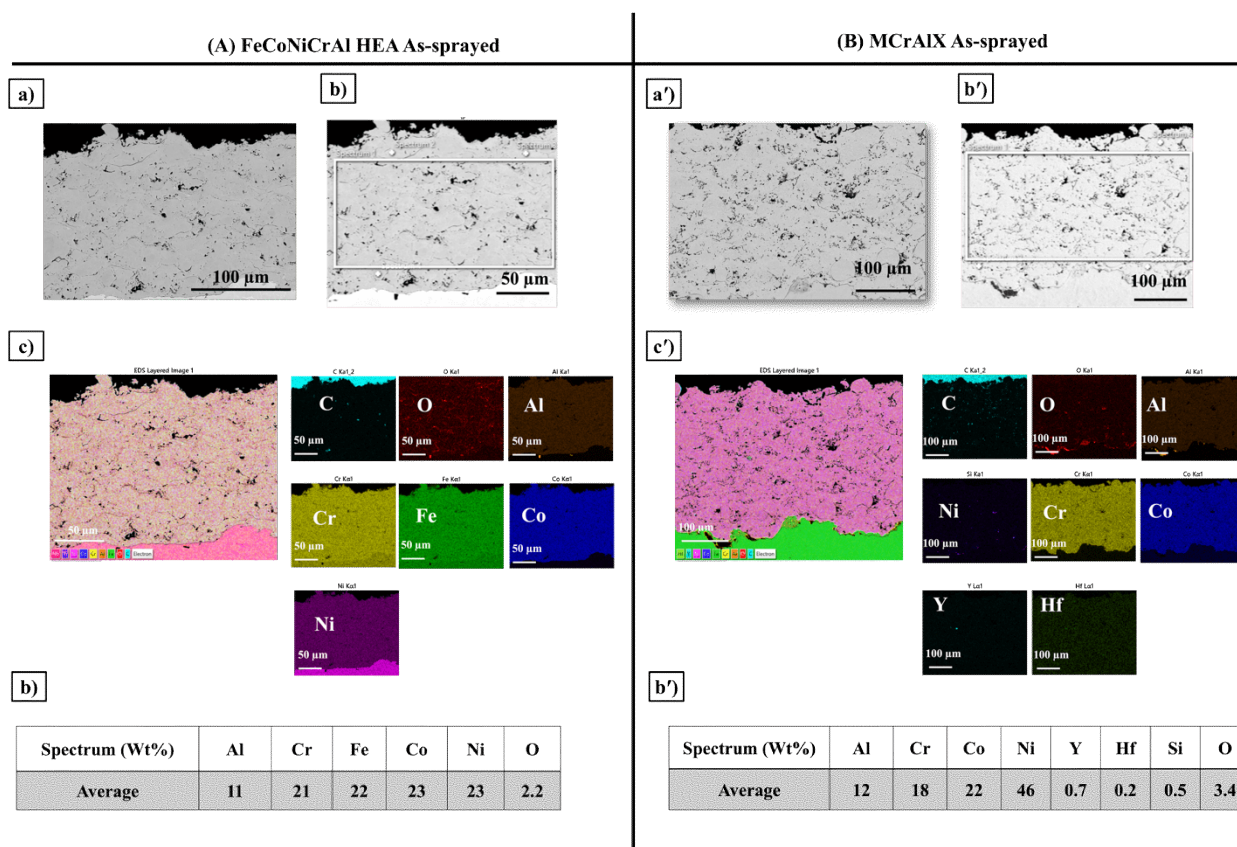


Figure 3-3As-sprayed cross-sections of: A) FeCoNiCrAl HEA bond coat: a) microstructure of the HEA bond coat sprayed via HVOF, b) EDS area analysis of the region outlined in white (values shown as average  $\pm$  SD in wt%, based on  $\geq 5$  measurements), c) Elemental mapping showing distribution of key elements. B) MCrAlX bond coat: a') Microstructure of the MCrAlX bond coat sprayed via HVOF, b') EDS area analysis of the rectangular region (average  $\pm$  SD in wt%,  $n \geq 5$ ), c') Elemental mapping of primary elements.

### 3.3.3 TGO Microstructure Dynamics

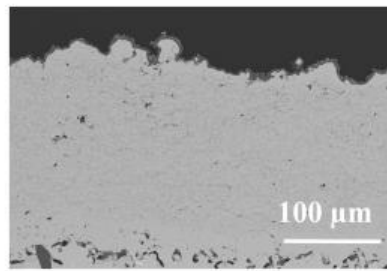
A key requirement for bond coats in TBC systems is the formation of a dense, continuous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> TGO layer. In contrast, the presence of mixed oxides such as spinels like Ni(Cr, Al)<sub>2</sub>O<sub>4</sub> can be detrimental, as they: (a) reduce adhesion and increase the risk of spallation, (b) induce higher growth stresses that accelerate failure under thermal cycling, (c) allow faster oxidation rates leading to excessive TGO thickening, and (d) lower the thermal stability of the coating, ultimately reducing durability at elevated temperatures [8,32,86,107,108,114,122]. TGO forms during high-temperature exposure due to the oxidation of aluminum in the bond coat. When oxygen diffuses through the top coat or reaches the surface of the bond coat, it reacts primarily with aluminum to form a dense layer of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (alumina). This layer acts as a protective barrier, limiting further oxidation. The formation and growth of TGO depend on factors such as temperature, time, and the availability of reactive elements like Al, Y, or Hf that promote adherence and slow growth. Optimizing HEA compositions helps suppress undesirable oxides while ensuring stable TGO growth. Studies have shown that HEA bond coats, such as AlCoCrFeNiY, exhibit lower oxidation rates and reduced oxide spallation compared to conventional NiCoCrAlY coatings due to their columnar grain structure and reduced aluminum activity[83,99,123]. Both FeCoNiCrAl HEA and NiCoCrAlYHfSi (MCrAlX) as-sprayed samples were subjected to isothermal oxidation at 1150 °C for 150 hours to evaluate TGO growth, oxide formation, and microstructural evolution. As shown in **Figure 3-4**, the oxidation process led to pore healing in both coatings. In **Figure3-4(Aa)**, the FeCoNiCrAl HEA bond coat reveals the formation of a dense, continuous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> TGO layer. EDS analysis at selected points along the TGO (Fig. 4(Ab)) confirms that the oxide scale is predominantly composed of Al and O, suggesting the formation of an Al<sub>2</sub>O<sub>3</sub>-rich layer. While no significant amounts of Fe, Co, Ni, or Cr were detected at these locations, we acknowledge that localized microsegregation or minor mixed oxides—such as spinels—may still be present, especially in regions of contrast observed in the microstructure. This interpretation is supported by elemental mapping in **Figure3-4(Ac)**, which shows strong Al and O enrichment, though the possibility of undetected or overlapping

signals from minor oxides cannot be ruled out. Internal oxides are observed within the diffusion layer, indicating localized elemental depletion, but no severe degradation is evident.

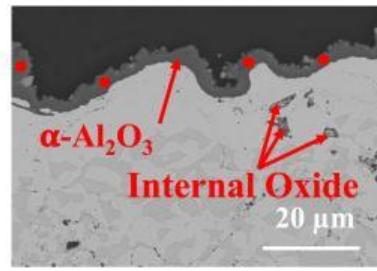
Conversely, **Figure3-4(Ba')** shows that the MCrAlX bond coat exhibits not only  $\alpha$ - $\text{Al}_2\text{O}_3$  but also a secondary layer of mixed spinel oxides. This mixed oxide formation, highlighted in **Figure3-4(Bc')**, is attributed to the relatively faster elemental diffusion in the MCrAlX coating, which contrasts with the sluggish diffusion behavior typically observed in HEAs. The reduced atomic mobility in the HEA system likely contributes to the preferential and more gradual formation of a stable  $\text{Al}_2\text{O}_3$  layer. EDS point analysis in **Figure3-4(Bb')** confirms the presence of Cr, Ni, and other oxides within the TGO. Notably, TGO spallation is visible in the MCrAlX coating, unlike in the HEA bond coat, where the alumina layer remains intact. After isothermal oxidation at 1150 °C for 150 hours, the FeCoNiCrAl HEA bond coat exhibited a dual-phase microstructure, as evident from the contrast between bright and dark regions in the SEM images (**Figure3-4Aa**). This contrast is attributed to the coexistence of  $\gamma$  (FCC) and  $\beta$  (B2) phases, which are commonly reported in FeCoNiCrAl-type HEAs [14,61]. The  $\gamma$  phase appears as the ductile matrix, providing structural support, while the  $\beta$  phase, enriched in aluminum, plays a critical role in supplying Al for the formation of the protective  $\alpha$ - $\text{Al}_2\text{O}_3$  TGO. In bond coats, the presence of both  $\gamma$  and  $\beta$  phases ensures a balance between mechanical integrity and oxidation resistance. The formation and stability of these two phases after thermal exposure reflect the alloy's ability to maintain phase separation and functional performance under high-temperature conditions.

**(A) FeCoNiCrAl\_HEA\_TGO Microstructure**

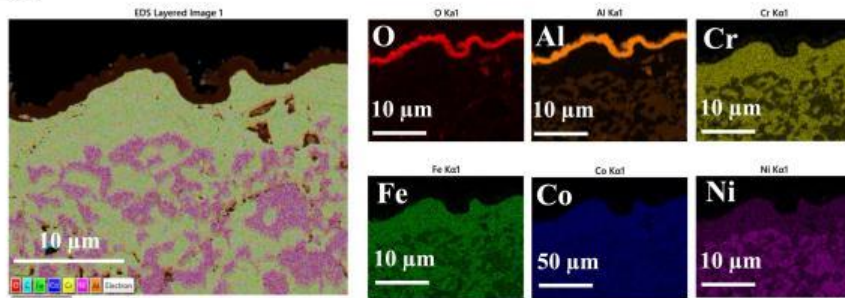
**a)**



**b)**



**c)**



**b)**

| Spectrum (Wt%) | Al | Cr | Fe | Co | Ni | O  |
|----------------|----|----|----|----|----|----|
| Average        | 48 | 0  | 0  | 0  | 0  | 50 |

## (B) MCrAlX\_TGO Microstructure

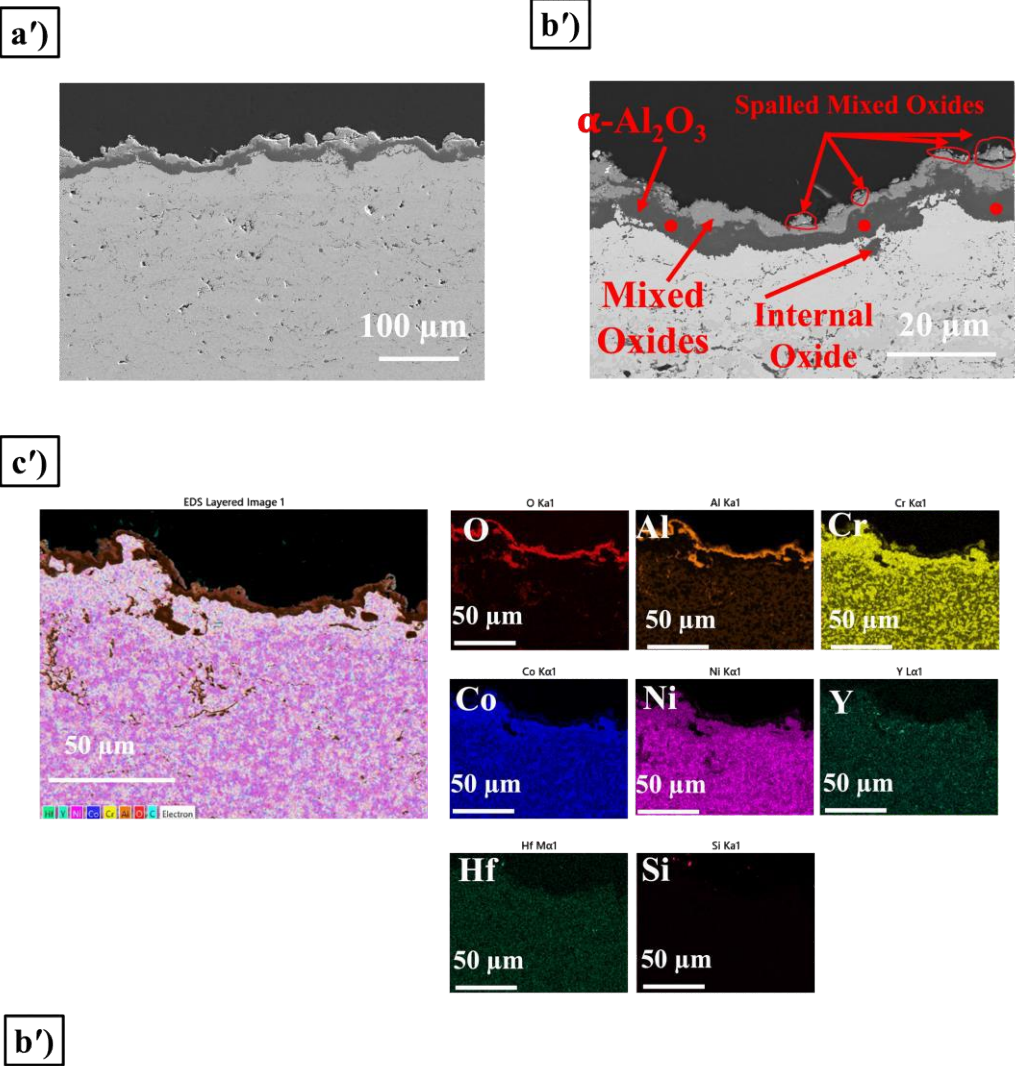


Figure 3-4 Cross-sectional microstructures and EDS analyses after isothermal oxidation at 1150 °C for 150 hours: A) FeCoNiCrAl HEA bond coat: a) Microstructure of the oxidized bond coat showing the formation of the TGO layer, b) EDS point analysis of red-marked regions (values averaged and shown in table), c) Elemental mapping of the same region, showing Al enrichment along the TGO. B) MCrAlX bond coat: a') Microstructure of the oxidized bond coat with visible TGO and internal oxides, b') EDS point analysis of red-marked regions (average values shown in table), c') Corresponding elemental mapping of the same area, showing distributions of Al, Cr, Ni, and other elements.

The TGO thickness measurements indicate that the FeCoNiCrAl HEA bond coat forms a thinner oxide layer (3.6 μm) compared to the MCrAlX bond coat (5.7 μm) over a 300 μm

section, as illustrated in **Figure 3-5**. This difference of 2.1  $\mu\text{m}$  aligns with the depletion zone observations, further demonstrating the superior oxidation resistance of HEAs [90,98].

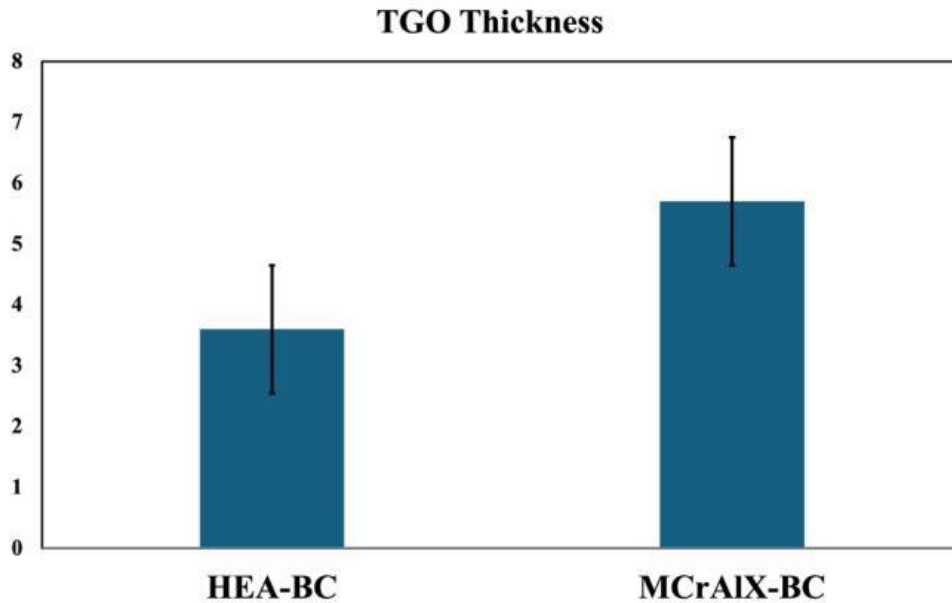


Figure 3-5 TGO thickness of heat-treated samples sprayed via HVOF with different compositions (FeCoNiCrAl HEA and NiCoCrAlYHfSi medium entropy alloy) at 1150 °C after 150 hours. Measurements were taken using FESEM at high magnification (2000x) with an average of 10 measurements for each bond coat. The TGO of the MCrAlX comprises a mix of spinel and alumina layers, whereas the TGO of the HEA bond coat is solely alumina.

**Figure 3-6** presents the EDX line analysis performed across the TGO and underlying bond coat regions of FeCoNiCrAl HEA and NiCoCrAlYHfSi (MCrAlX) coatings after isothermal oxidation. The elemental distribution profiles (Fig. 6) provide a detailed comparison of depletion zones and oxide scale growth across the TGO–bond coat interface in both coatings. In the FeCoNiCrAl HEA, a gradual elemental gradient and thinner depletion zone ( $\sim 5.1 \mu\text{m}$ ) are observed, consistent with the sluggish diffusion effect. In contrast, the MCrAlX coating exhibits sharper elemental transitions and a thicker depletion zone ( $\sim 8.4 \mu\text{m}$ ), marked by significant Al and Cr depletion near the TGO. All line scan data were normalized and carbon signals removed to enhance accuracy, and element colors were reassigned to avoid overlap.

The observed microsegregation in the HEA powder, particularly of Al and Cr, is attributed to the sluggish diffusion effect inherent in high entropy alloys. This characteristic can influence TGO formation by slowing the outward diffusion of Al during oxidation,

thereby promoting the gradual and stable growth of a continuous  $\alpha\text{-Al}_2\text{O}_3$  scale. In contrast, the faster diffusion behavior in the NiCoCrAlYHfSi (MCrAlX) powder may result in less controlled oxidation kinetics, leading to the formation of mixed spinel oxides and an increased likelihood of TGO spallation under prolonged exposure. These diffusion-related differences in elemental behavior may help explain the superior oxidation resistance and TGO stability observed in the FeCoNiCrAl HEA coatings.

The FeCoNiCrAl HEA bond coat (Fig. 6a) exhibits a thinner depletion zone, measuring approximately 5.1  $\mu\text{m}$ , while the depletion zone in the MCrAlX coating (Fig. 6b) extends to 8.4  $\mu\text{m}$ . The sharper compositional gradients in the MCrAlX coating reflect faster diffusion rates and greater material consumption, contributing to the formation of mixed oxides and thicker TGO layers. In contrast, the HEA profile shows a more gradual elemental transition across the TGO and bond coat interface, suggesting slower diffusion and enhanced elemental retention. The thinner depletion zone in the HEA coating correlates with the formation of a stable, continuous alumina ( $\alpha\text{-Al}_2\text{O}_3$ ) TGO layer. This limited depletion minimizes phase destabilization and enhances long-term oxidation resistance, reducing the risk of premature failure. On the other hand, the thicker depletion zone in the MCrAlX coating promotes the growth of spinel oxides and mixed phases, accelerating TGO thickening and increasing the likelihood of oxide spallation during thermal cycling.

These results underscore the advantage of HEAs in suppressing diffusion-driven degradation, contributing to superior TGO adherence and prolonged coating lifespan in high-temperature environments. The EDX analysis further substantiates the role of sluggish diffusion in HEAs, reinforcing their potential as next-generation bond coat materials for TBC systems.

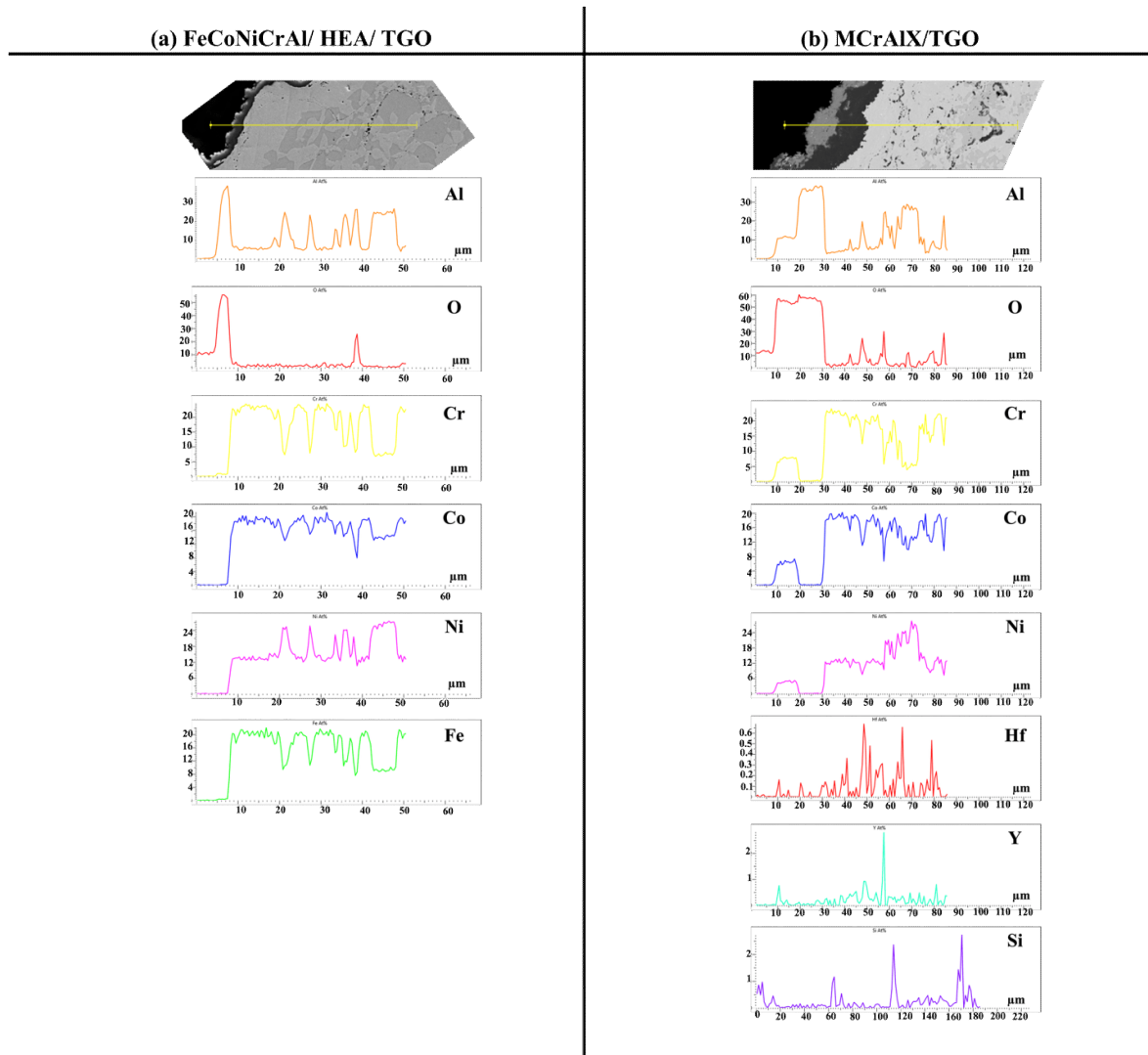


Figure 3-6EDX line analysis of TGO and depletion zones in FeCoNiCrAl HEA (a) and NiCoCrAlYHfSi MCrAlX (b) bond coats after isothermal oxidation at 1150°C for 150 hours.

**Figure 3-7** presents the specific mass gain results, measured after isothermal oxidation at 1150 °C for 150 hours, comparing the oxidation behavior of FeCoNiCrAl HEA and NiCoCrAlYHfSi (MCrAlX) bond coats. In the first 10 hours, both coatings exhibit a similar oxidation rate, resulting in only a slight difference in mass gain. This is primarily due to the low rate of diffusion during the initial stage, where oxidation is mainly controlled by surface reaction kinetics rather than bulk diffusion.

However, after 10 hours, a significant difference emerges. The HEA bond coat develops a dense and protective  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> TGO layer, which acts as a diffusion barrier, slowing the oxidation rate. In contrast, the MCrAlX bond coat forms mixed spinel oxides, which allow for continued oxygen diffusion, leading to a higher mass gain rate over time.

Over the entire exposure period, the HEA bond coat exhibits consistently lower mass gain, with an approximately 40–50% reduction compared to MCrAlX after 150 hours. This behavior highlights the superior oxidation resistance of HEAs, which can be attributed to their sluggish diffusion effect. The slower atomic mobility in HEAs limits the outward diffusion of elements, such as Al and Cr, thereby reducing the rate of oxide growth.

The formation of a dense and continuous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> TGO layer in the FeCoNiCrAl HEA bond coat serves as an effective diffusion barrier, minimizing further oxidation. This behavior is attributed to the sustained availability of aluminum and the sluggish diffusion of transition metals (Ni, Co, Cr), which suppresses the formation of transient oxides and mixed spinels. In contrast, the MCrAlX bond coat exhibits faster diffusion kinetics, leading to the outward migration of Ni, Co, and Cr, which readily react with alumina to form mixed spinel oxides such as (Ni,Co)(Cr,Al)<sub>2</sub>O<sub>4</sub>. These spinels disrupt the integrity of the oxide layer, resulting in increased oxide scale thickness and a higher likelihood of TGO spallation. The thinner depletion zone observed in the HEA further reflects lower elemental consumption, preserving the integrity of the coating. These combined factors suggest that HEA bond coats offer enhanced long-term stability and durability in high-temperature environments, making them promising candidates for next-generation TBC systems.

The slightly lower porosity observed in the HEA bond coat contributes to reduced oxygen ingress during high-temperature exposure, thereby influencing the oxidation kinetics and promoting the formation of a more stable and continuous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> layer. Furthermore, the denser microstructure of the HEA coating suppresses the formation of internal oxides, supporting the integrity of the TGO/bond coat interface. These microstructural features are consistent with the observed reduction in TGO thickness, limited depletion zone, and improved oxidation resistance compared to the MCrAlX coating.

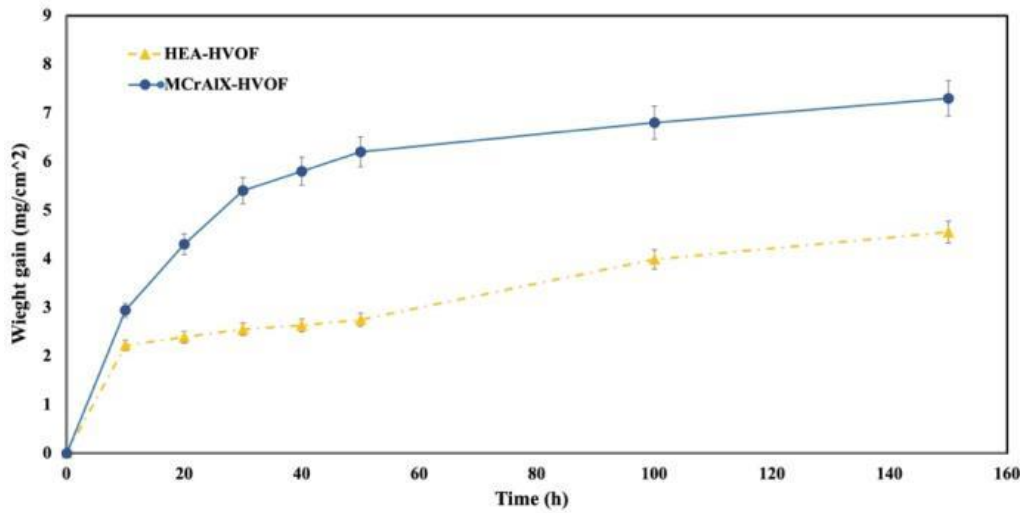


Figure 3-7 Isothermal oxidation test results for HEA and MCrAlX bond coats applied using HVOF. Error bars indicate the standard deviation.

### 3.4 Conclusion

In this study, FeCoNiCrAl HEA, and MCrAlX, a commercial material, were utilized for bond coats prepared via HVOF techniques. Following the HVOF technique parameters, dense coatings with low porosity values were achieved (3.4-4.2%). The research focused on the oxidation behavior of FeCoNiCrAl HEA and MCrAlX bond coats at 1150 °C for 150 hours, examining oxide growth, spallation, and microstructural evolution. The key conclusions are as follows:

1. The FeCoNiCrAl HEA bond coat, sprayed via HVOF, exhibits a thinner TGO layer compared to the MCrAlX bond coat, most likely due to the lower diffusion rate of HEA materials, which were approximately 3.6 and 5.7  $\mu\text{m}$  respectively.

2. The alumina oxide scale formed on the FeCoNiCrAl HEA remained intact throughout the oxidation process, demonstrating robust resistance to oxide scale spallation. Notably, no spinel oxide was observed on the HEA bond coat. In contrast, both alumina oxide and mixed oxides formed on the MCrAlX bond coat, attributed to the higher diffusion rate at elevated temperatures.

3. The as-sprayed FeCoNiCrAl HEA coating exhibited a dense and uniform microstructure with a predominant solid solution phase, indicating that the HVOF process effectively minimized oxidation during deposition. While in-flight oxidation (IFO) was not directly quantified using Oxygen–Nitrogen–Hydrogen (ONH) analysis, the lack of detectable

oxide phases and the elemental uniformity observed in EDS mapping suggest that oxygen pickup during spraying was minimal. These features, combined with the low measured porosity, support the conclusion that IFO was limited, contributing to the overall coating quality typically associated with HVOF-sprayed HEA systems.

These findings advance our understanding of the oxidation behavior, elemental diffusion at high temperatures, and microstructural evolution of FeCoNiCrAl HEA bond coats, highlighting their potential for enhanced performance in high-temperature applications. Future research should focus on modifying the FeCoNiCrAl HEA composition by incorporating reactive elements such as Y or Hf to further improve oxidation resistance and long-term stability at elevated temperatures.

## **4 Chapter Four: Optimization of HVOF Process Parameters for Enhancing FeCoNiCrAl HEA Bond Coatings in Thermal Barrier Systems**

The content of this chapter has been published in the Journal of Thermal Spray Technology in January 2025.

- Hossein Shahbazi performed the experimental work, data analysis, and manuscript preparation.
- Dr. Lima, Dr. Stoyanov, and Prof. Moreau provided supervision, technical input, and critical revisions.



## 4.1 Introduction

In order to improve the efficiency and power generation of gas turbines, it is essential to gradually increase the temperature of the incoming gas that powers the turbine. Consequently, there is a growing demand for materials with high-temperature resistance to be used in the hot section components [1,2,15,31,41,44,124,125]. Thermal barrier coatings (TBCs) have emerged as primary methods to ensure that the main components of the hot section (e.g., combustor, nozzles, and blades) operating under high temperatures meet necessary requirements. The main function of TBCs is to act as insulators against heat and protect against oxidation, effectively safeguarding the superalloy substrates from harmful effects [4,10,82,91]. MCrAlY coatings, which consist of Ni and/or Co, have gained widespread use in safeguarding superalloy components from oxidation and hot corrosion in gas turbine hot sections. The pursuit of enhanced engine combustion efficiency and emission reduction through higher operating temperatures poses a major coating design challenge. Therefore, it becomes crucial to improve bond coatings to enhance oxidation resistance. On the other hand, the bond coat failure is identified by the separation of the oxide scale from the interface between the bond coat and the oxide scale. This separation is triggered by the accumulated strain energy within the oxide scale, which intensifies as the oxide thickens during exposure to high-temperature oxidation [10,126]. Simultaneously, the concentration of impurities and the development of flaws at the interface would hasten the detachment of the oxide scale [127]. Hence, the exploration of advanced bond coats with heightened high-temperature resilience is a focal point of interest aimed at improving the stability and extending the service life of thermal barrier coatings under elevated temperatures. High Entropy Alloys (HEAs) exhibit remarkable properties at elevated temperatures, including synergistic effects and excellent resistance to oxidation and corrosion. Consequently, HEAs hold the potential to replace MCrAlY coatings effectively [128]. Utilizing a thermal spray method, such as High-Velocity Air Fuel (HVOF), can produce high quality bond coats thanks to their high density and reduced in-flight oxidation (IFO) [90]. HVOF-sprayed coatings tend to exhibit denser microstructures and contains fewer oxides compared to High-Velocity Oxygen Fuel (HVOF). Moreover, HVOF operates at relatively lower temperatures and employs air, as opposed to pure oxygen, as the oxidizing gas for combustion [53,54,59,129]. **Figure 4-1** illustrates the features of HVOF and the critical components of its two guns (M3

and i7). Furthermore, it identifies various variable parameters that can be optimized to obtain high-quality coatings.

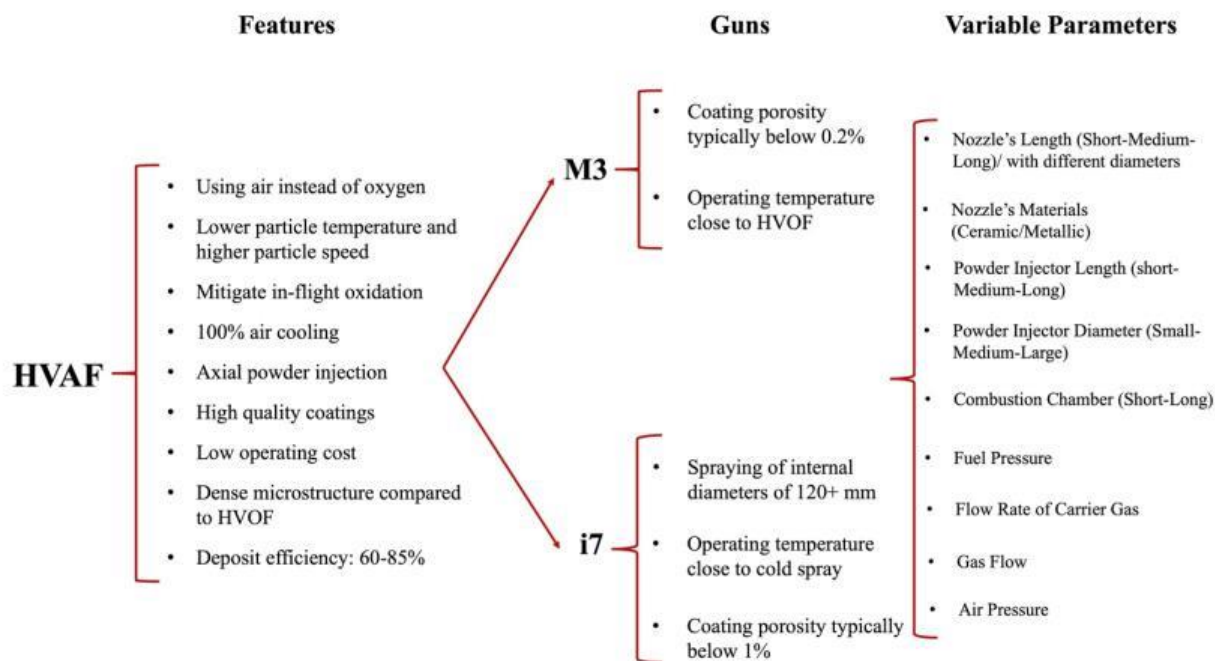


Figure 4-1 Identifying HVOF critical features and aspects of guns, with emphasis on variable parameters for coating quality optimization.

In this paper, FeCoNiCrAl equimolar HEA composition is investigated as a bond coat material owing to its remarkable combination of strength, ductility, and outstanding resistance to oxidation in elevated temperatures [90,130]. **Figure 4-2** illustrates the role of the elements in the bond coat. Crucially, the FeCoNiCrAl HEA, characterized by a significant Al content, is anticipated to exhibit robust resistance to oxidation. This resilience is attributed to its capacity to generate a protective alumina ( $\text{Al}_2\text{O}_3$ ) scale, similar to traditional MCrAlY bond coats. This high Al content, combined with the unique properties of HEAs, enhances the oxidation resistance and overall performance of the bond coat. Currently, considerable research efforts have been dedicated to comprehensively exploring the oxidation behavior of FeCoNiCrAl HEA [90,96,131,132].

In this study, FeCoNiCrAl HEA was utilized as a bond coat and applied using the HVOF technique. Various parameters were adjusted to optimize the process and achieve a dense coating with high deposit efficiency (83%) and low porosity (0.3%). An isothermal oxidation test was conducted to assess the behavior of the thermally grown oxide (TGO) layer

and the mass gain at elevated temperatures (1000°C after 50 hours). The results revealed the formation of a uniform and dense Al<sub>2</sub>O<sub>3</sub> TGO layer without any spinel oxide.

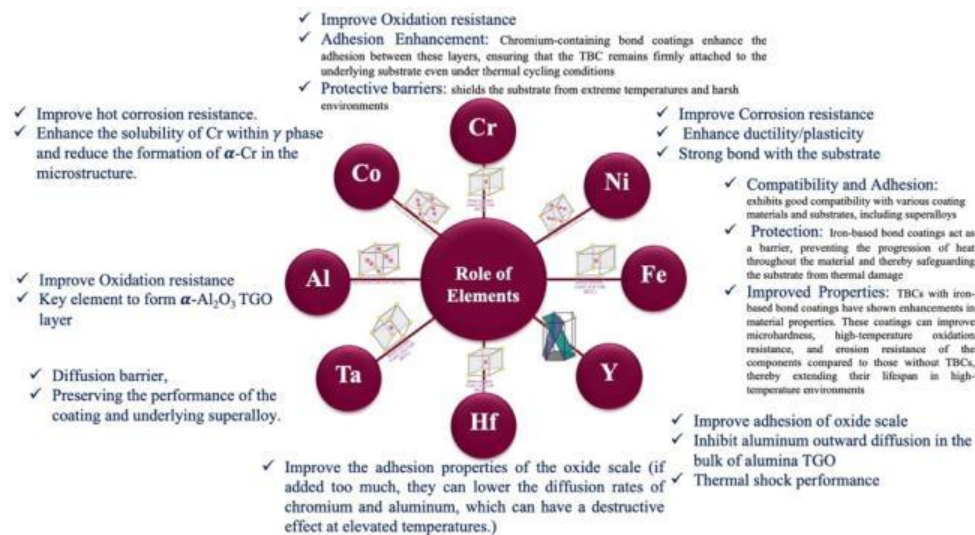


Figure 4-2 Role of elements in bond coat compositions.

## 4.2 Materials and methods

This study investigated a gas atomized FeCoNiCrAl HEA with an equimolar composition obtained from Heeger Co. USA, featuring a particle size distribution ranging from -45+15  $\mu\text{m}$  (d10: 21.3  $\mu\text{m}$ , d50: 34  $\mu\text{m}$ , d90: 53.28  $\mu\text{m}$ ). The powder characterization results, including particle size distribution measured through a wet laser diffraction particle size analyzer (Spraytec, Malvern Panalytical, Malvern, United Kingdom) and powder morphology analyzed via scanning electron microscopy SEM (S-3400 N, Hitachi High Technologies America, Inc., Japan) fitted with a photodiode BSE detector. Likewise, the chemical composition was analyzed through the use of energy-dispersive X-ray spectroscopy (EDS). Powder and coating phase analyses were conducted through X-ray diffraction (XRD) using Co-K $\alpha$  radiation ( $\lambda = 1.78 \text{ \AA}$ ,  $2\theta$  range of  $10^\circ$ – $120^\circ$ ) with a Bruker system from Germany, operated at 40 kV and 40 mA, 2 deg/min. Before applying the bond coat, the substrates underwent grit-blasting with Al<sub>2</sub>O<sub>3</sub> grit #80 at 4.1 bar (60 psi) to enhance surface roughness and promote better adherence of the coatings to the substrate. The Inconel and low carbon steel substrates exhibited a roughness (Ra) value of  $3.5 \pm 0.3 \mu\text{m}$  after the grit-blasting process. The cut-off length used for measuring Ra was 2.5 mm, with ten measurements taken to calculate the average Ra value. Measurements were conducted using a Mitutoyo-SJ.210 profilometer from Japan. To analyze the microstructure test, bond coats were produced on

low carbon steel substrates (25.4 \* 25.4 and 3 mm thick) and to perform the isothermal oxidation test bond coats were produced on Inconel-718 substrates puck-shape (25.4 mm in diameter and 6 mm thick). The FeCoNiCrAl HEA powder was sprayed using the HVAF coating process. To achieve this objective, M3-HVAF and i7-HVAF spray systems (from UniqueCoat Technologies LLC, VA, US) have been utilized. Various nozzles and powder injectors were employed in both preheating the substrates and the actual spraying process, with propylene selected as the fuel. The M3 gun is capable of producing high-quality coatings with porosity typically below 0.2%, and its operating temperature closely resembles that of HVOF. Featuring four nozzles (4L2C, 4L4C, 5L2C, 5L4C) with varying lengths and diameters, the M3 gun's performance is influenced by the coating quality. **Figure 4-3** illustrates the schematic of the M3 gun along with its different nozzles and powder injectors. It can be observed that, in the long nozzles, the particle residence time is increased, allowing them to spend more time in the hot combustion gas flow of the diverging section. Consequently, particles remain in the gas flow for a longer duration, leading to an increase in temperature and resulting in a less dense coating. The same principle applies to powder injectors; as their length increases, powder particles have less time to reach optimal temperatures. For instance, the long powder injector injects particles into the combustion chamber, which is close to the inner converging-diverging parts of the nozzle. **Table 4-1** depicts the HVAF parameters utilized by the M3 gun. Due to the limited range of pressure with which we could work, we maintained these parameters—providing favorable spray conditions—constant across all conditions.

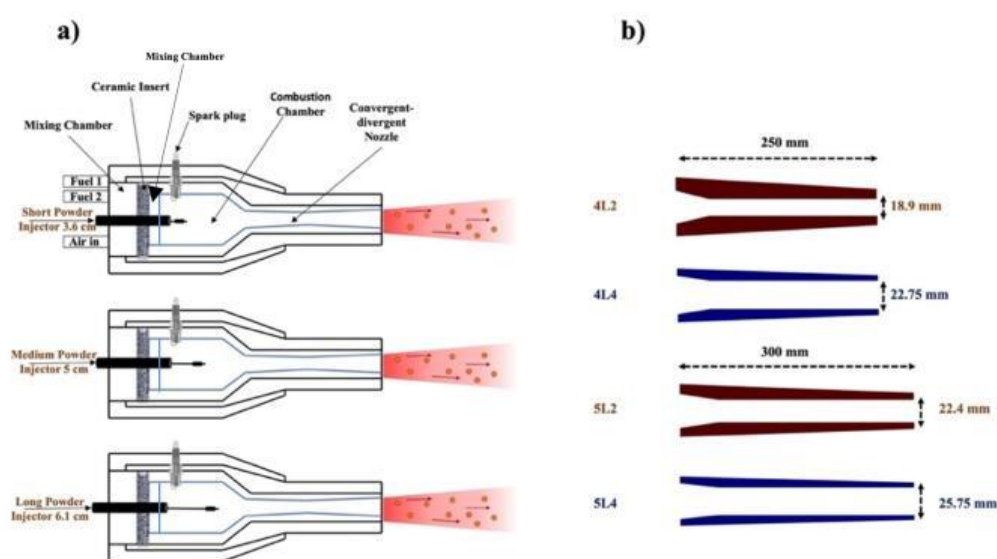


Figure 4-3 Simpled Schematic of HVOF M3 gun, a) schematics of M3 gun include powder injectors length, b) Schematics of M3 gun's nozzles.

Table 4-1 Overall summary of the spray parameters for the bond coat manufacturing via HVOF M3 gun.

|                                             |                           |
|---------------------------------------------|---------------------------|
| <b>Fuel 1 (Propylene) pressure (Psi)</b>    | 86                        |
| <b>Fuel 2 (Propylene) pressure (Psi)</b>    | 86                        |
| <b>Air pressure (Psi)</b>                   | 100                       |
| <b>Carrier gas flow rate (L/min)</b>        | 45                        |
| <b>Powder feed rate (g/min)</b>             | 120                       |
| <b>No. of passes</b>                        | 4                         |
| <b>Preheat (passes)</b>                     | 4                         |
| <b>Torch traverse speed (mm/s)</b>          | 1000                      |
| <b>Spray distance (mm)</b>                  | 300                       |
| <b>Nozzle Models</b>                        | 4L4, 4L2, 5L4, 5L2        |
| <b>Powder Injector Length</b>               | Short (36mm), Long (61mm) |
| <b>Substrate Temperature (FLIR Systems)</b> | 150 °C                    |

Furthermore, **Figure 4-4** displays the schematic of the i7 gun, showcasing its various nozzles and powder injectors with different diameters. In the i7 gun, compressed air and propylene are introduced into a combustion chamber. Subsequently, upon igniting the i7 gun, the graphite sheet is preheated to the ignition temperature of the gas mixture. Following this, the output from the mixing chamber enters the combustion chamber through the porous ceramic sheet [103]. Ultimately, an axially-fed nitrogen gas is employed to propel the HEA powder. The i7 gun, measuring 95 mm in length, is a scaled-down counterpart of the high-power HVOF-M3 gun. Its compact size enables the spraying of internal diameters exceeding 140 mm at a stand-off distance of 50 mm [103,104,133]. The i7 gun can produce coatings with high quality and porosity of less than 1%, and the operating temperature of this method is close to that of cold spray [129]. For the i7 gun, a 3L4 nozzle was paired with an elongated powder injector featuring a substantial diameter (2.75 mm) to prevent potential clogging, which may occur with a smaller diameter (0.875 mm). **Table 4-2** illustrates the HVOF parameters employed with the i7 gun. Fuel and air pressure start at low levels and increase to

higher values. The significant difference in standoff distances between the M3 (300mm) and i7 (50mm) HVOF guns is primarily due to their design, operational parameters, and intended applications. The M3 gun, with its longer standoff distance, is optimized for coating large surfaces, allowing particles to achieve optimal acceleration and heating, which is necessary for high deposition efficiency (DE) in large-scale applications. In contrast, the i7 gun is designed for precise applications with higher particle velocities and lower operating temperatures. The shorter standoff distance minimizes in-flight oxidation (IFO) and maintains the high kinetic energy of particles, ensuring dense and well-adhered coatings in intricate and confined space applications. Additionally, the standoff distances have been optimized to achieve the best results for each gun, considering the limited range of pressures that provide consistent and high-quality spray conditions.

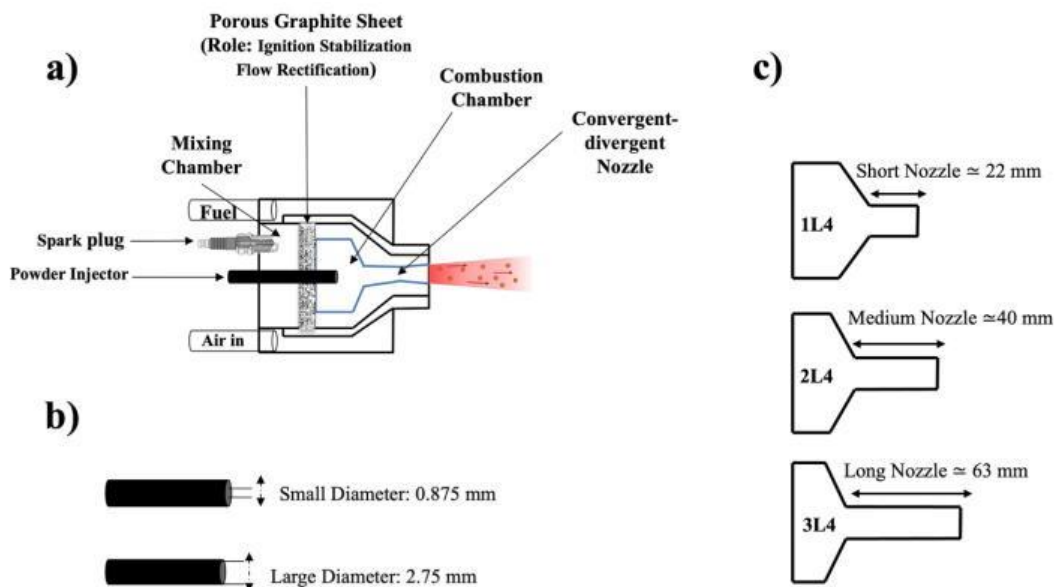


Figure 4-4 Schematic of HVOF i7 gun, a) i7 gun, b) powder injectors schematics in case of diameter variety, c) i7 nozzles schematics.

Table 4-2 Comprehensive overview of the spray parameters employed in the production of the bond coat using the HVAF i7 gun.

|                                             |                |
|---------------------------------------------|----------------|
| <b>Fuel pressure (Psi)</b>                  | 112            |
| <b>Air pressure (Psi)(P1/P2)</b>            | 130            |
| <b>Carrier gas flow rate (L/min)</b>        | 17             |
| <b>Powder feed rate (g/min)</b>             | 117            |
| <b>No. of passes</b>                        | 5              |
| <b>Preheat (passes)</b>                     | 5              |
| <b>Torch traverse speed (mm/s)</b>          | 1000           |
| <b>Spray distance (mm)</b>                  | 50.8           |
| <b>Powder Injector/Diameter</b>             | Large: 2.75 mm |
| <b>Substrate Temperature (FLIR Systems)</b> | 150 °C         |

The A320 ThermoVision infrared camera (FLIR Systems, MA) was utilized to observe and track the surface temperature of the coating during the preheating of the substrate. The Accuraspray system from Tecnar, Quebec, Canada was employed to track the temperature and velocity of particles in flight for each procedure. To enhance the preservation of their actual microstructures, the as-sprayed bond coat samples underwent a vacuum impregnation process in epoxy resin and hardener (ANAMET, Canada). Subsequently, they were ground and polished following standard metallography procedures commonly employed for TBCs, using SiC abrasive paper ranging from 220 to 4000 grit. This was followed by 9  $\mu\text{m}$ , 5  $\mu\text{m}$ , and 1  $\mu\text{m}$  water-based diamond suspensions, all applied with an automatic grinding-polishing machine (Struers, Canada). A final polishing step involved using a 0.4  $\mu\text{m}$  colloidal silica suspension on the polishing machine. The specimens were then cleaned in soapy water, sonicated in acetone to eliminate any remaining colloidal silica, and dried using hot air. The cross-sectional microstructural characteristics of the bond coats were examined using a Field Emission Scanning Electron Microscope (FESEM, Hitachi, Regulus 8230, Japan). Additionally, the elemental composition of the FeCoNiCrAl HEA bond coat was assessed

through energy dispersive x-ray spectroscopy (EDS) and mapping techniques. A tubular furnace with a maximum operating temperature of 1200 °C (Barnstead, F21135, USA) was used for the isothermal oxidation test.

### 4.3 Results and discussion

#### 4.3.1 Bond Coat Manufacturing via High Power Gun (M3)

**Figure 4-5** shows the powder morphology and characterization of FeCoNiCrAl HEA. All bond coats produced for this study were sprayed using HVAF with different guns and nozzles to optimize spray parameters and achieve a dense and uniform microstructure. The reasons for using different nozzles and powder injectors were fully explained in the last section, covering all aspects of the methodology. As it has been presented in **Table 4-3**, the influence of the nozzle and powder injector's length fully makes sense. By using the short powder injector and 4L4 nozzle, deposit efficiency (DE) was obtained 73 %. The measurement of DE involved assessing the weight of the strips before and after bond coat deposition. Additionally, it considered the powder feed rate and the total duration that the torch was over the strip during the spraying process [134]. After that, the powder injector was changed to the longer one, and the DE increased to 78%. This indicates that the powders were injected into a smaller area of the combustion chamber, allowing less time for them to reach higher temperatures. Finally, long powder injectors with various nozzles were continued to be used. Furthermore, the amount of porosity was measured using Image-J analysis, and the number of pores decreased when changing from a short powder injector to a long one from 3.6 % to 0.7 %. Ossiansson *et al.* [16] conducted a study on AlCrFeCoNi HEA as a bond coat for TBCs. In their research, they employed the HVAF technique, utilizing 4L4C and 5L4C nozzles. A key distinction between their study and ours lies in the use of different particle sizes and fuel types, contributing to achieving a denser and higher DE. Specifically, they employed a particle size distribution of -33+15 µm and propane as a fuel. In contrast, as detailed in **Table 4-1** and previously mentioned, our study utilized a -45+15 µm particle size distribution and propylene as a fuel. This choice proved more effective and beneficial for the HVAF M3 guns, facilitating the attainment of a dense and uniform microstructure. Furthermore, Lobel *et al.* [59] employed a 4L4C nozzle and propane as a fuel in their investigation into the microstructure and corrosion properties of AlCrFeCoNi HEA coating, utilizing a particle size distribution of -45+15 µm. The examination revealed a dense

microstructure with some pores and unmolten particles at high magnification. In comparison to our study, the pore content in our results is slightly lower (approximately 0.7%) than that reported by Lobel *et al.* This difference is attributed to the use of propylene as the fuel in our study. In conclusion, the alteration of nozzles to 4L2C resulted in a deposition efficiency (DE) of 83%, accompanied by a porosity level of 0.3%.

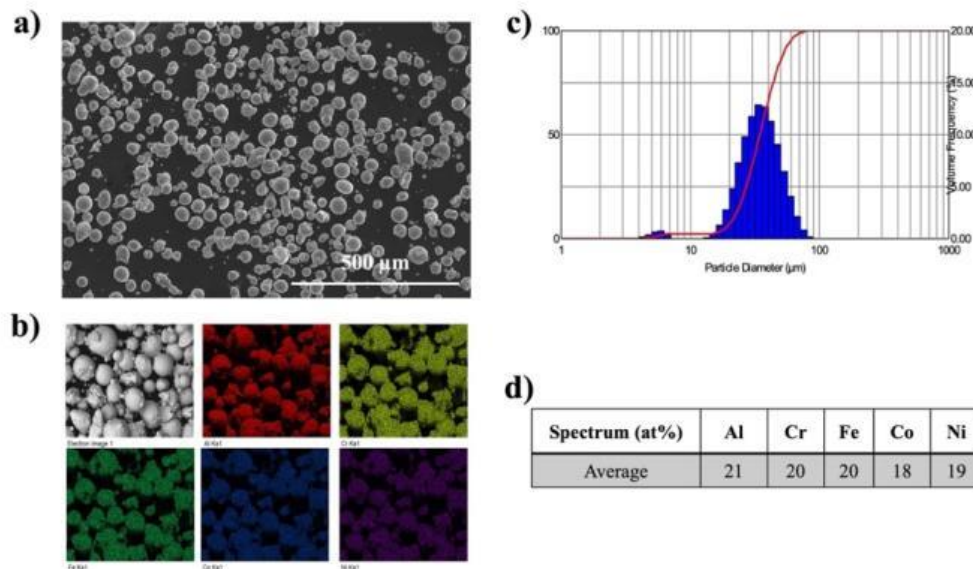


Figure 4-5 Characterization of FeCoNiCrAl HEA powder: a) SEM image, b) mapping, c) particle size distribution, d) EDS point analysis.

Table 4-3 Influence of nozzle and powder injector variations on deposition efficiency (DE) and porosity of coatings sprayed using the HVAF-M3 gun. Each value represents the mean  $\pm$  standard deviation (SD), calculated from six DE measurements and approximately one hundred porosity measurements taken from five distinct locations across the coating cross-section.

|                       | 4L4C/Short<br>Powder<br>Injector | 4L4C/Long<br>Powder<br>Injector | 4L2C/Long<br>Powder<br>Injector | 5L4C/Long<br>Powder<br>Injector | 5L2C/Long<br>Powder<br>Injector |
|-----------------------|----------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| <b>D.E. (%)</b>       | 73 $\pm$ 0.1                     | 78 $\pm$ 1.2                    | 83 $\pm$ 1.2                    | 80 $\pm$ 1.3                    | 81 $\pm$ 1.0                    |
| <b>Porosities (%)</b> | 3.6 $\pm$ .3                     | 0.7 $\pm$ .1                    | 0.3 $\pm$ .1                    | 0.5 $\pm$ .1                    | 1.9 $\pm$ .2                    |

**Figure 4-6** exhibits the FESEM cross-sectional micrograph of the FeCoNiCrAl HEA bond coat sprayed via the HVAF M3 gun with the 4L2C nozzle and long powder injector.

The maximum temperature reached by substrates in the pre-heated process was 150 °C at a distance of 3.2 m tracked by the IR camera (FLIR Systems). **Figure 4-7** depicts the particle velocities and temperatures. The average particle temperatures of the bond coat reached approximately 1456 °C, 1488 °C, 1578 °C, and 1460 °C during spraying, as monitored by Accuraspray for 4L2, 4L4, 5L2, and 5L4 nozzles, respectively. Additionally, the average particle velocity was recorded as 625 m/s, 653 m/s, 687 m/s, and 710 m/s by Accuraspray for 4L2, 4L4, 5L2, and 5L4 nozzles. As evident, particles in shorter nozzles obtain lower temperatures because they have less time to reach the desired temperature. Conversely, in longer nozzles, we observe that the temperature of particles is higher than that in short nozzles. When examining the nozzle diameter, it becomes apparent that as the diameter decreases, particles gain more acceleration and speed. Given the significance of minimizing IFO (In-Flight Oxidation) and its positive impact on reducing oxidation, thereby enhancing coating density, it is recommended to use nozzles such as 4L2 and 5L2. This recommendation is crucial as one must adhere to optimal temperature and particle speed for effective results. Besides, mapping demonstrates the uniform distribution of each element in as-sprayed samples under various conditions. However, there are some bright areas in the aluminum and oxygen mapping images, indicating the presence of alumina from the grit blasting process. In addition, EDS analysis indicates that the composition of each element in the HEA powder is consistent with that in the as-sprayed material. Furthermore, the oxygen content is consistently below 3 at%, underscoring the effectiveness of the HVAF technique in mitigating in-flight oxides through controlled processes [135,136]. Consequently, based on the XRD characterization presented in **Figure 4-8**, it is evident that a random solid-solution phase microstructure, characterized by high density, was achieved using the HVAF M3 gun [116]. Moreover, the sprayed coating produced by the i7 gun, as depicted in this figure, exhibits a phase similar to that produced by the M3 gun and the HEA powder. Additionally, some broad peaks can be observed, possibly indicating the presence of finer particles, a rougher surface, or particle recrystallization. This characteristic is intrinsic to HEA, where the elements are in a disorderly configuration in the atomic radius neighborhoods, unlike conventional materials formed based on one or two principal elements with an ordered configuration [90]. This distinction is evident in the various area (dark and bright) observed in the microstructure under high magnification in each condition. The best result was obtained with 4L2, which involves long powder injectors. EDS line analysis in **Figure 4-9** reveals bright areas rich in Cr and dark areas rich in Al, illustrating microsegregation. It is evident that light elements, such as Al, appear as dark areas in the microstructure, while heavy elements, like Cr, manifest as

bright areas. Hence, it is advisable not to definitively categorize these areas as distinct phases, as the fluctuation graphs in the line EDS analysis do not show significant deviations, and caution should be exercised in making such distinctions. Therefore, it can be suggested that random solid solution phases were obtained by using the HVOF technique for the FeCoNiCrAl HEA composition. The beauty of using HEA as a bond coat lies in the avoidance of the  $\beta$ -phase (NiAl-rich phase). In conventional bond coats, the presence of this phase can lead to brittleness, particularly at lower temperatures. As the temperature surpasses a critical point, typically around 750°C for NiAl, the brittleness diminishes, and the material can withstand more strain before fracturing. This temperature, known as the "ductile to brittle transition temperature" (DBTT), plays a crucial role. However, when coatings containing  $\beta$ -NiAl are used in applications such as TBCs that undergo temperature variations, a challenge emerges[90]. These coatings are susceptible to developing cracks as the temperature drops below the DBTT [95,100]. This is especially problematic for TBCs subjected to heating and cooling cycles, as cracks can form during the cooling phase. By selecting FeCoNiCrAl HEA over the conventional MCrAlY bond coat, the occurrence of brittle  $\beta$ -NiAl rich phases can be prevented, addressing the challenges associated with the ductile-to-brittle transition temperature.

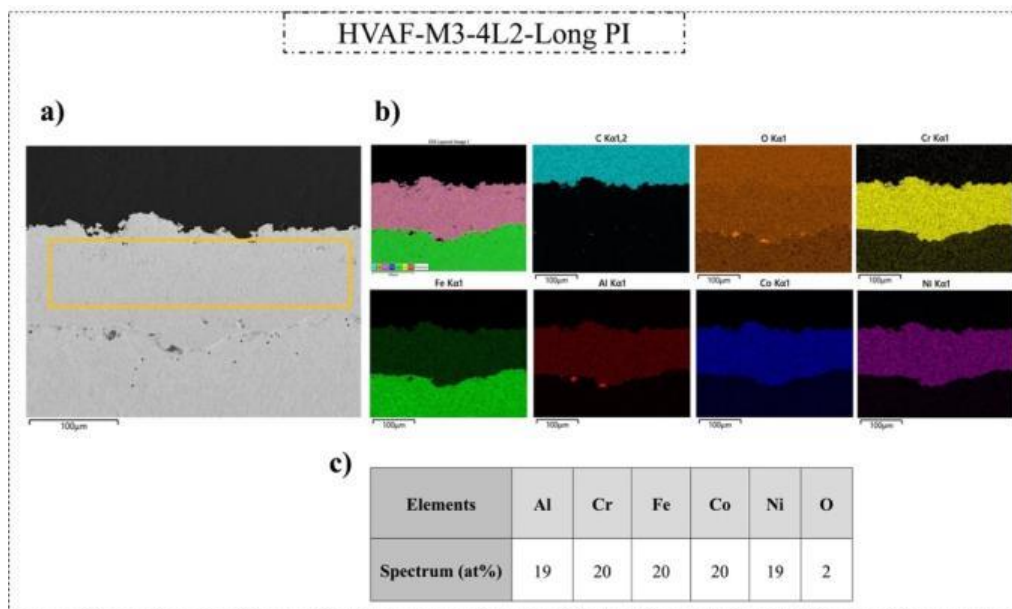


Figure 4-6 FESEM of the as-sprayed microstructure of FeCoNiCrAl HEA using HVOF M3 gun employing 4L2C nozzle with long powder injector: a) Cross-sectional as-sprayed HEA bond coat, b) Mapping analysis representing the uniformity of elements and random solid solution, c) EDS area analysis (Orange rectangle identifying the EDS area).

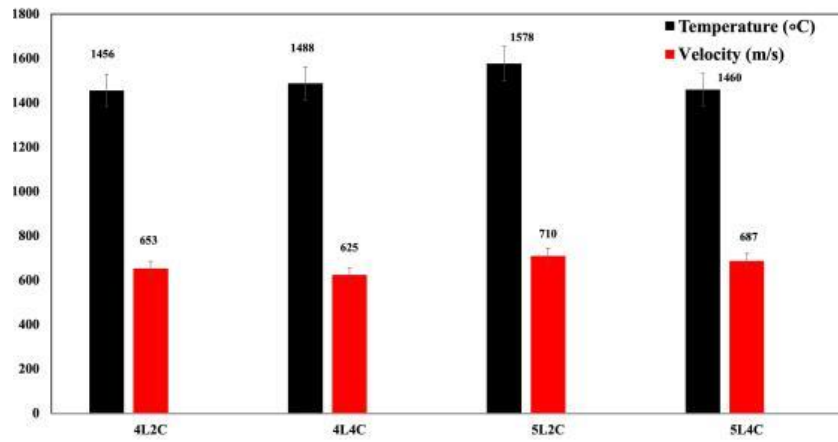


Figure 4-7 Particle velocities and temperatures recorded by Accuraspray.

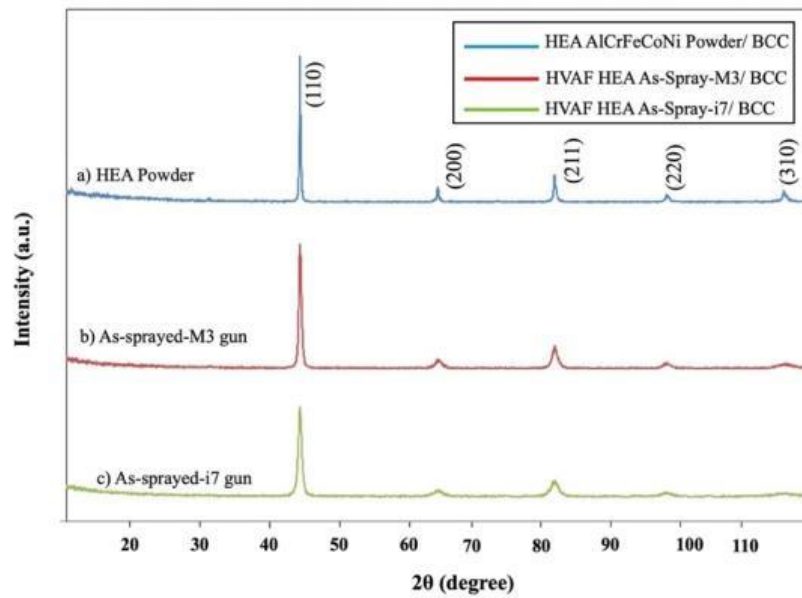


Figure 4-8 XRD of a) FeCoNiCrAl HEA powder, b) As-sprayed bond coat manufactured by the M3 gun, c) As-sprayed FeCoNiCrAl HEA bond coat manufactured by the i7 gun.

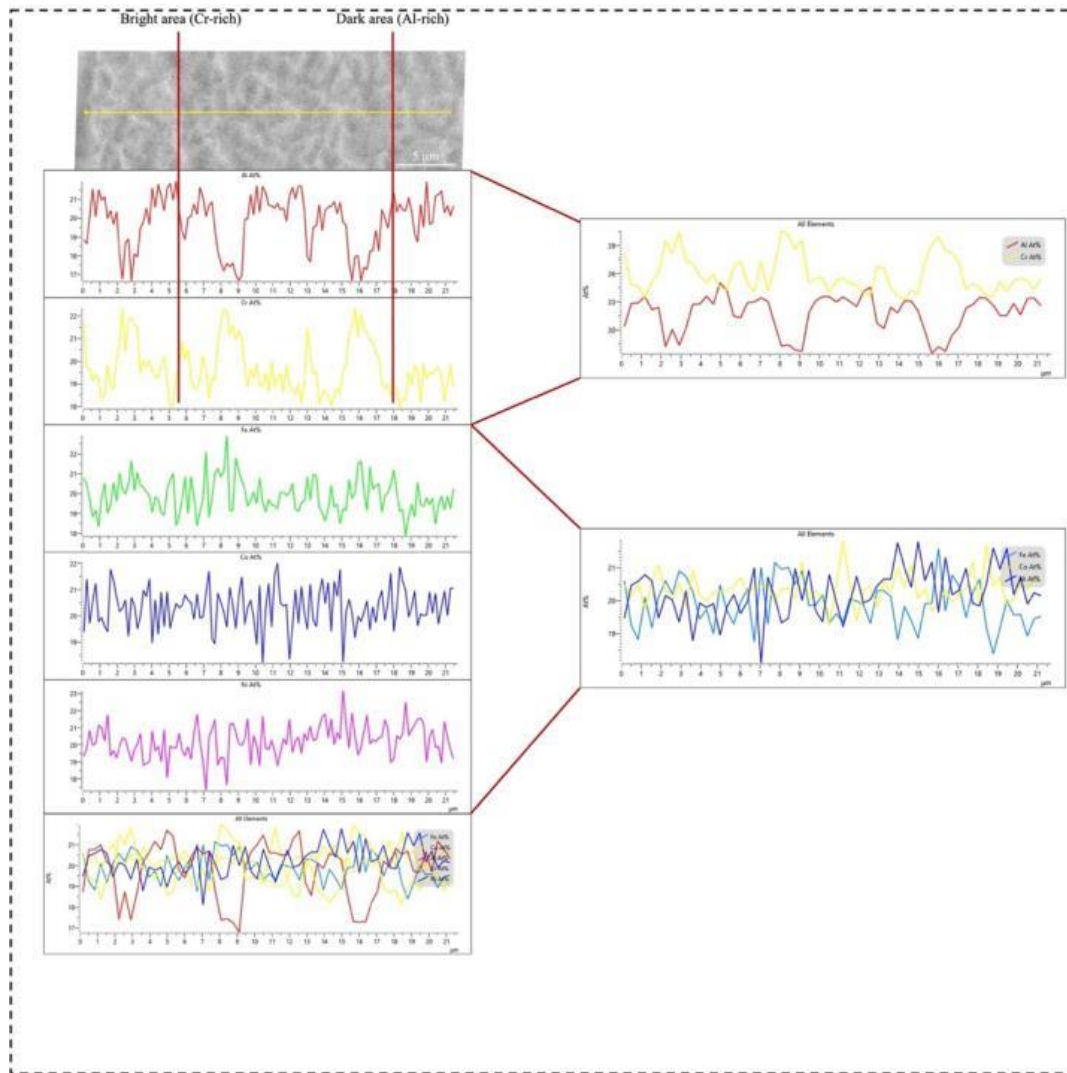


Figure 4-9 EDS line analysis for phase identification: Bright areas (Cr-rich) and dark areas (Al-rich).

#### 4.3.2 Bond Coat Manufacturing via Low Power Gun (i7)

The impact of pressure is further detailed in **Table 4-4**. **Figure 4-10** presents the cross-sectional FESEM micrograph of the FeCoNiCrAl HEA bond coat manufactured using the HVAF i7 gun with the 4L3 nozzle and medium pressure. The only alteration made involved adjusting the air and fuel pressure. Achieving a narrow and continuous flame is crucial when spraying with the i7 gun, and this is accomplished by modifying the air and fuel pressures. One of the advantages of using the i7 gun is its operating temperature, which is close to cold spray. This property aids in mitigating IFO formation and obtaining a dense structure [104,129,133]. However, challenges arise during the spraying process. For instance, the optimal particle size for this gun to achieve high DE and a dense microstructure is  $-30 \pm 5 \mu\text{m}$ . If the particle size exceeds this range, heavier particles would need to be accelerated at low temperatures, which is not feasible and results in a low deposition efficiency (DE). According

to the HVOF i7 mechanism, powder particles are accelerated and impinge on the substrate, producing a coating based on kinetic energy generated by the high velocity of particles. The utilization of a particle size distribution of  $-45+15\ \mu\text{m}$  was employed in the project, and finer particle sizes of  $-30+5\ \mu\text{m}$  are planned for future stages. Despite being unable to increase the thickness and deposit efficiency beyond  $35\ \mu\text{m}$  and 23%, respectively, an amazing outcome was achieved: a dense, random solid solution microstructure presented in **Figure 4-10**. This is evident in the uniformity of elements seen in mapping and EDX analysis, showcasing the equimolar concentration of elements. As depicted, the presence of splat boundaries and pores are more obvious compared to using the M3 gun, attributed to the chosen particle size distribution, as explained earlier. In **Figure 4-10**, some features are identified by red arrows. A comparison with the M3 gun reveals a similar pattern of bright (Cr-rich) and dark (Al-rich) areas. However, one notable difference is the decreased unmolten particles/area when using the i7 gun, owing to its lower temperature compared to the M3 gun. **Figure 4-11** illustrates an overall perspective of the microstructure achieved through the HVOF technique employing both i7 and M3 guns with FeCoNiCrAl HEA.

Table 4-4 Influence of variations in air and fuel pressure on deposition efficiency (DE) and porosity of coatings sprayed using the HVOF-i7 gun. Each DE value represents the mean  $\pm$  standard deviation calculated from six coating trials. Porosity values were determined from approximately 100 measurement points (20 per each of five distinct locations) across the polished cross-section of each coating.

|                             | Low Pressure | Medium Pressure | High Pressure |
|-----------------------------|--------------|-----------------|---------------|
| <b>Air Pressures (psi)</b>  | 118          | 130             | 140           |
| <b>Fuel Pressures (psi)</b> | 100          | 112             | 120           |
| <b>D.E (%)</b>              | $20\pm1.0$   | $23\pm1.2$      | $18\pm1.0$    |
| <b>Porosities (%)</b>       | $3.9\pm0.20$ | $3\pm0.20$      | $4.5\pm0.30$  |

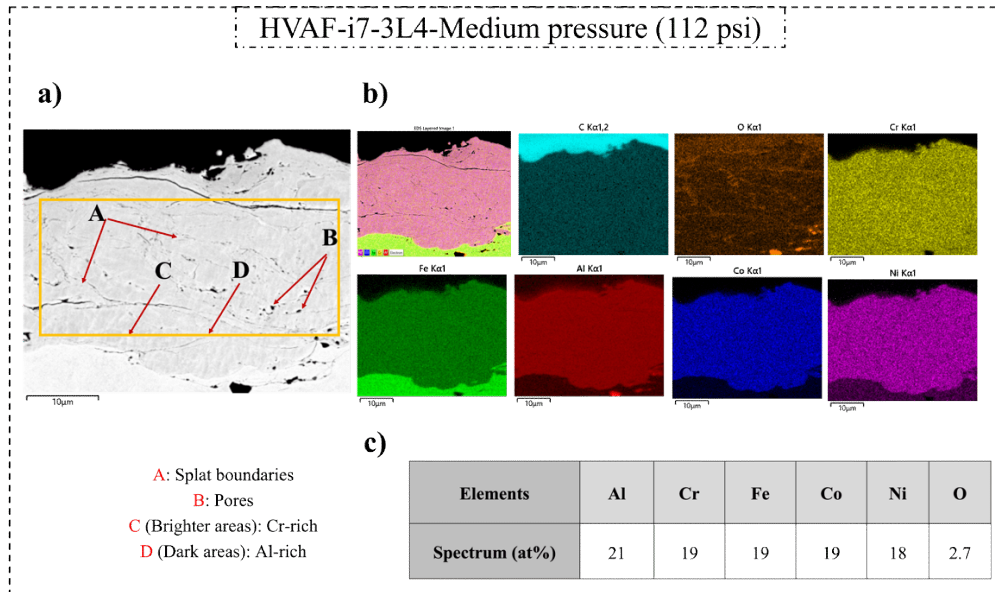


Figure 4-10 FESEM of the as-sprayed microstructure of FeCoNiCrAl HEA using HVAF i7 gun/medium pressure: (arrows indicating bond coat features), b) Mapping analysis representing the uniformity of elements and random solid solution, c) EDS area analysis (Orange rectangle identifying the EDX area).

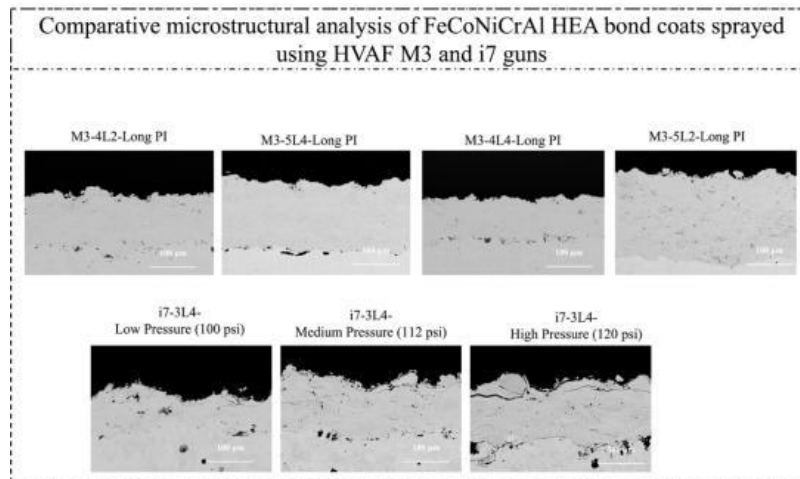


Figure 4-11 General view of the microstructure sprayed by the HVAF technique using i7 and M3 guns using FeCoNiCrAl HEA.

### 4.3.3 Isothermal Oxidation Test

To investigate the formation of the TGO layer at high temperatures, an isothermal oxidation test in ambient air at 1000 °C was conducted. This specific test was selected due to the extreme temperatures that turbine engines can be exposed to. It is crucial to note that while these high temperatures are encountered during certain phases of a turbine engine's operation, they are not sustained throughout its entire working cycle. The 50-hour test was performed using a programmable automated tube furnace from Barnstead. The FeCoNiCrAl HEA was

sprayed onto the Inconel-718 puck-shaped substrate, using the HVOF technique with M3 and i7 guns. The coated samples (M3-4L2C, M3-4L4C, M3-5L2C, M3-5L4C and i7-Low Pressure, i7-Medium Pressure, i7-High Pressure) were placed in ceramic alumina crucibles, then weighed four times using a Mettler Toledo, ME204E (220 g capacity; 0.1 mg readability, USA). The specimens were positioned in ceramic crucibles to collect any oxide scales that might have detached during the experiment. Following the test, the specimens were permitted to cool in the surrounding environment, after which the crucible-containing samples were reweighed. This process was carried out again for durations of 10, 20, 30, 40, and 50 hours. The disparity in weight [mg] for each sample was subsequently divided by the entire surface area of the sample (coating area + substrate) [cm<sup>2</sup>]. The results of the isothermal oxidation test, conducted at 1000°C, are depicted in **Figure 4-12**. In all samples, there was no apparent spallation observed, suggesting that the adherence of the oxide scales remained intact. The plotted data shows the oxidation rate in terms of the increase in mass per unit area of the sample. In an overall assessment, it can be observed that the coatings produced by the i7 gun exhibit a lower thickness compared to those obtained by the M3 gun. This difference in thickness results in the formation of oxides with a lower mass, as clearly illustrated in **Figure 4-12**. **Figure 4-13** illustrates the cross-sectional microstructure of the 4L4C sample from the isothermal oxidation test. To avoid repetition, similar results from other nozzles of the M3 gun and other conditions (low, medium, and high pressure) of the i7 gun have been omitted. Instead, the focus is entirely on presenting the final results concerning the thickness of the oxide layer, which will be thoroughly discussed in the following sections. As illustrated, the Al<sub>2</sub>O<sub>3</sub> TGO layer forms uniformly and exhibits a consistent scale in all spray conditions, showcasing the efficacy of the HVOF technique combined with the FeCoNiCrAl HEA composition. Moreover, No Al<sub>2</sub>O<sub>3</sub> oxide scale spallation was observed. The formation of the TGO layer results from the oxidation reaction between oxygen that permeates through the top coat and aluminum ions existing in the bond coat [137]. Furthermore, based on the EDS point analysis, it is evident that in the diffusion area, the amount of aluminum is lower than that of other elements. This indicates the presence of aluminum ions migrating from the bond coat to the top layer, contributing to the formation of the TGO layer. **Figure 4-14** illustrates that the thickness of the heat treatment samples produced by the M3 gun through nozzles 4L2C, 4L4C, and 5L2C are closely aligned, exhibiting reasonable behavior after 50 hours at 1000 °C. For the 5L4C nozzle, the test must be repeated because the sample was not placed in the middle of the crucible to obtain an accurate temperature gradient, but based on the microstructure, it is expected to exhibit the same behavior. Additionally, samples sprayed by the i7 gun using

different pressures indicate that the most favorable behavior is associated with medium pressure. However, both low and high pressures demonstrate remarkable TGO thickness behavior. To more accurately assess their behavior, it is necessary to achieve higher coating thicknesses (around 150  $\mu\text{m}$ ). In general, it is believed that the incorporation of reactive elements into the HEA composition and the use of the i7 gun, along with finer particles, have the potential to enhance oxidation resistance and mitigate oxide layer thickness at elevated temperatures and over extended periods. **Figure 4-15** displays the cross-sectional microstructures of the FeCoNiCrAl/substrate interfaces following 50 hours of oxidation at 1000  $^{\circ}\text{C}$ . Due to the substantial difference in chemical composition between the bond coat and the Inconel 718 superalloy substrate, diverse contrasts, microstructures, and distinct interfaces are clearly observed in the cross-sections after oxidation. As indicated in **Figure 4-15(a)**, there emerged an inner- $\beta$ -depletion zone (IBDZ) and an interdiffusion zone (IDZ) in the neighborhood of the interface [121]. The development of the IBDZ and IDZ in the proximity of the bond coat/substrate interface primarily results from the diffusion of Al (as well as Co and Cr) originating from the Al-rich bond coat and the diffusion of Ni from the Ni-rich superalloy, respectively [138]. Moreover, the examination of cross-sectional views indicates the presence of secondary phases, identified by the contrasting dark grey and white areas, which have precipitated in the IDZ (**Figure 4-15 (a)**). Based on the EDS line analysis in **Figure 4-15 (a)** and the point analysis in **Figure 4-15 (b)**, dark grey and white precipitates were identified. In summary, the results indicate distinct element interdiffusion behaviors correlated with chemical compositions. In certain areas, the volume of Ni increases, suggesting an inclination to diffuse into the coating. Conversely, the volume of Al decreases, implying consumption and diffusion to the top layer, contributing to the formation of the TGO scale layer. Liu *et al.* [121] conducted a study on the oxidation and interdiffusion of the AlCoCrFeNiY HEA bond coat on a Ni-based superalloy. They identified dark grey and white precipitates as (Ni, Al)-rich  $\beta$  phase and (Ti, Ta, W)-rich carbides, respectively. Additionally, they quantified the amount of  $\beta$  phase using Image J software and observed a decrease from 30% to 9% in the IDZ with an increase in temperature from 1050  $^{\circ}\text{C}$  to 1150  $^{\circ}\text{C}$ . This finding contributes to a reduction in the DBTT, showcasing the remarkable properties of HEAs. These materials exhibit a sluggish diffusion effect at elevated temperatures, aiding in minimizing transition phases and maintaining a solid solution state. Therefore, it is crucial to conduct tests such as isothermal oxidation tests and thermal cycling fatigue tests to understand the growth process and the type of oxide layer, as these factors can directly influence the failure of TBC.

Further discussion should acknowledge that the development of the TGO plays a pivotal role in the failure of the ceramic layer within a TBC system. The TGO typically consists of various oxides, such as  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, NiO, Cr<sub>2</sub>O<sub>3</sub>, and (Ni, Co)(Cr, Al)<sub>2</sub>O<sub>4</sub>, collectively known as mixed oxides [90]. In order to achieve effective oxidation resistance and prevent accelerated spalling of the ceramic layer in TBC systems, it is crucial to establish a continuous, dense, and slow-growing TGO layer. Recent studies have shown that the rapid growth of mixed oxides can result in local cracks and peeling of the ceramic layer [139–141].  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is widely regarded as an optimal component of the TGO due to its exceptional stability at high temperatures, low ion diffusion rate, and strong compactness. Extensive research has shown that once the TGO thickness surpasses a critical threshold of 10-15  $\mu$ m, it triggers the formation of cracks within the ceramic layer, ultimately resulting in the failure of TBCs [108,141]. Therefore, it is crucial to avoid the formation of mixed oxides and the creation of a dense and uniform TGO consisting entirely of pure  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. So, it is essential to control the TGO thickness, ensuring it reaches a specific threshold, and maintain a slow growth rate. These measures are instrumental in reducing stress within the neighboring ceramic layer and extending the lifespan while enhancing the performance of TBCs [142].

The time between overhaul (TBO) represents the number of flying hours and/or cycles (i.e., one flight equals one cycle) a turbine can stay on the wing before requiring a major overhaul. This complexity depends on factors such as the type of turbine (e.g., power), environmental conditions (e.g., desert, volcano, sea), and aircraft type (e.g., business jet or wide-body). During each flight, a plane cannot operate at maximum take-off thrust for more than 5 minutes, as exceeding this limit renders the plane not airworthy. Following take-off, the engine power is reduced to about 1/3 of the maximum take-off thrust, resulting in lower stress, strain, and TGO thickening. Consequently, during take-off, the engine experiences the highest stresses and strains, including those affecting TBCs. In practical terms, commercial jets do not always operate at maximum take-off power for the entire flight duration. The 5-minute limit for full power usage is the maximum duration pilots are allowed to extend the engine to its full power during any single flight. Typically, using the engine at maximum power for the full 5 minutes is not a common occurrence in commercial jets. The 5-minute mark is used as a reference for estimating the time engines may spend at peak temperatures. In real-world scenarios, pilots often take off without utilizing the maximum take-off thrust [143]. This practice, known as de-rated take-off thrust, is implemented when conditions permit, such as when the runway is sufficiently long or the aircraft is lightly loaded. De-rated take-off thrust is employed to preserve the engine's life, as operating at maximum thrust for take-off puts significant stress and strain on engine components. The existence of de-

rated take-off thrust is motivated by the desire to avoid the high stress/strain intensity experienced by jet engines at maximum take-off power [144]. Incidents of engines blowing or catching fire in the air, leading to emergency returns to the airport, are more likely during take-off and are rare during cruise flight when turbine power operates at around 30% of its maximum power [143].

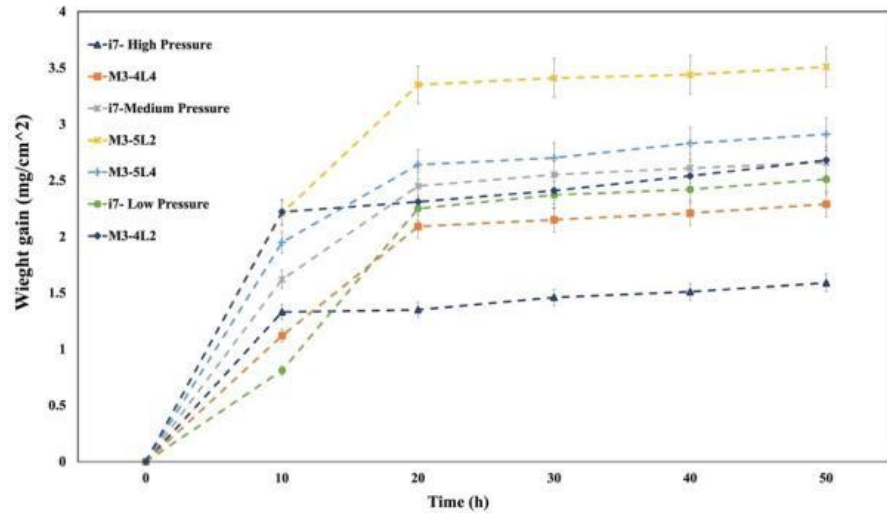


Figure 4-12 Isothermal oxidation test of the HEA bond coat using HVOF via M3 and i7 guns. Error bars represent the standard deviation.

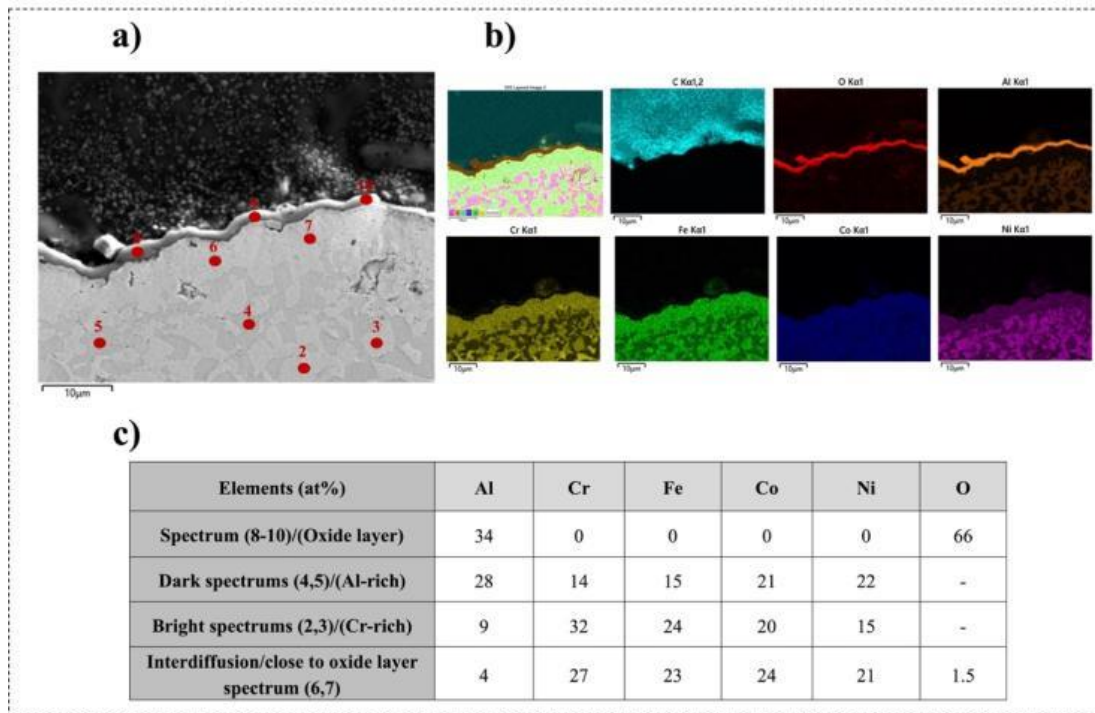


Figure 4-13 FESEM images illustrating the isothermal oxidation microstructure of FeCoNiCrAl HEA using the HVOF M3 gun with nozzle 4L4C: a) Microstructure of the heat-treated 4L4C sample and the TGO layer, with point analysis by EDS; b) Mapping of the cross-section of the heat-treated 4L4C sample, depicting the  $\text{Al}_2\text{O}_3$  TGO layer; c) EDS analysis confirming the formation of the alumina TGO layer after 50 hours at 1000 °C.

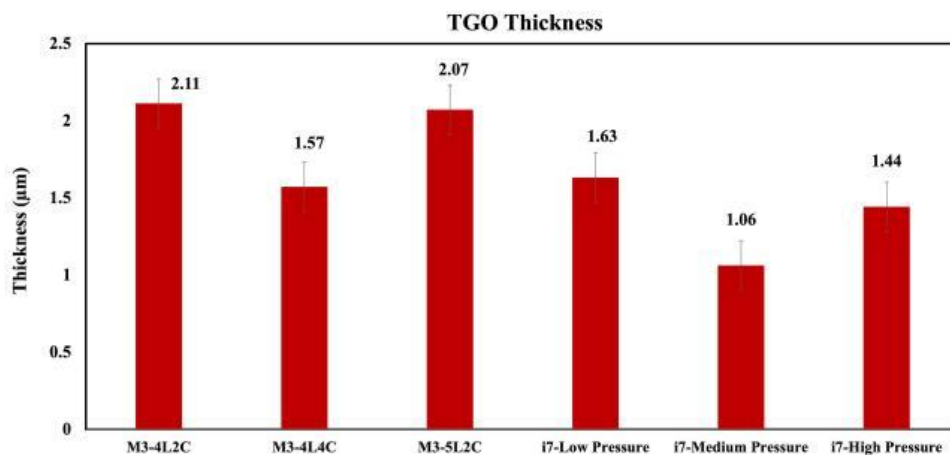


Figure 4-14 TGO thickness of heat-treated samples sprayed via HVOF using different guns (M3 and i7) under various configurations (M3: 4L2C, 4L4C, 5L2C; i7: low, medium, and high pressure conditions).

Error bars represent the standard deviation (SD) of thickness measurements obtained from approximately 20 points per cross-section at five different locations.

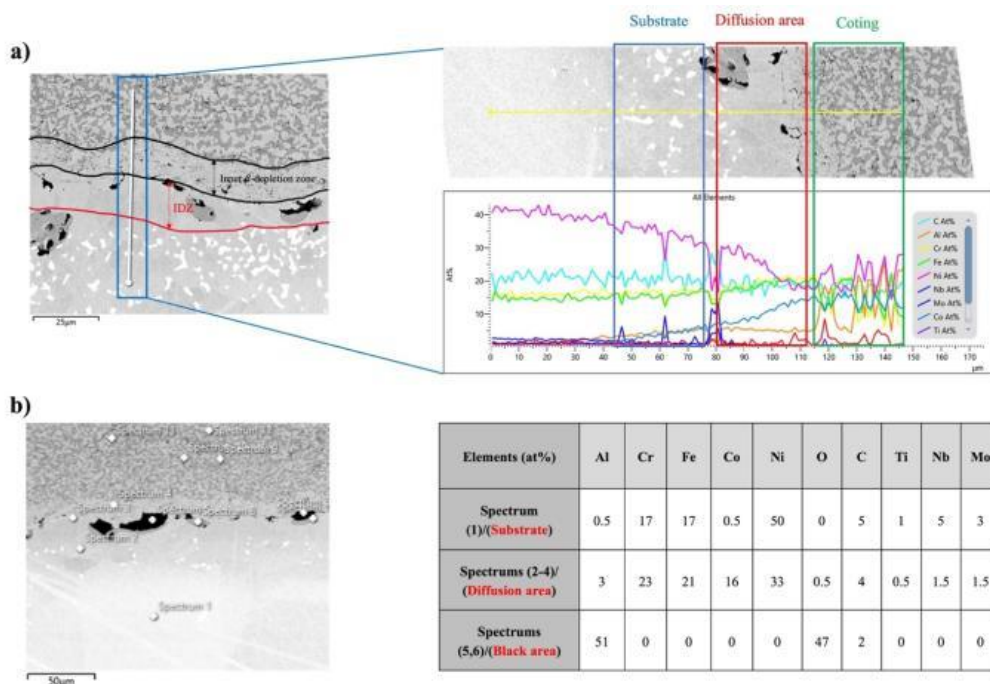


Figure 4-15 Cross-sectional microstructure (M3-5L2) of the bond coat/substrate interface after 50 hours of oxidation at 1000°C. (a) EDS line analysis, (b) EDS point analysis.

#### 4.4 Conclusion

In this study, a FeCoNiCrAl HEA bond coat with a dense and uniform microstructure was prepared using HVOF techniques, employing different nozzles, powder injectors, and fuel pressures on both carbon steel and Inconel 718 superalloy substrates. The investigation focused on the oxidation behavior of the FeCoNiCrAl bond coat at 1000 °C, encompassing oxide growth, spallation, and the evolution of microstructure, as well as the interdiffusion behavior between the bond coat and the superalloy substrate. The following conclusions can be drawn from this work:

1. The FeCoNiCrAl HEA bond coat demonstrates effective control over oxidation rates across all seven tested conditions (four with the M3 gun and three with the i7 gun). Optimal results were achieved with the M3 gun, particularly when using the 4L2C nozzle. While minor variations were observed among the results, the 5L4C condition notably stands out.
2. The microstructure obtained is dense, uniform, and exhibits a solid solution, underscoring the efficacy of using HVOF in mitigating In-Flight Oxidation (IFO).
3. The alumina oxide scale formed on FeCoNiCrAl remains intact throughout the oxidation process, indicating robust resistance to oxide scale spallation. Notably, no spinel oxide was observed. This resilience is attributed to the increased strain energy within the oxide scales and the formation of interfacial defects. In comparison to MCrAlY, as reported in the literature, FeCoNiCrAl HEA has the potential to serve as a suitable alternative for commercial bond coats when reactive elements are incorporated into the HEA composition.

These findings contribute to our understanding of the oxidation behavior and microstructural evolution of FeCoNiCrAl HEA bond coats, highlighting the potential for improved performance in high-temperature applications. Moreover, incorporating reactive elements into the composition is anticipated to enhance oxidation resistance at higher temperatures, a direction for future research. Additionally, the use of finer

particles with the i7 gun contributes to achieving a denser microstructure in the bond coat. Notably, this project marks the first application of the HEA bond coat sprayed by the i7 gun, representing a pioneering development in the field.

## **5 Chapter Five: Effect of Microstructure on Oxidation Resistance and TGO Formation in FeCoNiCrAl HEA Coatings Deposited by Low-Temperature HVOF Spraying**

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- Hossein Shahbazi conducted the experimental design, oxidation tests, and data interpretation.
- Dr. Lima, Dr. Stoyanov, and Prof. Moreau contributed to discussion and manuscript editing.

## 5.1 Introduction

Thermal barrier coatings (TBCs) play a critical role in modern gas turbines, aerospace engines, and other high-temperature applications by protecting essential components from thermal degradation and extending their operational lifespan. A key element of TBCs is the bond coat, which serves as an intermediate layer that enhances adhesion between the substrate and the thermal barrier top coat. Additionally, the bond coat provides essential resistance to oxidation and corrosion, ensuring durability in demanding operating conditions [90,94]. While traditional bond coat materials, such as MCrAlX alloys, where M represents Ni, Co, or NiCo, and X includes elements such as Y, Hf, Ta, and Si, have shown satisfactory performance, ongoing research continues to explore alternative materials with superior properties to enhance the durability and reliability of TBC systems further[23,128,145,146]. Among the promising candidates, FeCoNiCrAl high-entropy alloys (HEAs) stand out because of their exceptional mechanical properties and outstanding oxidation resistance at elevated temperatures[7,11,14,16,28,35,39,40,45,59,80,85,90,96–98,121,125,132,147]. In the realm of thermal spray techniques employed for applying bond coats, several methods have been developed, each offering unique advantages and challenges[8,14,34,61,83,84,90,142]. Notably, high-velocity air fuel (HVOF) stands out for its ability to produce coatings with dense microstructures, which is a very desired characteristic for improving TBC performance[42,54,59,103,104,129,133]; by reducing coating porosity, unlike conventional techniques such as high-velocity oxy-fuel (HVOF), HVOF utilizes air instead of oxygen as the combustion medium, resulting in lower particle temperatures and higher particle velocities during the spraying process[59]. This advanced approach effectively minimizes in-flight oxidation and promotes the formation of high-quality, dense coatings with low as-sprayed oxidation levels. Among HVOF systems, the ID-HVOF i7 torch enables the deposition of coatings within internal diameters as small as 120 mm while maintaining precise control over coating quality and porosity levels[90]. A critical factor influencing HVOF performance is the selection of an appropriate particle size distribution (PSD), which plays a key role in determining the quality of the resulting microstructure. In their study, Shahbazi et al. investigated the HEA bond coat deposited using the HVOF process with an M3 gun, identifying an optimal PSD of 15–45  $\mu\text{m}$  for achieving high-quality coatings [98]. Additionally, they examined the same FeCoNiCrAl HEA composition with a 15–45  $\mu\text{m}$  PSD using the HVOF-i7 gun to assess the impact of a lower-temperature spray system. While this

approach resulted in a dense and uniform bond coat, it did not achieve significant coating thickness. Based on the findings in the literature and the experimental experience of our team, a PSD of 5–30  $\mu\text{m}$  was identified as optimal for the HVAF-i7 gun and was thus selected for this study[101]. Mauer et al. investigated the potential of the HVAF-M3 system for producing bond coats in TBC applications, focusing on conventional MCrAlY materials[148]. Their findings highlighted several advantages of HVAF over traditional methods. For example, atmospheric plasma spraying (APS) operates at high temperatures, leading to oxide formation during and after spraying, while HVOF uses oxygen in its fuel system, further promoting oxidation and increasing operational costs. As a result, HVAF emerges as a more cost-effective and efficient alternative. Additionally, the study compared the performance of two HVAF nozzles, 4L2 and 4L4, revealing a slight increase in deposition efficiency with higher particle velocities. The 4L4 nozzle achieved the maximum particle velocity at a spray distance of 350 mm, approximately 50 mm farther downstream than the optimal 300 mm spray distance for the 4L2 nozzle.

This study explores the potential of FeCoNiCrAl HEA as a replacement for conventional bond coats in TBC systems. By leveraging the unique properties of FeCoNiCrAl HEA and the advanced capabilities of HVAF technology, the goal is to develop dense microstructures that minimize spallation and facilitate the formation of a continuous, slow-growing thermally grown oxide (TGO) layer. To achieve this, the isothermal oxidation behavior of FeCoNiCrAl HEA coatings is systematically examined at temperatures ranging from 1000 °C to 1150 °C for 50 h. This investigation provides comprehensive insights into the TGO layer's evolution under high-temperature conditions, evaluating the feasibility of FeCoNiCrAl HEA for enhancing TBC performance in demanding applications.

## **5.2 Materials and methods**

This study investigated the effects of microstructure, density, and porosity of FeCoNiCrAl HEA coatings fabricated using the ID-HVAF i7 torch (UniqueCoat Technologies, Oilville, VA, USA) on the isothermal oxidation behavior. To the best of the authors' knowledge, this is the first study to employ the i7 ID torch to spray a FeCoNiCrAl HEA bond coat for TBC applications. The research examined the coating's microstructure and chemistry, TGO growth, alumina phase transformation, and oxidation rate at different temperatures. The characterization of the powder included particle size distribution analysis using a wet laser diffraction particle size analyzer (Spraytec, Malvern Panalytical Ltd.,

Malvern, UK) and cross-sectional powder morphology analysis via scanning electron microscopy (SEM) (S-3400N, Hitachi High Technologies America, Inc., Tokyo, Japan), equipped with a photodiode BSE detector, as shown in **Figure 5-1**. The chemical composition was determined using energy-dispersive X-ray spectroscopy (EDS). The EDX line scan in **Figure 5-1** confirms the presence of Cr-rich and Al-rich regions within individual HEA powder particles, indicating microsegregation due to the sluggish diffusion effect inherent in HEAs. This segregation leads to compositional variations within the particles yet prevents significant phase separation after spraying, contributing to a more stable and uniform microstructure.

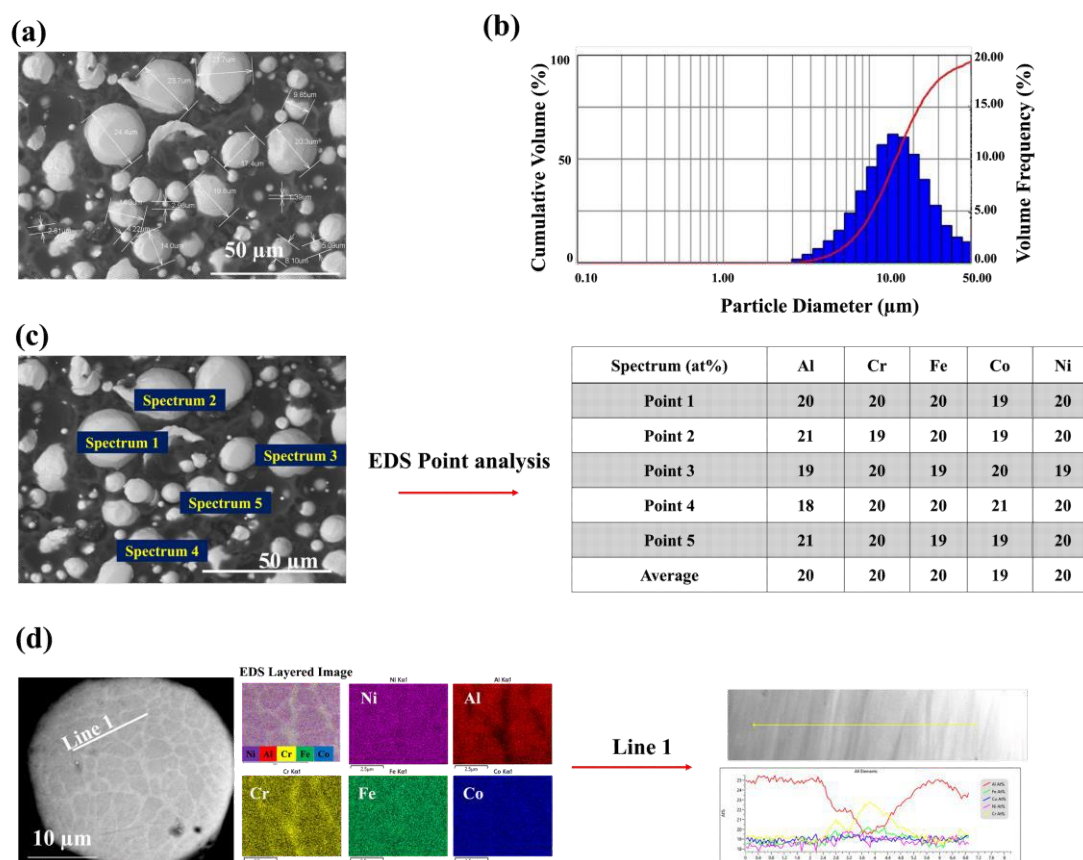


Figure 5-1 Characterization of FeCoNiCrAl HEA powder: (a) SEM image showing particle morphology and size measurements; (b) Particle size distribution measured using laser diffraction; (c) SEM-EDS image with marked spectrum points and corresponding elemental composition (at%) from point analysis; (d) Cross-sectional SEM image of a particle showing EDS elemental mapping (Al, Cr, Fe, Co, Ni) and EDS line scan across Line 1.

Before applying the bond coat, the substrates underwent grit blasting with Al<sub>2</sub>O<sub>3</sub> grit #80 at 4.1 bar (60 psi) to increase surface roughness and enhance coating adhesion. The substrate's roughness plays a critical role in how thermal spray particles interact with the surface during deposition. In HVAF and HVOF processes, particles impacting a rough surface can deform and fill surface irregularities more effectively, contributing to a denser microstructure. However, if the surface is too smooth, particle adhesion may be insufficient, leading to a lower coating density. Conversely, an excessively rough surface may prevent particles from fully filling the valleys, potentially increasing coating porosity[84]. This process resulted in an average surface roughness (Ra) of  $3.9 \pm 0.6 \mu\text{m}$  on the Inconel 718 substrate. The Ra measurements were performed using a Mitutoyo-SJ.210 profilometer (Mitutoyo Corporation, Kawasaki, Japan) with a cut-off length of 2.5 mm, averaging ten measurements.

Isothermal oxidation tests were conducted on puck-shaped Inconel 718 substrates with a 25.4 mm diameter and 6 mm thickness. The ID-HVAF i7 system employs large converging-diverging nozzles and long, large-diameter powder injectors for both preheating and spraying, using propylene as fuel. The extended nozzle increases particle residence time in the hot combustion gas, promoting a dense microstructure. This torch produces high-quality coatings with porosity levels below 1%.

To prevent clogging issues associated with smaller injectors, the 3L4 nozzle (long nozzle: 63 mm) was paired with a large-diameter powder injector (2.75 mm). The HVAF parameters used with the i7 gun are summarized in **Table 5-1**.

Table 5-1 Spray parameters for bond coat production using the HVAF i7 ID torch.

|                                      |        |
|--------------------------------------|--------|
| Fuel pressure (Psi)                  | 112    |
| Air pressure (Psi) (P1/P2)           | 130    |
| Carrier gas flow rate (L/min)        | 25     |
| Powder feed rate (g/min)             | 120    |
| No. of passes                        | 5      |
| Preheat (passes)                     | 5      |
| Torch traverse speed (mm/s)          | 1000   |
| Spray distance (mm)                  | 50.8   |
| Substrate temperature (FLIR systems) | 155 °C |

During the spraying process, a ThermoVision A320 infrared camera (FLIR Systems, Inc., North Billerica, MA, USA) was used to monitor the substrate's surface temperature, with a preheating temperature recorded at 155 °C. To preserve the actual microstructures, the as-sprayed bond coat samples were vacuum-impregnated in epoxy resin and hardener (ANAMET, Frankford, ON, Canada). The samples were then mounted, cut, and polished following standard metallographic procedures.

The cross-sectional microstructure of the bond coats was analyzed using a Field Emission Scanning Electron Microscope (FESEM, Hitachi, Regulus 8230, Tokyo, Japan). The elemental compositions of the FeCoNiCrAl HEA bond coat and the TGO layer were assessed using energy-dispersive X-ray spectroscopy (EDS) and elemental mapping techniques. For isothermal oxidation testing, a tubular furnace with a maximum operating temperature of 1200 °C (Barnstead Thermolyne, Model F21135, Dubuque, IA, USA) was used.

## 5.3 Results and discussions

### 5.3.1 The microstructure of the coatings

**Figure 5-2** shows the cross-sectional microstructure of the HEA bond coat sprayed via an HVAF-i7 torch with a long nozzle and large-diameter powder injectors. Based on our previous study, FeCoNiCrAl HEA was sprayed with different air and fuel pressure parameters[98]. The highest deposition efficiency and lowest porosity in the microstructure were achieved using medium air and fuel pressure, as detailed in **Table 5-1**. The deposition efficiencies (DEs) for low, medium, and high air and fuel pressures were 73%, 79%, and 53%, respectively, while the corresponding porosity levels were 0.8%, 0.2%, and 1.8%. Porosity measurements were conducted using ImageJ (Version 1.53t) analysis. As mentioned earlier, the porosity of HVAF-i7 coatings typically falls around 1%. However, the use of propylene as a fuel—due to its higher calorific value and ability to generate a narrow, stable flame—combined with optimized spray parameters enabled the achievement of a significantly lower porosity of 0.2% and a dense microstructure. This dense structure minimizes oxygen ingress, thereby substantially reducing internal oxidation in the bond coat compared with coatings with higher porosity (>6%). While it does not directly mitigate TGO thickening, the reduction in internal oxidation helps maintain the bond coat's integrity and delays spallation

at high temperatures[149]. Examining the microstructure reveals that the intermediate inter-diffusion zone (IDZ) at the coating/substrate interface is approximately 3  $\mu\text{m}$  thick, indicating a similar level of inter-diffusion throughout. Due to the relatively thin inter-diffusion layer ( $\sim 3\ \mu\text{m}$ ) compared with the thicker coating ( $\sim 150\ \mu\text{m}$ ), the impact of inter-diffusion on the oxidation behavior can be considered negligible[150]. As shown in **Figure 5-2**, the cross-sectional low-magnification image reveals a fully dense micro-structure, demonstrating the effectiveness of the HVAF-i7 process in producing high-density coatings because of its low-temperature operation. At higher magnification, some semi-molten areas are visible. These features result from the high-velocity impact of particles onto the substrate, where kinetic energy facilitates coating densification. In some cases, the temperature generated by particle collisions may lead to the presence of semi-molten or unmolten regions within the microstructure.

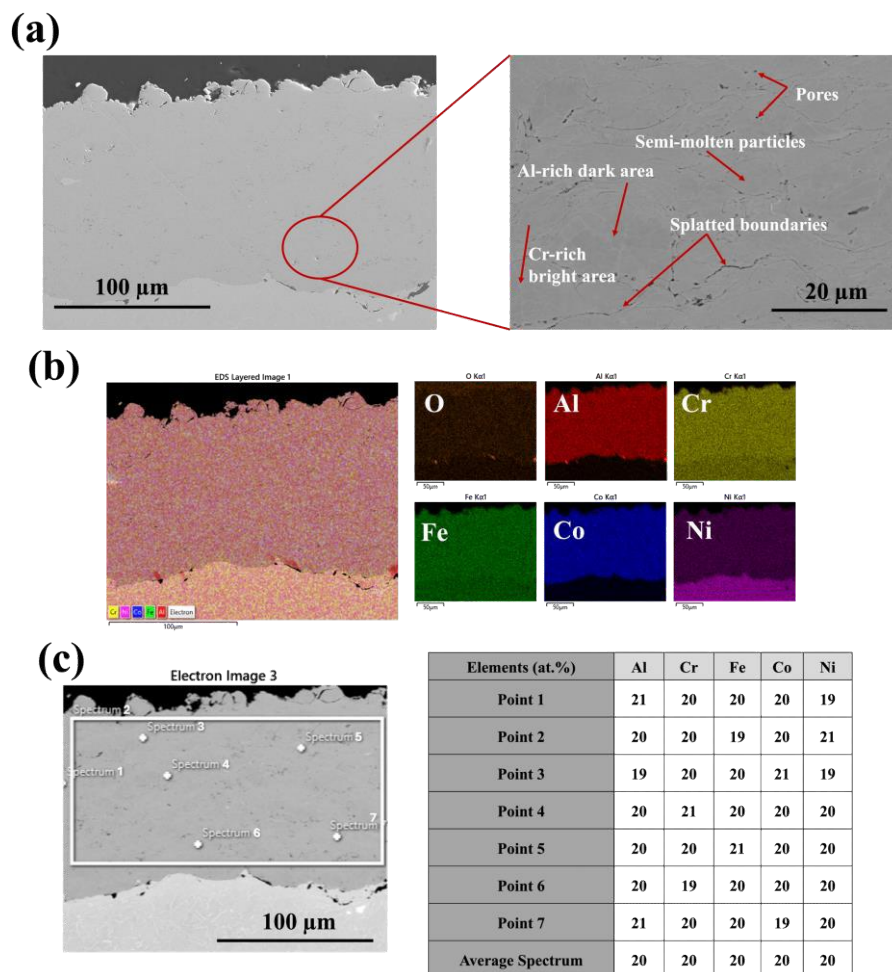


Figure 5-2 FESEM images of the as-sprayed microstructure of FeCoNiCrAl HEA using the HVOF i7 gun: (a) Cross-sectional view of the as-sprayed HEA bond coat, (b) Elemental mapping showing uniform distribution and random solid solution, (c) EDS area and point analysis (white rectangle indicating the EDS area).

In **Figure 5-1**, two distinct areas—dark and bright—are visible, corresponding to Al-rich and Cr-rich regions, respectively. This suggests microsegregation within the cross-sectional powder. Light elements such as Al appear as dark areas in the microstructure, while heavy elements such as Cr stand out as bright areas. Therefore, it is advisable not to categorically identify these areas as distinct phases without significant deviations in the EDS line analysis fluctuation graphs. Instead, it indicates that random solid solution phases were achieved using the HVOF technique for the FeCoNiCrAl HEA composition. The advantage of using HEA as a bond coat is the absence of the  $\beta$ -phase (NiAl-rich phase), which is often found in conventional bond coats and can cause brittleness at lower temperatures [98]. As temperatures exceed the ductile-to-brittle transition temperature (DBTT), around 750 °C for NiAl, this brittleness reduces, allowing the material to endure more strain before fracturing[90]. Moreover, the  $\beta$ -NiAl phase, which typically appears as granules, is less apparent or missing near defects such as splat boundaries, voids, oxide stringers, and unmelted particles in APS and HVOF bond coats. The disappearance of the  $\beta$ -NiAl phase near these defects suggests that they negatively impact the phase's integrity or consistency. Generally, the  $\beta$ -NiAl phase is valued for its high-temperature oxidation resistance and mechanical properties. However, its presence has both advantages and disadvantages, as discussed earlier[151]. By using HEA, the issues associated with the  $\beta$ -NiAl phase are avoided, resulting in improved oxidation resistance. This benefit will be further detailed in the subsequent section of this study.

**Figure 5-3** shows the XRD patterns of the HEA powder and the HVOF-i7 deposited coating, indicating that no significant phase transformations occurred during the spraying process. Both conditions exhibit a body-centred cubic (BCC) structure, confirming that the high-velocity spraying process effectively preserves the original phase composition and promotes the formation of a random solid solution.

Moreover, pseudo-Voigt fitting was performed on the four main diffraction peaks to analyze the peak profiles quantitatively. The extracted FWHM values for the powder and the coating are provided in **Table 5-2**. The results reveal that the FWHM values of the coating are nearly identical to those of the feedstock powder, indicating that no considerable crystallite refinement or strain evolution occurred during deposition. This observation suggests that the

HVAF-i7 process preserves not only the phase composition but also the crystallite characteristics of the initial powder. Consequently, the process produces a dense and phase-stable coating with minimal micro-structural changes, reinforcing its potential as a suitable HEA bond coat for thermal barrier coating applications.

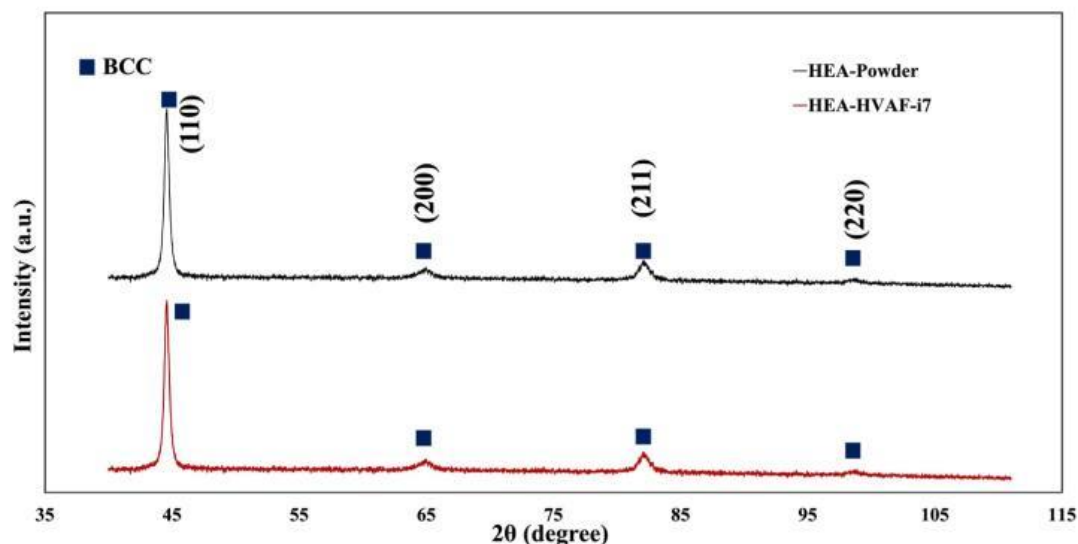


Figure 5-3 XRD patterns of FeCoNiCrAl HEA powder and HVAF-sprayed coating.

Table 5-2 FWHM values of the four major peaks for the powder and HVAF-i7 coating obtained by pseudo-Voigt fitting.

| Peak (hkl) | FWHM (Powder) (°) | FWHM (HVAF-i7 Coating) (°) | Difference (°) |
|------------|-------------------|----------------------------|----------------|
| (110)      | 0.46124           | 0.46131                    | 0.00007        |
| (200)      | 1.123             | 1.123                      | 0.00000        |
| (211)      | 0.882             | 0.896                      | 0.01400        |
| (220)      | 1.684             | 1.703                      | 0.01900        |

Furthermore, based on **Figure 5-2**, EDS mapping and area analysis confirm the formation of a random solid solution phase with a uniform elemental distribution after coating. This highlights the effectiveness of the HVAF technique and the intrinsic high-entropy effect, which promotes the development of a solid solution phase within a simple crystalline structure[90,152]. As previously mentioned, roughness plays a critical role in determining coating quality in TBCs. Both substrate and bond coat roughness are essential for enhancing adhesion, increasing bonding strength, and reducing stress at the bond coat–top coat interface. A rougher bond coat surface promotes mechanical interlocking with the ceramic top coat, improving adhesion and minimizing the risk of delamination[84]. Increased

roughness also enhances the surface area available for top coat adhesion, further improving bonding strength. A rough bond coat surface helps distribute thermal stress more evenly, reducing localized stress concentrations that could lead to cracking and spallation. Controlled roughness promotes the formation of a uniform and well-adhered thermally grown oxide (TGO) layer, which is essential for oxidation resistance. However, excessive roughness may introduce stress concentrations, increasing the risk of premature failure[153].

Optimal roughness enhances thermal barrier properties by strengthening the bond between layers and improving the system's overall thermal insulation efficiency. Enhanced adhesion due to optimal roughness also increases fatigue resistance, particularly under cyclic thermal and mechanical loads, such as those experienced in gas turbines and aeroengines. Achieving the ideal roughness through techniques such as grit blasting is crucial for ensuring reliable TBC performance in high-temperature applications. Generally, an average roughness ( $R_a$ ) of 3 to 5  $\mu\text{m}$  provides a balance between mechanical interlocking and maintaining a smooth surface to prevent stress concentrations. In this study, coating roughness was measured using a Mitutoyo-SJ.210 profilometer with a 2.5 mm cut-off length, averaged over ten measurements, yielding an  $R_a$  value of 4.7  $\mu\text{m}$ .

### 5.3.2 TGO microstructure and growth kinetics

Prolonged exposure to high temperatures (exceeding 100 h) resulted in unsatisfactory outcomes, likely because of the melting point limitations of the Inconel 718 substrate. This led to partial substrate melting, which compromised coating integrity. To address this issue, Inconel 625 has been selected for future studies, with further investigations planned to evaluate its performance under similar conditions.

Gupta et al. explored strategies to enhance the lifespan of SPS thermal barrier coatings, focusing on bond coats deposited using the HVOF process with the M3 supersonic gun (10, 50, 100, and 200 hours). Isothermal oxidation tests were conducted at 1100 °C for 10, 50, 100, and 200 h. Their results revealed the formation of a uniform, dense, and continuous alumina TGO layer after 50 h of exposure. Additionally, a mixed oxide TGO began to develop in the MCrAlY bond coat as the test progressed. Notably, even after 200 h of oxidation, the TGO thickness remained well-controlled at approximately 6 µm[154].

In contrast, the present study observed no formation of mixed oxides after 50 h at 1150 °C. This can likely be attributed to two key factors: (i) the sluggish diffusion characteristics inherent to HEAs, which reduce the transport of elements such as Cr and Al, thereby limiting the formation of complex oxides, and (ii) the use of the HVOF-i7 gun, a lower-temperature spraying technique that minimizes oxidation during deposition. However, a thermally grown oxide (TGO), primarily Al<sub>2</sub>O<sub>3</sub>, was observed on the surface of the HEA bond coat over time, indicating that oxidation occurred but remained largely limited to the formation of a protective alumina scale rather than mixed oxide phases. The HVOF-i7 gun operates at reduced particle temperatures compared with the HVOF-M3, minimizing the formation of oxides during spraying and promoting the development of a more uniform, oxide-free microstructure. This reduced oxidation at the deposition stage further delays the formation of mixed oxides during subsequent high-temperature exposure[98]. After 50 h at 1000 °C, 1100 °C, and 1150 °C, a dense, uniform, and thin alumina TGO layer was observed in the HEA bond coat. These results suggest that the enhanced oxidation resistance of the HEA coating is likely attributable to the dense microstructure achieved using the HVOF-i7 process. While a direct comparison with benchmark bond coat systems (e.g., MCrAlY) is not available within this study, evidence from the literature indicates that the HVOF-M3 gun, which operates at higher particle temperatures, tends to introduce more oxides during deposition. By contrast, the lower operating temperature of the HVOF-i7 gun minimizes oxide formation during

spraying, thereby promoting a more uniform and oxide-free bond coat microstructure. Additionally, the inherent sluggish diffusion characteristics of HEAs further suppress the transport of alloying elements such as Cr and Al, which are critical for forming protective oxides, thereby delaying the formation of mixed oxides during high-temperature exposure. Collectively, these factors likely contribute to the observed differences in TGO characteristics and highlight the potential advantages of combining HEAs with the HVOF-i7 spraying technique.

The growth of the TGO layer remained controlled, resulting in a dense and continuous alumina TGO layer. In conventional bond coats, alumina TGO layers often spall at higher temperatures when reactive elements are absent. However, the FeCoNiCrAl HEA bond coat demonstrated enhanced oxidation resistance by promoting the formation of a uniform and adherent alumina TGO layer. This behavior may be attributed to the unique properties of HEAs, particularly sluggish diffusion, which can slow the movement of elements, thereby controlling TGO growth and reducing spallation risk, as observed in this study.

To monitor oxidation behavior, specimens were placed in alumina ceramic crucibles to collect any detached oxide scales during testing. After each specified exposure time, samples were removed from the furnace, air-cooled to room temperature for approximately 5 min, and reweighed while still in their respective crucibles. Each sample was weighed five times, with precautions taken to prevent oxide and ash weight loss. The weight gain due to TGO formation was recorded at each time interval, and the total weight difference (mg) for each sample was divided by the total surface area (coating + substrate) [cm<sup>2</sup>] to determine the specific weight gain[34,50,84,155,156]. This process ensured accurate measurement of the oxidation behavior and the development of the TGO layer over various durations and temperatures.

The results of the isothermal oxidation tests at 1000, 1100, and 1150 °C after 50 h are shown in **Figure 5-4**. No visible spallation was observed in any sample, indicating that the oxide scales remained intact. These plotted data represent the oxidation rate as an increase in mass per unit area. The coatings deposited using the HVOF-i7 gun with HEA exhibit low thickness, attributed to the dense microstructure achieved through this process. As shown in **Figures 5-5, 5-6, and 5-7** the oxide growth increases with temperature at 1000 °C, 1100 °C, and 1150 °C, respectively. The HVOF-i7 technique, combined with HEA, effectively controls the growth of the TGO layer. Future research in our group will explore the incorporation of reactive elements such as Y and Hf to further regulate TGO growth. The Al<sub>2</sub>O<sub>3</sub> TGO layer

formed uniformly and consistently across all isothermal oxidation tests, demonstrating the effectiveness of the HVOF-i7 process in conjunction with the FeCoNiCrAl HEA composition. No  $\text{Al}_2\text{O}_3$  oxide scale spallation was detected. The TGO layer formation results from the oxidation reaction between oxygen diffusing through the top coat and aluminum ions in the bond coat. EDS point analysis confirms that in the diffusion zone, the aluminum content is lower than that of other elements, indicating that aluminum ions migrate from the bond coat to the top layer, contributing to TGO layer formation.

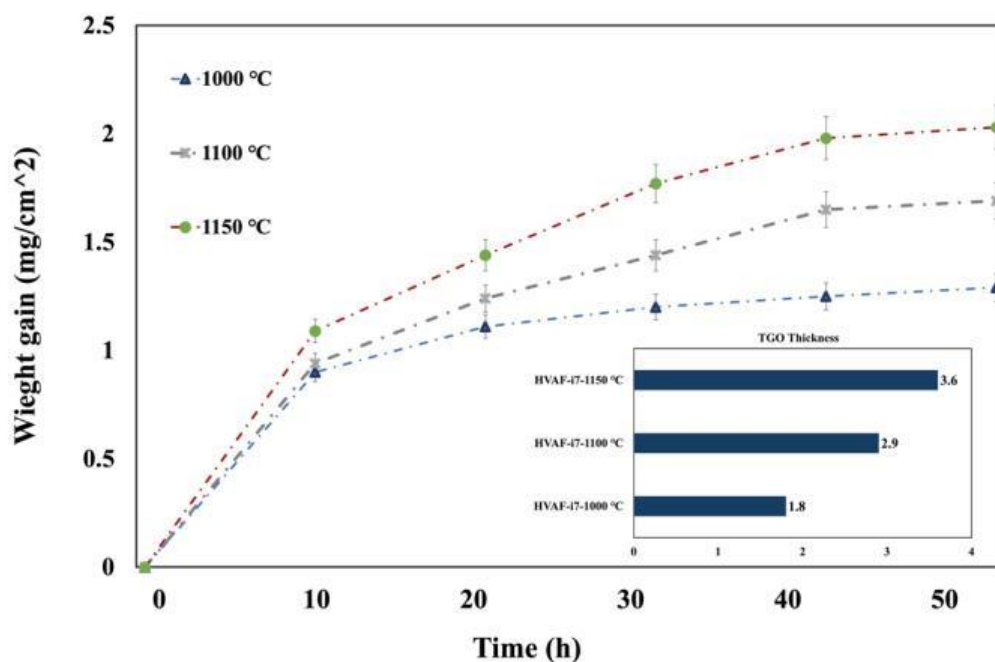
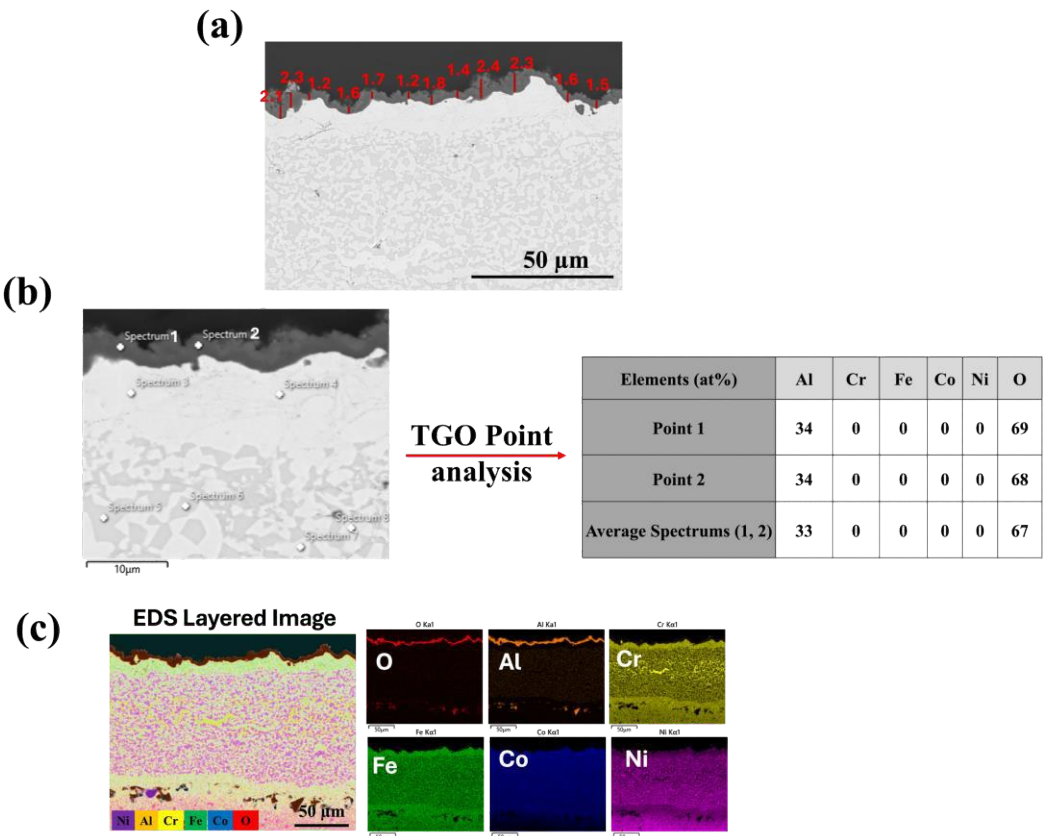
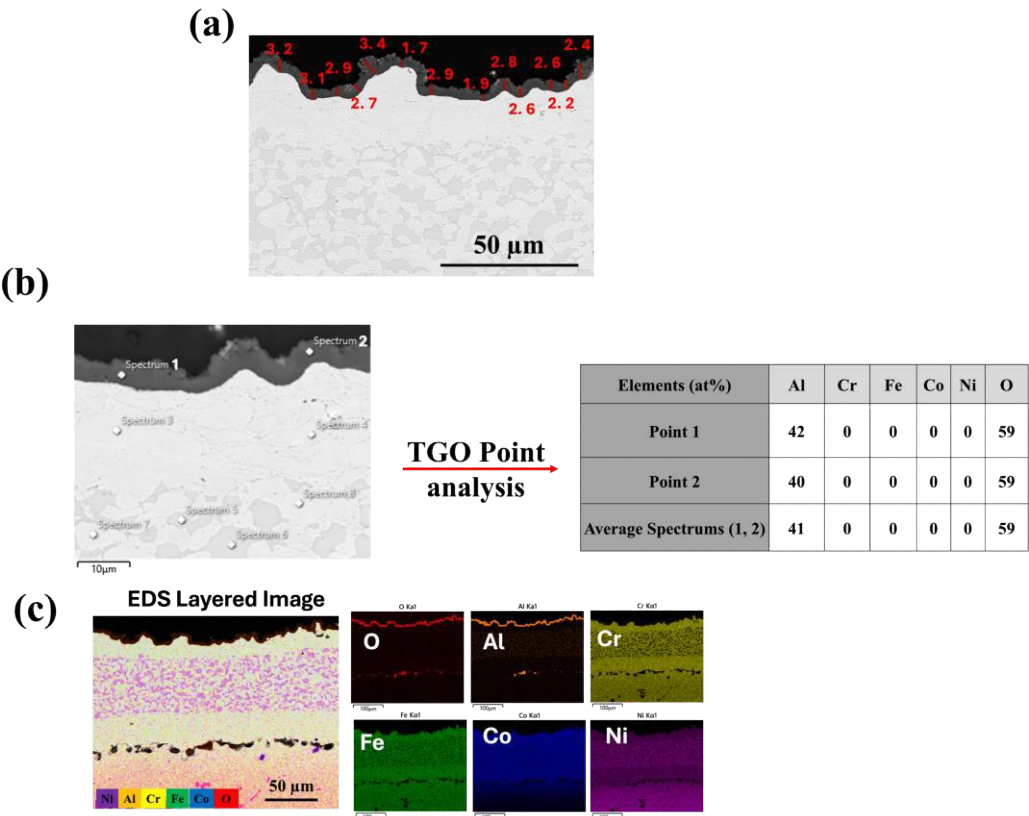


Figure 5-4 Isothermal oxidation test of the HEA bond coat applied using the HVOF i7 gun. Error bars indicate the standard deviation.

Alumina TGO layer 1000 °C-50 h



Alumina TGO layer 1100 °C-50 h



### Alumina TGO layer 1150 °C-50 h

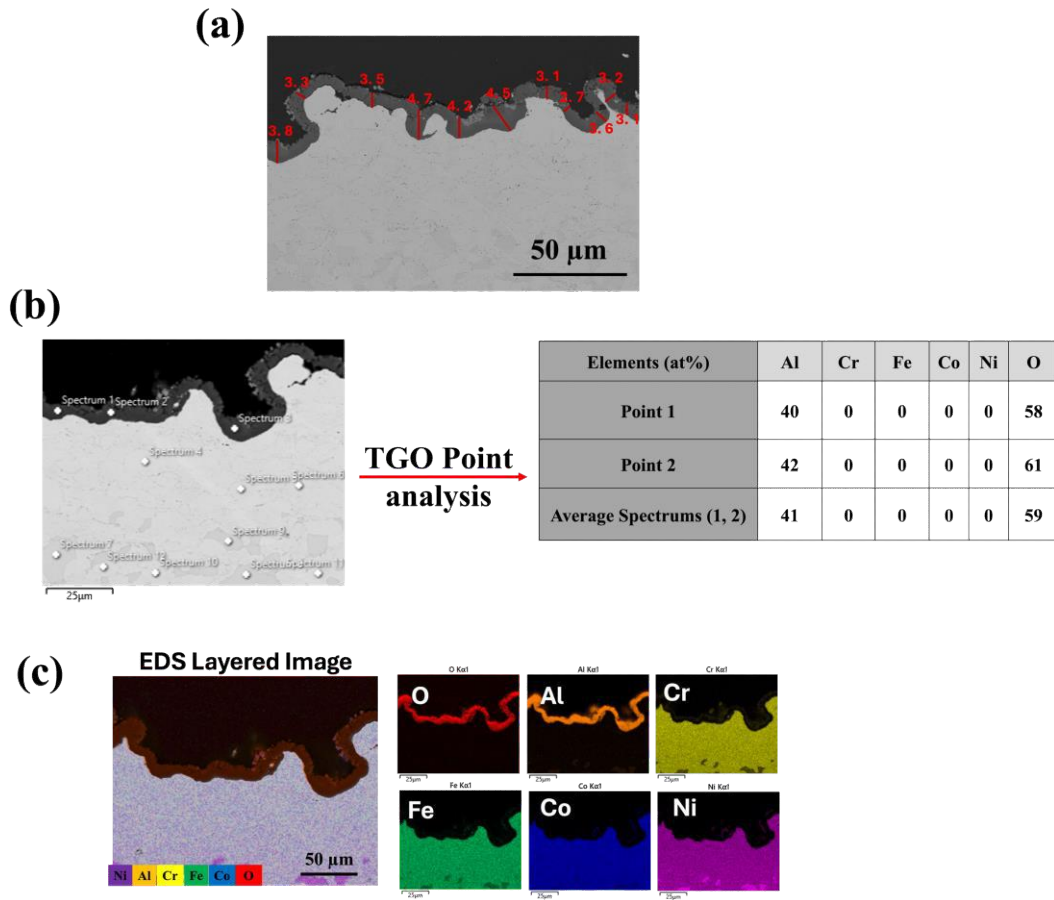


Figure 5-7 Characterization of thermally grown oxide (TGO) layer formed at 1150 °C for 50 h: (a) SEM cross-sectional image of the TGO layer with thickness measurements (in  $\mu\text{m}$ ); (b) SEM image showing EDS point analysis locations with corresponding elemental compositions (at%) of selected points within the TGO; (c) EDS layered image and individual elemental maps showing the distribution of O, Al, Cr, Fe, Co, and Ni in the oxidized region.

Shahbazi et al. investigated FeCoNiCrAl HEA coatings deposited using HVOF M3 and HVOF-i7 guns. Their study utilized a particle size distribution (PSD) of 15–45  $\mu\text{m}$ , which was suitable for the M3 gun because of its higher operating temperature, similar to HVOF. However, this PSD was not ideal for the HVOF-i7 gun, which operates at a lower temperature and requires finer particles (5–30  $\mu\text{m}$ ). As a result, they were unable to achieve significant coating thickness or high deposition efficiency with HVOF-i7. The TGO layer formed at 1000 °C after 50 h measured 1.06  $\mu\text{m}$ , but its accuracy was affected by the thin bond coat thickness ( $\sim 20$   $\mu\text{m}$ ). In contrast, this study used finer particles (5–30  $\mu\text{m}$ ), allowing the coating thickness to reach 150  $\mu\text{m}$ , which is within the standard range for TBC systems (150–200  $\mu\text{m}$ ). The resulting TGO layer was thin, dense, continuous, and uniform, demonstrating excellent high-temperature performance. This improvement is attributed to the sluggish

diffusion properties of HEAs, which regulate elemental diffusion at high temperatures. The unique atomic configuration of HEAs creates local energy variations, trapping atoms in low-energy regions and making the slowest-diffusing element the rate-determining factor for oxidation resistance[11,39,45,90,96].

**Figure 5-8** presents the cross-sectional microstructure and EDX line analysis of the FeCoNiCrAl/TGO interface following 50 hours of oxidation at 1000 °C, providing a more detailed view of elemental diffusion and TGO formation, complementing the observations in **Figures 5-5, 5-6, and 5-7**. In **Figures 5-5, 5-6, and 5-7**, the formation of a dense alumina TGO layer at the bond coat interface is evident, establishing the basis for analyzing the interdiffusion zone. **Figure 5-8** expands on this by highlighting the elemental migration critical to TGO growth. The EDX profiles show a sharp increase in oxygen (O) concentration at the TGO interface, which aligns with the alumina ( $\text{Al}_2\text{O}_3$ ) formation observed in **Figures 5-5, 5-6, and 5-7**, confirming the presence of a protective oxide scale. The aluminum (Al) profile shows noticeable fluctuations, with a significant drop at the oxide front, indicating outward diffusion from the bond coat to sustain the alumina layer. This depletion of Al in the bond coat, along with its accumulation at the oxide interface, reflects ongoing inter-diffusion, driving the growth of the alumina TGO layer[107,157]. The gradual decline and variability in the aluminum profile suggest regions of continuous TGO thickening, while the oxygen profile stabilizes past the TGO layer, reinforcing the barrier effect of alumina. These compositional trends validate that the alumina scale formed is dense, adherent, and resistant to further oxidation. The absence of significant chromia or spinel oxide peaks, as previously observed in **Figure 5-5, 5-6, and 5-7**, underscores the superior oxidation resistance of alumina-based TGO compared to mixed oxide layers. This reinforces the role of FeCoNiCrAl coatings in promoting long-term TBC performance by limiting oxygen diffusion, reducing spallation risks, and ensuring enhanced stability under high-temperature exposure [8,32].

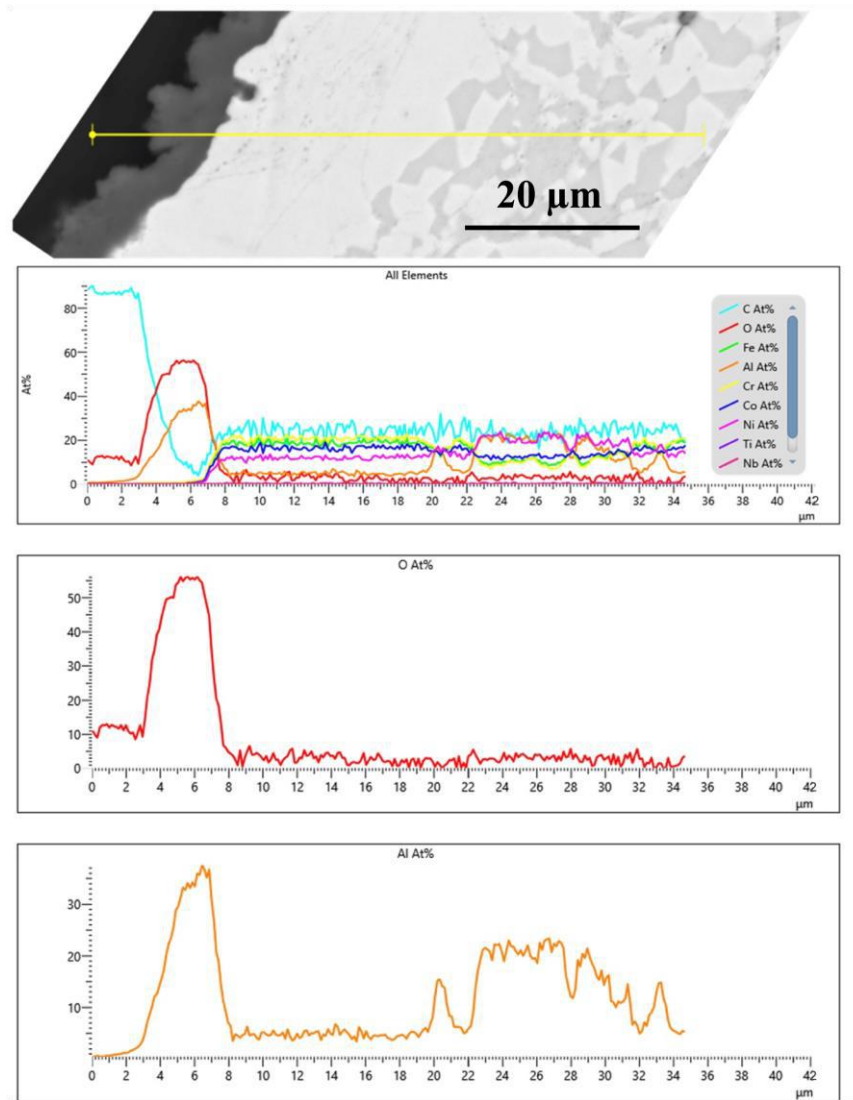


Figure 5-8 EDS line analysis of the cross-sectional microstructure (HVAF-i7) of the bond coat/TGO interface after 50 hours of oxidation at 1000 °C.

## 5.4 Conclusion

This study investigates the influence of microstructure, density, and porosity of fine FeCoNiCrAl HEA coatings, manufactured through HVAF-i7, on their isothermal oxidation behavior.

- Utilizing the HVAF-i7 gun, we achieved a highly dense microstructure comparable to that of cold spray techniques, highlighting the efficacy of the fabrication method.
- The microstructure and chemistry of the coating, along with the growth of the thermally grown oxide (TGO) layer, were investigated across different temperatures, revealing a dense, uniform, and thin alumina TGO layer after 50

hours at 1000°C, 1100°C, and 1150°C. It was observed that with increasing temperature, the TGO layer increased, albeit not significantly.

- The oxidation resistance of the HEA coating was significantly enhanced by the dense microstructure achieved via HVAF-i7, which contributed to the controlled growth of the TGO layer and the formation of a continuous alumina scale. While no direct benchmark bond coat was included for comparison, the observed microstructural characteristics and TGO behavior align with the known performance benefits associated with dense coatings produced through HVAF processes.
- The absence of reactive elements contributed to the spalling of the alumina TGO layer at higher temperatures, which will be further explored in future research.
- Analysis of deposit efficiency (79%) and porosity (0.2%) indicated that the best deposition efficiency and lowest porosity were achieved with medium air and fuel pressure, resulting in a dense, uniform, and random solid solution phase.
- Investigation of the microstructure revealed a relatively thin inter-diffusion layer compared to the coating thickness, suggesting negligible impact on oxidation behavior.
- EDS mapping and area analysis confirmed the presence of a random solid solution phase and uniform element distribution after coating, highlighting the efficacy of the HVAF technique and the high entropy properties.

## **6 Chapter Six: Enhanced Oxidation Resistance of High-Entropy Alloy Bond Coats via Low-Temperature Spray Processing and Vacuum Heat Treatment**

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- Hossein Shahbazi carried out all experiments, analysis, and manuscript writing.
- Dr. Lima, Dr. Stoyanov, and Prof. Moreau supervised and provided critical feedback.

## 6.1 Introduction

Thermal barrier coatings (TBCs) exemplify the engineering principle that incremental advancements can drive transformative outcomes. These systems, consisting of a metallic bond coat and a ceramic top coat, are designed to protect critical components operating in high-temperature environments, enhancing both efficiency and durability [143]. However, innovation has become essential as the demand for higher efficiency in extreme environments continues to grow. In TBC systems, the limitations of conventional bond coat materials, particularly their susceptibility to oxidation and degradation at elevated temperatures, have prompted researchers to explore more advanced alternatives [4,36,90,94,97,98,143,153]. High-entropy alloys (HEAs), with their unique properties derived from the four core effects, high configurational entropy, sluggish diffusion, severe lattice distortion, and the cocktail effect, offer transformative potential for addressing these challenges [11,28,39,45,96,147,158,159]. In this context, HEAs have emerged as a promising new class of materials due to their ability to form stable microstructures and resist oxidation under severe thermal conditions. Their unique compositional and microstructural characteristics provide opportunities to enhance the performance and durability of bond coats in TBC systems. These features enable the formation of uniform solid-solution phases and help mitigate elemental segregation during oxidation, which is critical for bond coat durability.

The microstructure of the bond coat plays a critical role, directly influencing its properties such as adhesion, oxidation resistance, and thermal expansion compatibility. The crystallographic structure of HEA powders, whether body-centered cubic (BCC), face-centered cubic (FCC), or a combination of both (BCC + FCC), has a profound impact on these performance metrics. Researchers have the opportunity to design bond coats that excel in demanding high-temperature environments by tailoring the structure of HEAs to meet application-specific requirements, such as operating temperatures, mechanical stresses, and thermal cycling demands. These advancements firmly position HEAs as a promising candidate to replace conventional bond coats, ensuring enhanced efficiency and reliability in modern TBC systems [82,90,98,160,161]. The chemical composition of the bond coat plays a critical role in determining its effectiveness under high-temperature conditions [90]. Aluminum (Al) is essential for forming the protective  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> thermally grown oxide (TGO) layer, which provides outstanding resistance to oxidation. Chromium (Cr) strengthens the adhesion between the TGO and the underlying layers, ensuring that the TBC remains firmly

attached to the substrate during thermal cycling [98,101,110]. Moreover, Cr acts as a barrier, shielding the substrate from harsh environments and extreme heat. Nickel (Ni) enhances the mechanical properties of the bond coat by improving ductility and plasticity, enabling the coating to accommodate thermal stresses more effectively[36]. Ni also establishes a robust bond with the substrate, critical for maintaining integrity during prolonged service [90,101]. Cobalt (Co), on the other hand, facilitates the solubility of Cr in the  $\gamma$  phase and suppresses the formation of  $\alpha$ -Cr in the microstructure, contributing to improved thermal stability and reduced phase transformations at elevated temperatures [22,90]. Originally, iron (Fe) was used as the base metal in some early MCrAlY bond coat alloys (notably the FeCrAlY systems of the 1960s), but modern high-temperature bond coats have transitioned to nickel- or cobalt-based MCrAlY compositions due to their superior oxidation and corrosion resistance [162]. Today, Fe-containing MCrAlY coatings are mainly applied in moderate-temperature environments ( $\sim 400\text{--}800\text{ }^{\circ}\text{C}$ ), for example, as cost-effective oxidation-resistant coatings on steel components, since they can form protective alumina/chromia scales up to roughly  $800\text{ }^{\circ}\text{C}$  [163,164]. Furthermore, iron is increasingly utilized in HEA compositions to reduce cost while maintaining oxidation resistance, making Fe-rich HEAs a compelling alternative to conventional Ni/Co-rich alloys[165]. For instance, turbine blades coated with Fe-rich bond coats demonstrate superior performance in jet engines by resisting wear and thermal degradation. In addition to these foundational elements, reactive elements such as yttrium (Y), hafnium (Hf), tantalum (Ta), and silicon (Si) are integral to the success of modern bond coats. Reactive elements refine the oxide scale, stabilize the TGO layer, and enhance the adhesion at the metal-oxide interface [121,166,167]. For example, in commercial MCrAlY coatings used in aerospace applications, the addition of Y has been shown to reduce spallation and improve oxide adherence, directly contributing to the durability of turbine engine components under severe thermal cycling [167,168]. Heat treatment is a vital step in enhancing the microstructure and performance of bond coats in TBC systems. By stabilizing phases, reducing residual stresses, and refining elemental distribution, it improves adhesion, density, and microstructural uniformity. For instance, in NiCoCrAlYHfSi coatings, heat treatment promotes the formation of stable  $\alpha\text{-Al}_2\text{O}_3$  layers, boosting oxidation resistance and shielding against high-temperature degradation. Vacuum heat treatment (VHT), in particular, further enhances high-temperature performance by reducing internal oxidation and creating a uniform oxide scale. These advancements highlight the essential role of heat treatment in optimizing TBC systems for extreme environments [32,61,99].

Although the number of studies on HEA bond coats is limited, the potential for innovation and discovery remains vast. High-entropy alloys (HEAs) have increasingly attracted attention as bond coat materials for thermal barrier coating (TBC) systems due to their potential to combine high-temperature stability with excellent oxidation resistance. Although early studies were fewer in number, the research field has been expanding, revealing significant opportunities for innovation and discovery. For example, Yu *et al.*, investigated the effects of heat treatment at 1200 °C on the microstructure and mechanical properties of AlCoCrFeNiSiYHf HEAs. These alloys were specifically designed and synthesized as advanced bond coat materials for TBC systems, addressing the stringent high-temperature performance demands of turbine engines. Their work highlights the promise of HEAs in meeting the challenging requirements of modern high-temperature applications. The study revealed that heat played a crucial role in driving elemental diffusion and achieving homogenization in the alloy. A transformation from the FCC to the BCC phase was observed in the AlCoCrFeNiSiYHf HEA following a one-hour exposure to 1200 °C. Additionally, the mechanical properties of the alloy exhibited significant improvements across various parameters after heat treatment [62]. Abdullah *et al.*, explored the effects of heat treatment on the adhesion strength and mechanical properties of TBC systems. They observed that increasing the temperature and duration of heat treatment enhanced both adhesion strength and hardness, with greater improvements seen in TBCs utilizing High-Velocity Oxygen Fuel (HVOF)-applied bond coats. The bond coat/ceramic interface remained the primary failure location, but heat treatment reduced internal stresses, contributing to better adhesive strength. Additionally, microstructural changes and decreased porosity in the ceramic top coat improved its densification and microhardness [169]. HVOF, widely used in industry, serves as a benchmark, while the High-Velocity air Fuel(HVAF)-M3 system, operating at a lower temperature than HVOF, enables a comparative analysis of reduced thermal input. Furthermore, the HVAF-i7 system allows for an extended evaluation of the effects of progressively lower-temperature deposition on coating characteristics. The ability of HVAF to balance moderate temperatures with high particle velocities makes it ideal for producing bond coats with minimal oxidation, improved adhesion, and a more homogeneous microstructure, ensuring superior coating quality in applications requiring high oxidation resistance and bond strength [2,42,67,90,98,100,103,112,120,133,170]. Lower temperatures minimize the oxidation of powder particles during spraying, preserving the material's original microstructure and preventing the formation of unwanted oxide phases. This results in coatings with improved properties, including higher density and lower porosity

[46,60,171,172]. Additionally, HVAF produces extremely high particle velocities, often comparable to or exceeding those of HVOF, enabling superior mechanical bonding with the substrate. This combination of lower thermal input and higher particle velocity makes HVAF particularly suitable for depositing high-quality coatings with minimal thermal damage to the substrate or the sprayed material. The process is also more energy-efficient, as compressed air is more readily available and cost-effective than oxygen. Given these advantages, the HVAF technique holds significant potential for enhancing coating performance, particularly in applications where preserving material properties and minimizing thermal effects are critical [117,173]. Shahbazi *et al.* optimized HVAF spray parameters for a FeCoNiCrAl HEA bond coat in a TBC system. Their study found that using a lower flame-temperature process (HVOF vs. HVAF) produced a dense microstructure with minimal oxides, which improves the coating's oxidation resistance. After 50 hours at 1000 °C, the HVAF-coated sample developed a continuous, dense alumina TGO layer, demonstrating that the FeCoNiCrAl HEA bond coat offers enhanced oxidation resistance at elevated temperatures [101].

To systematically investigate the suitability of HEAs as advanced bond coat materials, this study focuses on FeCoNiCrAl-based compositions with and without reactive elements (Hf and Y), deposited via two thermal spray processes: HVOF and HVAF. A commercial NiCoCrAlYHfSi bond coat is also incorporated as a benchmark to contextualize the performance of HEA-based systems. All coatings were subjected to VHT at 1050 °C for 4 hours under a pressure of  $6.8 \times 10^{-4}$  mbar to reduce porosity, relieve residual stresses, and enhance coating integrity. Subsequent isothermal oxidation tests were performed at 1150 °C for 200 hours, both before and after VHT, to assess the evolution and growth behavior of TGO layers. Accordingly, this study aims to: (i) examine the influence of reactive elements (Hf and Y) on the oxidation resistance of FeCoNiCrAl-based HEAs; (ii) evaluate the effect of thermal spray technique (HVOF vs. HVAF) on microstructural features and performance outcomes; and (iii) analyze the role of vacuum heat treatment in promoting stable and protective TGO formation under high-temperature conditions. The experimental design was structured to decouple the influence of process and composition by incorporating two variables: spraying technique (HVOF vs. HVAF) and alloy formulation (with vs. without reactive elements). This approach enables direct comparisons between different spray processes for the same alloy, as well as between different alloy compositions under identical processing conditions.

## 6.2 Materials and methods

### 6.2.1 Characterization of Chemical Compositions of Powders

The experimental matrix was developed to decouple the effects of alloy composition and spraying technique. Both high-entropy alloys (FeCoNiCrAl and FeCoNiCrAlYHf) were deposited using HVOF and HVAF processes to allow direct comparisons between spray methods for each composition. The benchmark NiCoCrAlYHfSi (MCrAlY-type) bond coat was sprayed only using HVOF, which remains the most widely adopted process in industrial applications. This choice ensured a realistic comparison with state-of-the-art coatings commonly used in gas turbines. It is worth noting that our research group has also applied HVAF to deposit MCrAlY coatings, and the results have been or will be published by our collaborators. This comparative setup enables a consistent and systematic evaluation of how both spray technique and alloy composition influence microstructural evolution and high-temperature oxidation behavior. The chemical compositions of the powders used in this study are summarized in **Table 6-1**. FeCoNiCrAl (HEA), FeCoNiCrAlYHf (HEA\_RE; with reactive elements), and commercial NiCoCrAlYHfSi (MCrAlX) powders are presented for direct comparison. All values are reported in atomic percent (at.%).

Table 6-1 Chemical compositions of the investigated bond coat powders.

| Materials (at.%)       | Fe | Co   | Ni   | Cr | Al | Hf   | Y    | Si   |
|------------------------|----|------|------|----|----|------|------|------|
| FeCoNiCrAl (HEA)       | 20 | 20   | 20   | 20 | 20 | -    | -    | -    |
| FeCoNiCrAlYHf (HEA_RE) | 20 | 20   | 20   | 20 | 20 | 0.22 | 0.35 | -    |
| NiCoCrAlYHfSi (MCrAlX) | -  | 19.5 | 39.8 | 17 | 23 | 0.14 | 0.28 | .071 |

The experimental matrix used in this study is summarized in **Table 6-2**, illustrating the comparative framework between different alloy compositions (with and without reactive elements) and thermal spray processes (HVOF and HVOF).

Table 6-2 Experimental plan outlining the deposition routes and compositional variables employed to decouple process and alloy effects in HEA and MCrAlX coatings.

| Coating Composition      | Spray Technique | Purpose                                    |
|--------------------------|-----------------|--------------------------------------------|
| FeCoNiCrAl               | HVOF            | Evaluate baseline HEA coating              |
| FeCoNiCrAl               | HVOF (M3, i7)   | Compare spray processes (HVOF vs HVOF)     |
| FeCoNiCrAlYHf            | HVOF            | Evaluate effect of reactive elements (REs) |
| FeCoNiCrAlYHf            | HVOF (M3, i7)   | Compare spray processes (HVOF vs HVOF)     |
| NiCoCrAlYHfSi<br>(AMDRY) | HVOF            | Benchmark MCrAlX coating                   |

**Figure 6-1** is a schematic representation of this study's process. The FeCoNiCrAl HEA and FeCoNiCrAlHfY HEA (referred to as HEA and HEA\_RE, respectively, in this study) were gas-atomized by Heeger Co. (USA) and used in two distinct particle size ranges: -15+45  $\mu\text{m}$  (with  $d_{50}$  values of 34  $\mu\text{m}$  and 25  $\mu\text{m}$ , respectively) and -5+30  $\mu\text{m}$  (with  $d_{50}$  values of 14  $\mu\text{m}$  and 13  $\mu\text{m}$ , respectively). Additionally, the medium entropy alloy  $\text{Ni}_{22}\text{Co}_{17}\text{Cr}_{12}\text{Al}_{10.5}\text{Hf}_{0.5}\text{Y}_{0.4}\text{Si}$  (referred to as MCrAlX in this study) was gas-atomized by Oerlikon Metco (Amdry 386-2) and utilized within a particle size range of -88+16  $\mu\text{m}$  ( $d_{50} = 36 \mu\text{m}$ ) [111]. Three powders were characterized in this study. The selection of particle size distribution (PSD) was based on spraying equipment compatibility and prior optimization studies. For instance, FeCoNiCrAl and FeCoNiCrAlYHf powders sprayed via HVOF (i7 gun) required a finer PSD (-5+30  $\mu\text{m}$ ) to achieve high deposition efficiency, whereas the -15+45  $\mu\text{m}$  range was used for HVOF spraying. The MCrAlX powder (Amdry 386-2), supplied in the -88+16  $\mu\text{m}$  range ( $d_{50} \approx 36 \mu\text{m}$ ), closely matched the -15+45  $\mu\text{m}$  PSD and reflected standard industrial usage.

However, due to the similarity of results with previous studies, only the characterization of HEA\_RE powders is presented here. Particle size distribution was analyzed using a wet laser diffraction particle size analyzer (Spraytec, Malvern Panalytical, United Kingdom). These materials were selected for their remarkable potential to enhance oxidation resistance at elevated temperatures. Notably, the HEAs were chosen due to their exceptional balance of strength, ductility, and oxidation resistance under high-temperature conditions.

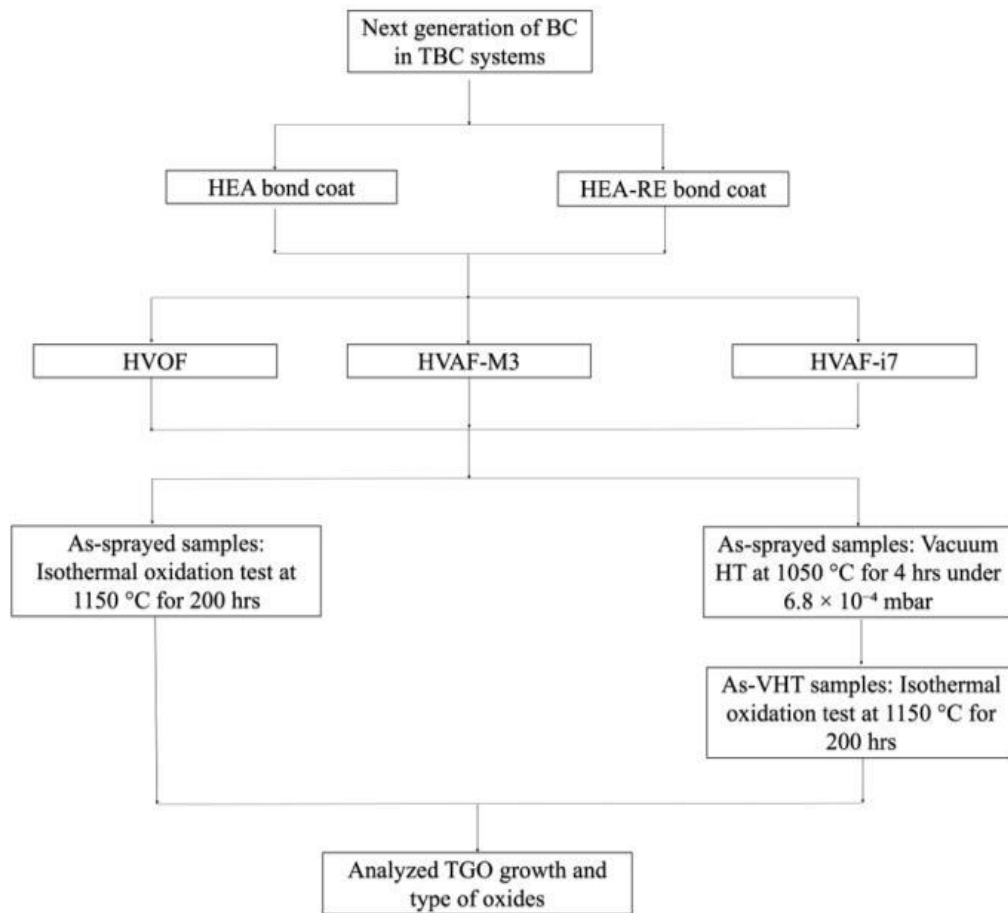


Figure 6-1 Schematic representation of the study process for evaluating the next-generation bond coats in thermal TBC systems.

The cross-sectional morphology of the powders was examined using a Field Emission Scanning Electron Microscope (FESEM, Hitachi, Regulus 8230, Japan) equipped with a photodiode BSE detector, as illustrated in **Figure 6-2**. The chemical compositions of the powders were determined using Energy-Dispersive X-ray spectroscopy (EDS). Phase analyses of both the powders and coatings were conducted using X-ray Diffraction (XRD) with Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) over a  $2\theta$  range of  $10^\circ$ – $120^\circ$ . The analysis was performed on a D8 Advance DaVinci system (Bruker, Germany) operated at 40 kV and 40 mA, with a  $1^\circ$  per minute scanning rate.

## 6.2.2 Coating Preparation and Optimize Parameters

This study investigates the influence of microstructure, density, and porosity on the isothermal oxidation performance of HEA and HEA\_RE coatings, applied using advanced low-temperature thermal spray techniques, including HVOF (Diamond Jet™ 2700) and HVOF (M3-4L2C and i7-4L3) [101,102]. To provide a comparative benchmark,

NiCoCrAlYHfSi medium entropy alloy coatings, deposited via HVOF, were included in the analysis, reflecting their widespread use in industrial applications as a standard bond coat. This approach ensures the findings align closely with practical, real-world scenarios. The deposition parameters were carefully optimized in previous studies for HVOF-M3, HVOF-i7, and HVOF processes [101,102].

Prior to bond coat application, the Inconel 625 substrates were treated with #80  $\text{Al}_2\text{O}_3$  grit blasting at a pressure of 4.13 bar (60 psi) to increase surface roughness and enhance coating adhesion. The samples were cleaned using ultrasonic agitation in ethanol for 15 minutes to remove residual dust and contaminants. This process resulted in an average surface roughness ( $R_a$ ) of  $3.6 \pm 0.3 \mu\text{m}$  on the Inconel 625 substrate. The  $R_a$  values were measured using a Mitutoyo-SJ.210 profilometer (Japan) with a cut-off length of 2.5 mm, and the results were averaged over ten measurements. The surface roughness of the bond coat is a key factor in determining the adhesion and performance of TBC systems. A properly roughened bond coat surface improves mechanical interlocking with the top coat, enhancing adhesion strength. However, excessive roughness can create stress points that may lead to coating delamination. The surface roughness of the bond coat was evaluated using a confocal microscope, with five measurements taken to determine an average  $R_a$  of  $9 \pm 0.8 \mu\text{m}$ .

The particle temperatures and velocities were characterized using DPV-2000 and Accuraspray diagnostic systems. The DPV-2000 system, operated in cold mode, was selected for HVOF-i7 due to its exceptionally high particle velocities and relatively low particle temperatures. Given that HVOF-i7 operates at lower flame temperatures and near-supersonic velocities, the emitted thermal radiation from the particles is weak, making traditional two-color pyrometry less effective. DPV-2000 compensates for this by employing laser illumination, enabling accurate velocity measurements via time-of-flight tracking and reliable temperature estimation, even for solid or partially molten particles. Conversely, Accuraspray was used for HVOF and HVOF-M3 samples, as these processes produce particles with sufficient thermal emission for two-color pyrometry. Accuraspray captures ensemble-averaged particle properties within a broader spray volume using optical cross-correlation for velocity and pyrometric analysis for temperature. This system is particularly well-suited for high-temperature thermal spray processes, such as HVOF and HVOF-M3, where particles remain fully or largely molten, ensuring reliable in-flight diagnostics[174,175].

### 6.2.3 Vacuum Heat Treatment

In this study, VHT was performed at 1050 °C for 4 hours under a pressure of  $6.8 \times 10^{-4}$  mbar to enhance the microstructural integrity of the bond coat by reducing porosity and stabilizing its structure. This process promotes the healing of internal pores, enhances adhesion to the top coat, and contributes to the development of a uniform TGO layer during oxidation exposure. Importantly, no phase transformation was observed after VHT, indicating that the existing phase constitution of the bond coat remained stable despite prolonged high-temperature exposure.

The primary mechanism responsible for porosity reduction during VHT is solid-state sintering, which is facilitated by atomic diffusion, grain boundary migration, and recrystallization. At elevated temperatures, the mobility of atoms increases, allowing diffusion-driven pore healing as metal atoms migrate into voids, reducing overall porosity. Grain boundaries serve as high-diffusion pathways, accelerating the redistribution of substitutional and interstitial atoms, which effectively fills microstructural defects such as pores and cracks. Additionally, grain boundary movement contributes to grain growth and densification, leading to a reduction in dislocation density and an overall strengthening of the bond coat [176,177].

### 6.2.4 Oxidation Test

Isothermal oxidation was selected to enable a controlled evaluation of TGO growth mechanisms and reactive element influence, without the added complexity of cyclic thermal stresses. The isothermal oxidation test was carried out in a tubular furnace (Barnstead, F21135, USA) with a maximum operating temperature of 1200°C. The samples were placed in ceramic alumina crucibles to maintain stability and collect any oxide scales that detached during the test. To ensure precise measurements, each sample was weighed five times using a high-precision balance (Mettler Toledo ME204E; 220 g capacity, 0.1 mg readability, USA). After heating, the samples were cooled naturally in ambient air, and the crucibles containing the samples were reweighed. This process was repeated at intervals of 10, 20, 30, 40, 50, 100, 150, and 200 hours. The weight change (in mg) for each sample was normalized to its total surface area, including the coating and substrate (in cm<sup>2</sup>). The study focused on understanding the formation of the TGO layer and mixed oxides caused by elemental diffusion. Detailed analyses were conducted to evaluate the coatings' microstructure, the growth and composition

of the TGO layer, alumina phase transformations, and the oxidation rate at 1150°C over a 200-hour duration.

### **6.2.5 Microstructure Characterization**

The samples were prepared using standard metallographic techniques, including mounting, cutting, and polishing. The cross-sectional microstructures of the bond coats were examined using a Field Emission Scanning Electron Microscope (FESEM, Hitachi, Regulus 8230, Japan). Elemental composition and distribution, including the TGO layer, were analyzed through energy-dispersive X-ray spectroscopy (EDS) and elemental mapping. Porosity distribution was quantified using Image-J analysis software, evaluating multiple regions across eight images to determine pore percentages.

## **6.3 Results and Discussions**

The following sections are structured to provide a coherent analysis of how processing parameters, compositional design, and reactive element incorporation affect the microstructure, deposition efficiency, and high-temperature oxidation performance of the investigated coatings. **Figure 6-2** shows the characterization results of the HEA\_RE powder with a particle size distribution of -5+30  $\mu\text{m}$ . The RE-containing sample is presented here, since the HEA without reactive elements has already been reported in earlier studies [98,101,102], and all powders showed similar features.

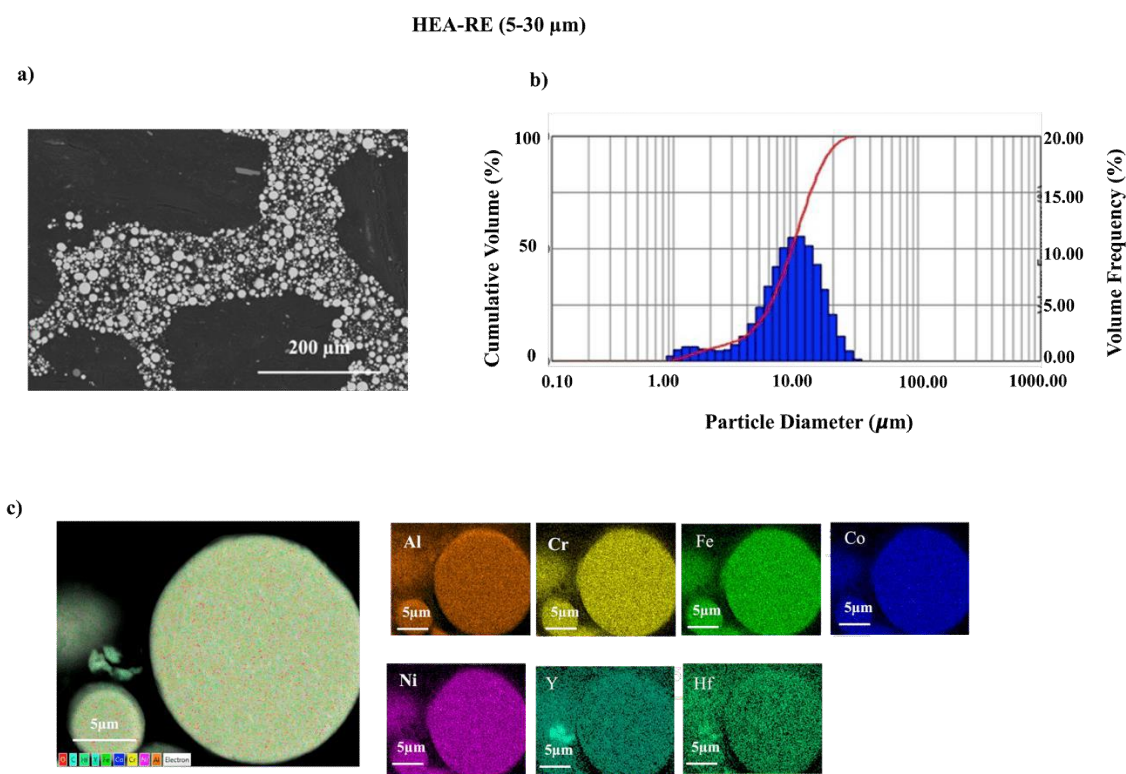


Figure 6-2As-received powder characterization: (a) Microstructure of HEA\_RE, (b) Particle size distribution (PSD) analysis, (c) Elemental mapping.

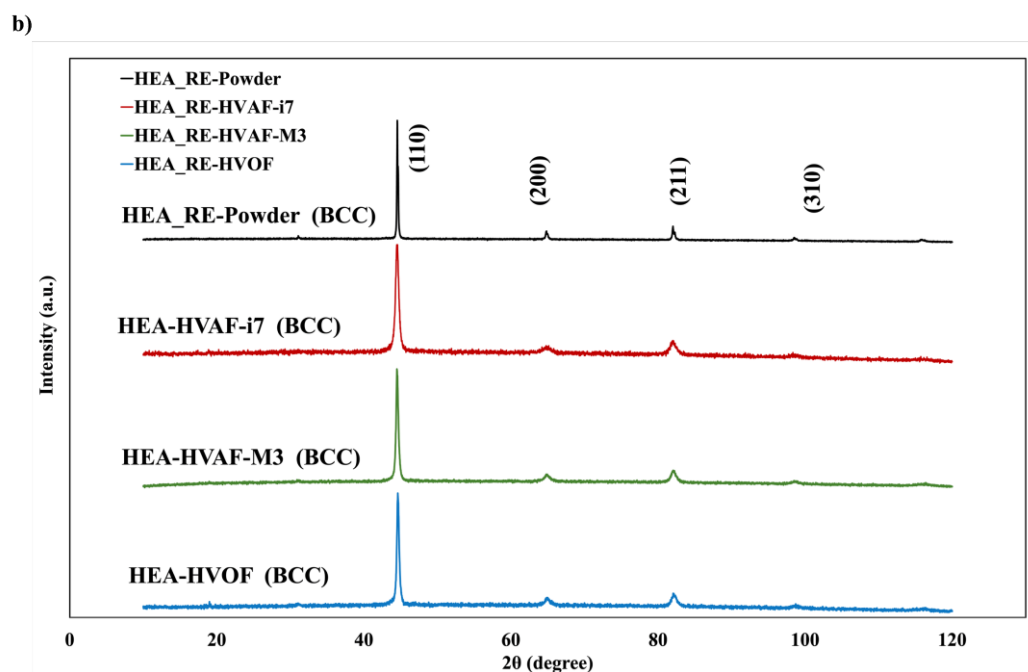
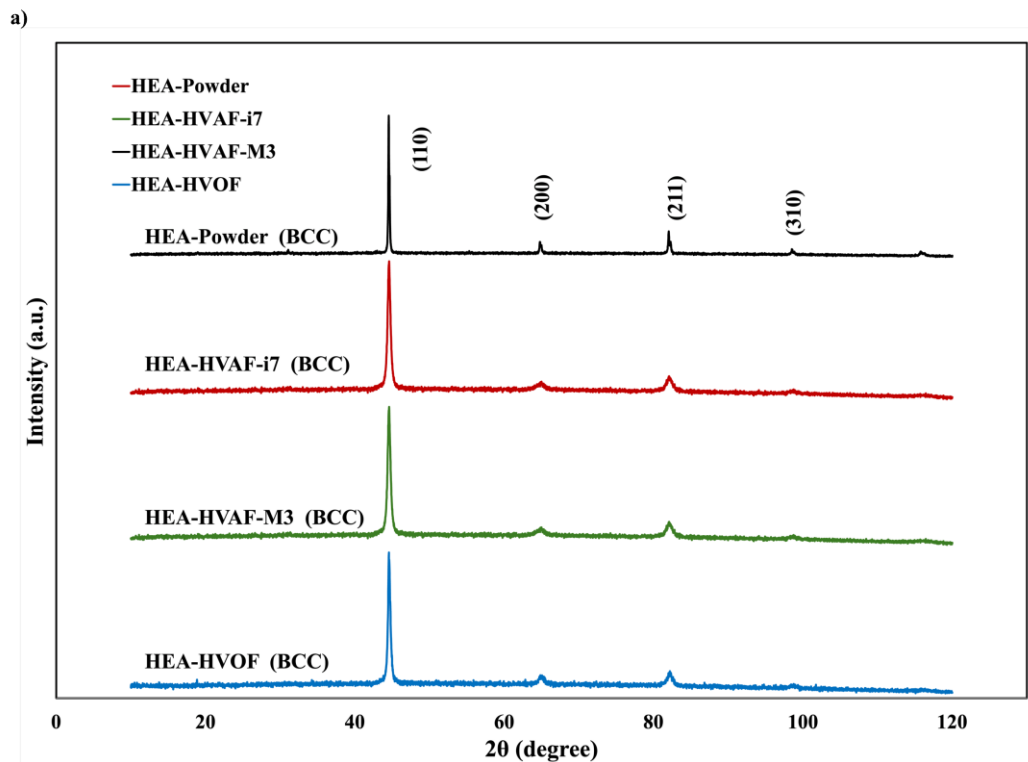
**Figure 6-3** presents the XRD patterns of both the feedstock powders and the corresponding as-sprayed coatings. The diffraction results confirm that a high-density random solid solution structure was effectively formed in the HEA bond coats sprayed via HVOF and HVOF processes. The broadening of diffraction peaks observed in the coatings may be attributed to a combination of microstructural features such as refined grain size, increased surface roughness, and particle recrystallization. These are hallmarks of high-entropy alloys, where severe lattice distortion and complex atomic configurations inherently disrupt long-range order, contrasting with the well-defined structures of conventional alloys containing one or two principal elements.

For the commercial NiCoCrAlYHfSi coatings, notable differences between the XRD patterns of the powder and the sprayed coating are observed. These changes arise from phase transformations, oxidation, and rapid solidification during the thermal spray process. Specifically, the reduction in peak intensity around  $2\theta \approx 40^\circ$  is mainly associated with a diminished  $\beta$ -NiAl phase fraction. The extreme particle temperatures ( $\sim 2500^\circ\text{C}$ ) followed by rapid quenching promote nanoscale  $\beta$ -phase precipitates, lattice strain, and microstructural refinement, all of which contribute to peak broadening. Furthermore, the partial oxidation of

Al during spraying depletes  $\beta$ -phase stabilizers, reducing  $\beta$ -phase content and peak intensity. Additional broadening may result from amorphous phase formation or increased residual stresses. Moreover, the process-induced texture, porosity, and surface roughness further attenuate peak sharpness and intensity[178]. Equiatomic FeCoNiCrAl HEAs also solidify into multi-phase structures, typically a disordered BCC (A2) matrix with an ordered BCC (B2) phase (NiAl-type) precipitating within it [179]. The MCrAlY bond coats typically consist of a dual-phase microstructure of  $\gamma$  (FCC Ni-Co solid solution) and  $\beta$  (BCC NiAl intermetallic) phases. The  $\gamma$ -phase matrix predominantly dissolves Cr and Co, providing ductility, while the  $\beta$ -NiAl phase serves as an Al reservoir critical for forming a continuous, protective  $\text{Al}_2\text{O}_3$  scale during high-temperature exposure. While the presence of the  $\beta$ -phase enhances oxidation resistance, excessive  $\beta$  content may lead to embrittlement due to its intrinsic brittleness[180,181]. The equiatomic FeCoNiCrAl HEAs form predominantly BCC-based microstructures composed of a disordered BCC A2 matrix and a coherent, ordered BCC B2 (NiAl-type) precipitate phase. The B2 precipitates, enriched in Ni and Al, are finely dispersed within the Fe–Cr-rich matrix, leading to enhanced hardness and high-temperature strength. Although the overall XRD profile reflects a single BCC structure, backscattered electron images often reveal dual contrast (dark and bright regions), indicating compositional variations or nanoscale secondary phases below XRD detection limits. These contrasts may arise from microsegregation or fine-scale precipitates that require high-resolution techniques (e.g., TEM or EBSD) for further elucidation. This dual contrast observed in the BSE micrographs, dark and bright regions, may not necessarily indicate distinct crystal structures but can rather stem from slight variations in lattice parameter, local composition (e.g., Ni/Al-rich vs. Fe/Cr-rich zones), or strain-induced contrast, all of which may arise due to minor differences in cell size or atomic packing within the same overall phase.

Upon addition of reactive elements (REs) such as Y and Hf in FeCoNiCrAlYHf, the BCC-dominated structure remains fundamentally unchanged, maintaining the A2 + B2 phase constitution. However, Y and Hf exhibit strong tendencies to segregate to grain and phase boundaries, forming minor Y/Hf-rich oxide inclusions during spraying or oxidation. These inclusions contribute to microstructural refinement and improved TGO adhesion and integrity. While the XRD pattern does not show significant differences due to the limited RE content ( $\sim 0.6$  at.%), the influence of these elements on oxidation resistance, particularly under thermal cycling, can be profound[180]. All investigated bond coats exhibited their typical phase structures. The MCrAlY bond coat consisted mainly of a  $\gamma$  (Ni–Co FCC) matrix with  $\beta$

(NiAl B2) precipitates, while the FeCoNiCrAl and FeCoNiCrAlYHf HEAs showed a BCC-dominant structure (A2 + B2). Minor reactive-element oxides were observed in the HEA containing Y and Hf after spraying or oxidation, consistent with prior reports.



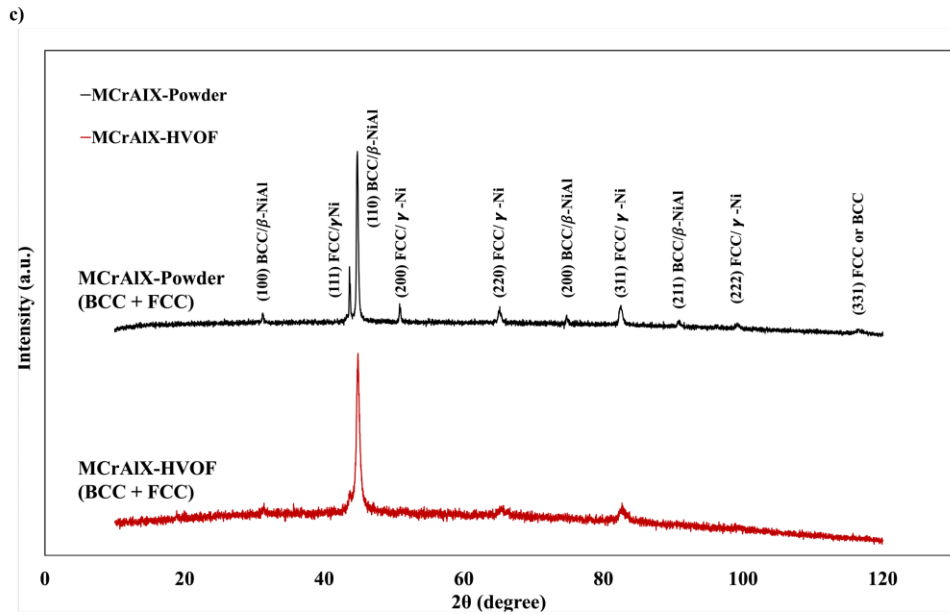


Figure 6-3 XRD patterns of powders and coatings obtained using various techniques and equipment; a) FeCoNiCrAl HEA, b) FeCoNiCrAlYHf HEA\_RE, and c) MCrAlX.

The surface roughness of the bond coat was evaluated using a confocal microscope. This level of roughness falls within the optimal range for promoting strong adhesion and ensuring the durability of the TBC system. The measured roughness for this bond coat is approximately 8  $\mu\text{m}$ , consistent with the average Ra obtained from multiple measurements. The color variation in the map represents different height levels of the bond coat surface, with peaks shown in warmer colors (e.g., red) and valleys in cooler colors (e.g., blue). This variation illustrates the uniform roughness profile achieved by the HVOF-M3 process, which contributes to the even distribution of stresses at the interface. Such uniformity minimizes stress concentrations, delays crack initiation, and prolongs the coating's lifetime. This map serves as a visual confirmation of the effectiveness of the HVOF-M3 process in producing a surface with optimal roughness characteristics. It demonstrates the process's ability to achieve a balance between sufficient roughness for adhesion and controlled morphology to prevent premature failure. Since no significant differences in roughness were observed between other materials and techniques, this map was selected as the representative for this study.

The HVOF method burns oxygen with fuel gases such as hydrogen, propane, propylene, LPG, natural gas, or kerosene. This combustion process generates high temperatures (2500–3500 °C) and ejects the exhaust gases at velocities up to 2000 m/s through a nozzle [41,117]. In contrast, the HVOF process uses compressed air instead of oxygen, reducing operating temperatures to 800–1400 °C, depending on the gun design, while

achieving high particle velocities due to the expansion of compressed air during combustion [90,98]. For example, the HVAF-M3 gun recorded an average temperature of 1480 °C and a velocity of 650 m/s, while the i7 gun, operating at lower temperatures, reached 1100 °C with a velocity of 700 m/s. For samples sprayed using the HVOF process, Accuraspray monitoring recorded an average temperature of 2450 °C and a velocity of 530 m/s. The high combustion temperatures in HVOF allow for effective particle melting, enabling them to flatten and adhere upon impact with the substrate. However, the prolonged thermal exposure increases the risk of oxidation during flight, potentially resulting in oxide inclusions at the coating-substrate interface or within the coating. In contrast, the lower temperatures in HVAF minimize particle oxidation while maintaining sufficient melting for coating deposition. The high velocities achieved, particularly with HVAF-M3 (650 m/s) and i7 (700 m/s), enhance the mechanical interlocking of particles, resulting in denser coatings with fewer defects, as shown in **Table 6-4**.

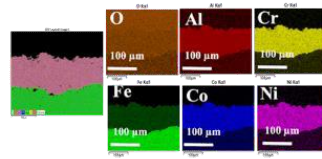
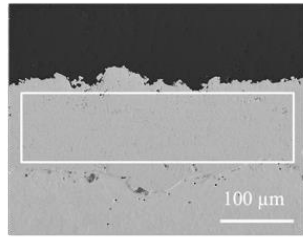
Table 6-3 Summary of the average particle temperatures and velocities measured using Accuraspray and DPV. HVOF and HVAF-M3 samples were monitored with Accuraspray, while HVAF-i7 samples were analyzed using DPV. Reported values represent the mean  $\pm$  measurement uncertainty based on the accuracy of the diagnostic systems used (Accuraspray and DPV).

| Sprayed Techniques            | Temperature (°C) | Velocity (m/s) |
|-------------------------------|------------------|----------------|
| HEA-HVAF-M3                   | 1480 $\pm$ 40    | 650 $\pm$ 20   |
| HEA-HVAF-i7                   | 1100 $\pm$ 30    | 700 $\pm$ 15   |
| HEA-HVOF                      | 2450 $\pm$ 50    | 530 $\pm$ 20   |
| MCrAlX (NiCoCrAlYHfSi) - HVOF | 2580 $\pm$ 50    | 510 $\pm$ 20   |

**Figure 6-4** presents the microstructure and elemental mapping of as-sprayed bond coats, including FeCoNiCrAl (HEA), FeCoNiCrAlYHf (HEA\_RE), and the conventional NiCoCrAlYHfSi medium entropy alloy. The selection of spray techniques (HVOF and HVAF) significantly influenced the bond coat properties. In **Figure 6-4(a)**, the porosity of the HEA bond coat decreased noticeably when switching from HVOF to HVAF-i7, a lower-temperature spray process.

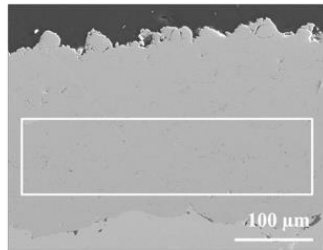
### a) HEA Bond coat

HVAF (M3)/ PSD 15-45 $\mu$ m

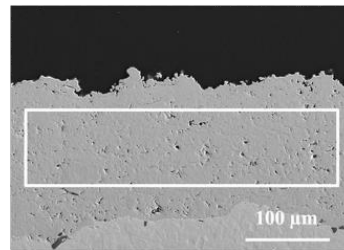


| Spectrum (at%) | Average |
|----------------|---------|
| Al             | 20      |
| Cr             | 20      |
| Fe             | 19      |
| Co             | 21      |
| Ni             | 20      |

HVAF (I7)/ PSD 5-30 $\mu$ m

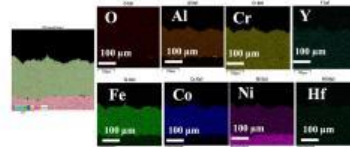
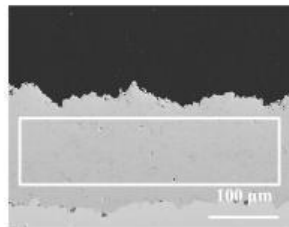


HVOF/ PSD 15-45 $\mu$ m



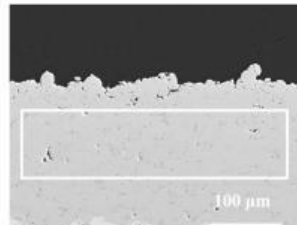
### b) HEA-RE Bond coat

HVAF (M3)/ PSD 15-45 $\mu$ m

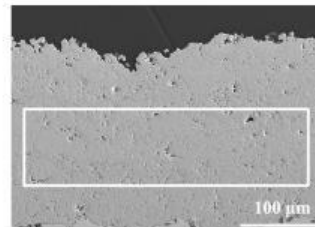


| Spectrum (at%) | Average |
|----------------|---------|
| Al             | 20      |
| Cr             | 21      |
| Fe             | 19      |
| Co             | 19.4    |
| Ni             | 20      |
| Y              | 0.34    |
| Hf             | 0.25    |

HVAF (I7)/ PSD 5-30 $\mu$ m



HVOF/ PSD 15-45 $\mu$ m



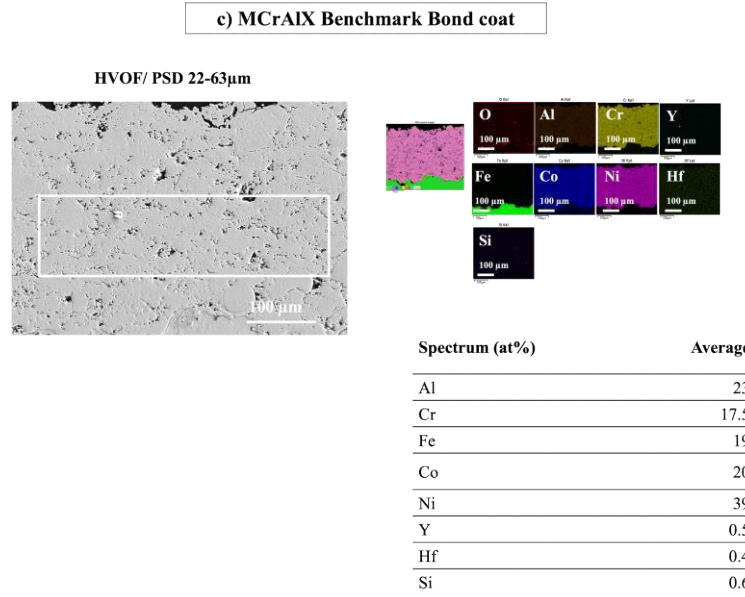


Figure 6-4 Cross-sectional FESEM images and corresponding EDX elemental mapping of as-sprayed bond coats: (a) FeCoNiCrAl HEA, (b) FeCoNiCrAlYHf HEA, and (c) NiCoCrAlYHfSi (benchmark MCrAlX). The coatings were deposited using HVOF-M3, HVOF-i7, and HVOF processes, with particle size distributions (PSD) of 5–30  $\mu$ m and 15–45  $\mu$ m, as indicated.

### 6.3.1 Deposition Efficiency and Porosity

Deposition efficiency (DE) was calculated based on the weight gain of the masked substrate before and after spraying. The DE percentage was determined using the following equation:

$$DE (\%) = \left( \frac{W_{\text{after}} - W_{\text{before}}}{W_{\text{powder fed}}} \right) * 100$$

where  $W_{\text{before}}$  and  $W_{\text{after}}$  denote the weights of the substrate before and after spraying, respectively, and  $W_{\text{powder fed}}$  represents the total amount of powder introduced into the spray gun. The coating area was properly masked to ensure only deposited material on the target surface was considered, and overspray losses were minimized during spraying.

Specifically, as shown in **Figure 6-5**, the porosity dropped from 3.4% (HVOF) to 0.2% (HVOF-i7), while the deposition efficiency (DE) improved from 64% to 79%, respectively. A

similar trend is evident in **Figure 6-4(b)** for the HEA\_RE bond coat. Porosity reduced significantly from 2.8% (HVOF) to 0.4% (HVAF-i7), with deposition efficiency increasing from 68% to 78%.

In contrast, the NiCoCrAlYHfSi bond coat shown in **Figure 6-4(c)** exhibits higher porosity (4.2%) and lower deposition efficiency (58%) when sprayed via HVOF. This performance is notably inferior compared to the HEA and HEA\_RE bond coats. While the melting points of individual elements may offer an approximate rationale, it is important to clarify that the values previously reported ( $\sim 1411$  °C for HEA and  $\sim 1544$  °C for HEA\_RE) were obtained through simple averaging of constituent elemental melting points, which does not accurately represent the thermodynamic behavior of multicomponent HEAs. Given the low concentration ( $\sim 0.6$  at.%) of reactive elements (Y, Hf), such a large increase in melting point is unlikely. Therefore, both HEA and HEA\_RE systems are expected to exhibit comparable melting ranges. The relatively lower melting behavior of these HEAs compared to the benchmark NiCoCrAlYHfSi ( $1526$  °C) may still contribute to better particle melting, but it is not the sole factor. Differences in porosity and deposition efficiency are also attributed to variations in particle size distribution, thermal conductivity, and spray dynamics. The HEA-based powders, due to their fine particle size and solid solution-dominated microstructure, tend to absorb heat more effectively, promoting enhanced melting, better splat formation, and improved cohesion on the substrate, resulting in denser coatings and higher deposition efficiency. In contrast, the benchmark NiCoCrAlYHfSi powder, with coarser particle size and higher thermal mass, may experience incomplete melting under identical HVOF conditions, leading to reduced splat deformation and increased porosity. However, this behavior is also strongly influenced by the selection of particle size distribution (PSD). In HVAF and HVOF processes, optimal PSD plays a critical role in deposition efficiency, porosity, and coating density. For example, using finer powders ( $5\text{--}30\text{ }\mu\text{m}$ ) in low-temperature HVAF systems (e.g., HVAF-i7) significantly enhances deposition efficiency (up to  $\sim 79\%$ ) and reduces porosity ( $<0.2\%$ ), whereas coarser powders ( $15\text{--}45\text{ }\mu\text{m}$ ) fail to adequately heat and deposit, resulting in thin or porous coatings [102,148]. In contrast, higher-flame systems such as HVAF-M3 or HVOF guns can accommodate coarser powders effectively due to their higher thermal energy and longer dwell times [148]. NiCoCrAlYHfSi coatings, known for higher porosity and incomplete melting, are similarly affected by PSD, as larger particles often exhibit poorer bonding. These findings underscore the importance of PSD optimization in achieving dense, low-porosity coatings with high deposition efficiency.

across different spray systems [148,182]. In contrast, the incomplete melting of NiCoCrAlYHfSi particles leads to coating defects, such as increased porosity, and limits overall performance. This emphasizes the critical interplay between material melting behavior and spray parameters in achieving coatings with optimal density and minimal porosity.

A key observation across all samples is the formation of uniform and random solid-solution phases, particularly in HEA and HEA\_RE bond coats. These phases contribute to improved microstructural stability and are less prone to cracking or phase separation, which often occur in conventional alloys. **Figure 6-5** provides a quantitative comparison, clearly showing that HEA and HEA\_RE bond coats outperform the NiCoCrAlYHfSi benchmark, achieving higher deposition efficiencies and significantly lower porosities. This highlights the superior performance of HEAs as bond coat materials for TBC systems, where coating density and reduced porosity are critical for long-term oxidation resistance and durability.

In a comprehensive review, Shahbazi *et al.* examined the application of HEAs as bond coats in TBC systems. Their study highlighted the superior oxidation resistance and thermal stability of HEA bond coats compared to traditional NiCoCrAlYHfSi alloys, attributing these enhancements to the unique multi-principal element composition of HEAs, which leads to the formation of stable oxide scales and improved mechanical properties at elevated temperatures [90]. Similarly, Nair *et al.* investigated the deposition of HEA coatings using thermal spray techniques and reported that HEA bond coats exhibit lower porosity and higher microhardness relative to conventional bond coat materials. These findings suggest that HEAs can provide more durable and reliable performance in high-temperature environments, making them promising candidates for next-generation TBC systems [79].

These studies reinforce the observations in the present work, where HEA and HEA\_RE bond coats demonstrated superior deposition efficiency and reduced porosity compared to the benchmark NiCoCrAlYHfSi bond coat. The unique properties of HEAs, including their sluggish diffusion and high configurational entropy, contribute to their enhanced performance as bond coats, offering improved protection for underlying substrates in high-temperature applications. In summary, the integration of HEAs as bond coats in TBC systems represents a significant advancement in materials engineering, providing coatings with enhanced thermal stability, oxidation resistance, and mechanical integrity, which are essential for the longevity and efficiency of components operating under extreme conditions. The superior deposition efficiency and reduced porosity of the HEA bond coats observed in this study are mainly attributed to their finer particle size distribution and more efficient melting behavior during

spraying. These microstructural features directly contributed to the improved coating density and oxidation resistance compared to the NiCoCrAlYHfSi benchmark. In addition, previous studies have reported that the intrinsic thermodynamic properties of HEAs, such as sluggish diffusion and high configurational entropy, promote microstructural stability and the preferential formation of protective alumina scales [98,101,102,183]. While these effects were not directly investigated here, they provide a framework that helps explain the superior performance of HEA bond coats in high-temperature applications.

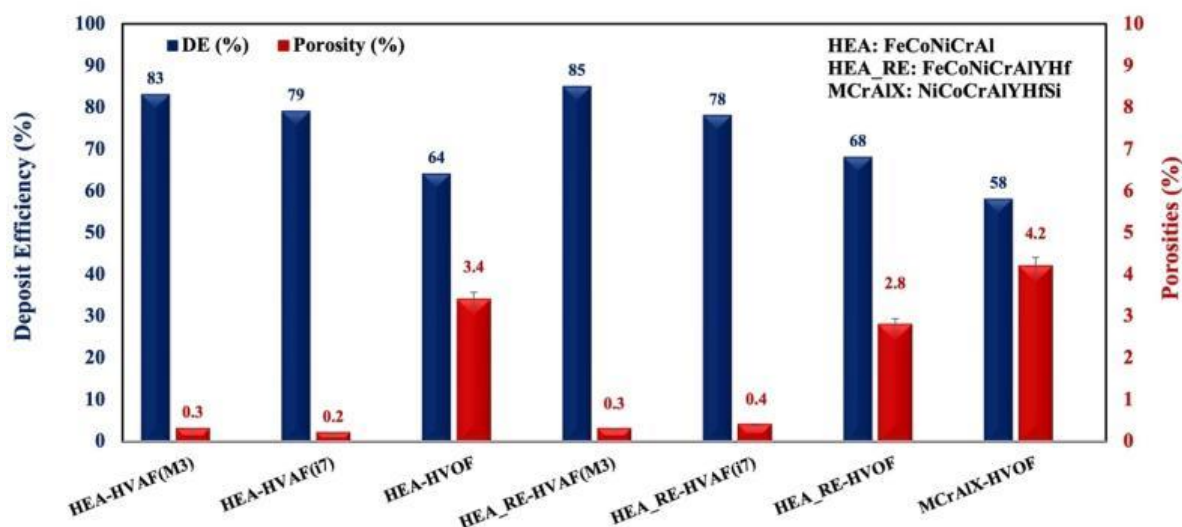


Figure 6-5 Comparison of deposition efficiency (DE) and porosity of as-sprayed bond coats: FeCoNiCrAl (HEA), FeCoNiCrAlYHf (HEA\_RE), and NiCoCrAlYHfSi (MCrAlX). The coatings were deposited using HVAF-M3, HVAF-i7, and HVOF processes. Error bars represent the standard deviation (SD) of DE and porosity values, obtained from six and approximately one hundred measurements per composition, respectively.

### 6.3.2 TGO Behavior

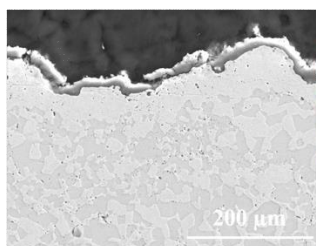
The isothermal oxidation test was conducted at 1150 °C for 200 hours to evaluate the behavior of the TGO layer and oxidation resistance of bond coats at temperatures exceeding typical gas turbine operating conditions (~850-1050 °C) [4,80,143]. As shown in **Figure 6-6**, the HEA and HEA\_RE bond coats deposited via HVAF (M3 and i7 guns) mainly developed a continuous  $\text{Al}_2\text{O}_3$  scale. However, for the HVOF/PSD 15–45  $\mu\text{m}$  condition (**Figure 6-6 (b)**), in addition to  $\text{Al}_2\text{O}_3$ , a  $\text{Cr}_2\text{O}_3$ -rich layer was also observed above the alumina. The formation of this secondary oxide is attributed to the higher flame temperature of the HVOF process compared to HVAF, which promotes increased in-flight oxidation of Cr during spraying. This explains the occurrence of mixed oxides at the bond coat surface under these conditions [8,32,90,107,108,149]. This alumina layer is highly desirable due to its slow growth rate and protective nature in high-temperature environments. In contrast, the benchmark

NiCoCrAlYHfSi bond coat (**Figure 6-6 (c)**) not only forms an alumina oxide layer but also shows the presence of mixed spinel oxides, confirmed through EDX mapping analysis. These spinel oxides are less stable, grow faster, and are often associated with increased oxidation rates and coating degradation [90,98,149]. Notably, spallation of the oxide layer was observed in the NiCoCrAlYHfSi bond coat, as shown in **Figure 6-6 (c)**, suggesting a potential reduction in durability and bond strength at elevated temperatures [150]. A critical observation is the absence of oxide spallation in the HEA and HEA\_RE bond coats. This superior performance can be attributed to the unique properties of HEAs, particularly the sluggish diffusion effect. In HEA systems, the multi-principal element composition significantly reduces the diffusion rates of alloying elements, effectively controlling oxidation kinetics and restricting the formation of undesirable mixed oxides. This leads to the preferential growth of a stable alumina TGO layer, enhancing the long-term oxidation resistance and structural integrity of the bond coats. These results demonstrate the advantages of HEA and HEA\_RE bond coats over traditional NiCoCrAlYHfSi systems in extreme high-temperature environments, highlighting their potential as next-generation bond coat materials for TBC systems.

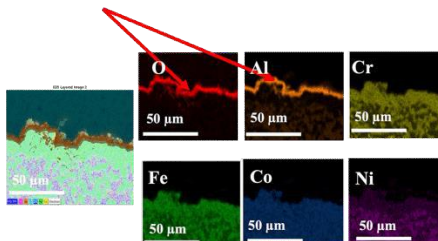
Although only cross-sectional morphologies were provided, visible signs of surface spallation were also noted on the oxidized top surface of the NiCoCrAlYHfSi samples, consistent with the detachment features seen in the cross-sections.

# a) HEA Bond coat

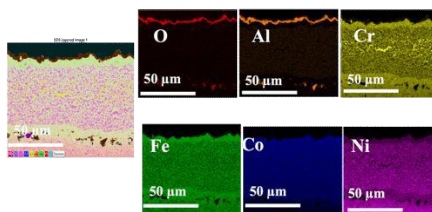
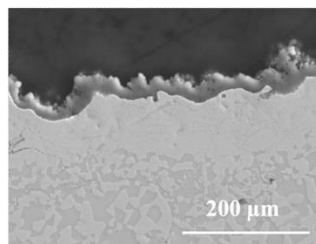
HVAF (M3)/ PSD 15-45μm



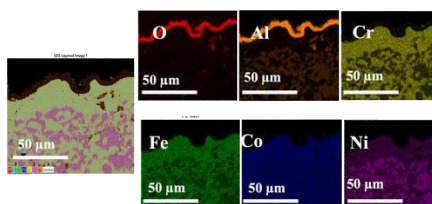
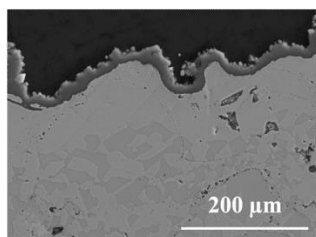
Alumina Oxide



HVAF (i7)/ PSD 5-30μm



HVOF/ PSD 15-45μm



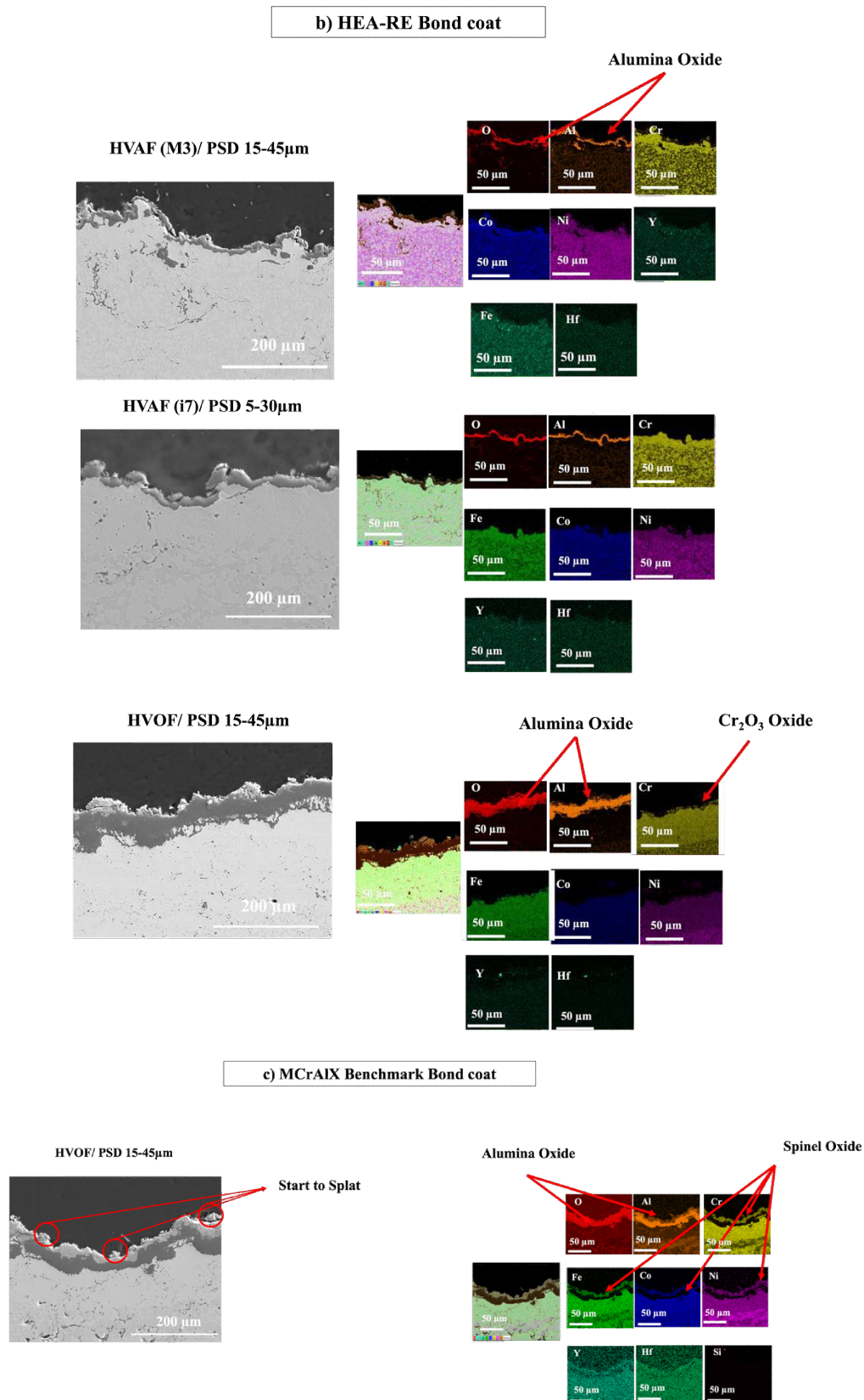


Figure 6-6 Cross-sectional FESEM images and EDX mapping analysis of as-sprayed bond coats. (a) FeCoNiCrAl HEA bond coats deposited via HVAF-M3, HVAF-i7, and HVOF. (b) FeCoNiCrAlYHf HEA\_RE bond coats deposited via HVAF-M3, HVAF-i7, and HVOF, showing the formation of a continuous Al<sub>2</sub>O<sub>3</sub> scale and, in the case of HVOF/PSD 15–45  $\mu$ m, an additional Cr<sub>2</sub>O<sub>3</sub>-rich layer. (c) Benchmark NiCoCrAlYHfSi medium entropy

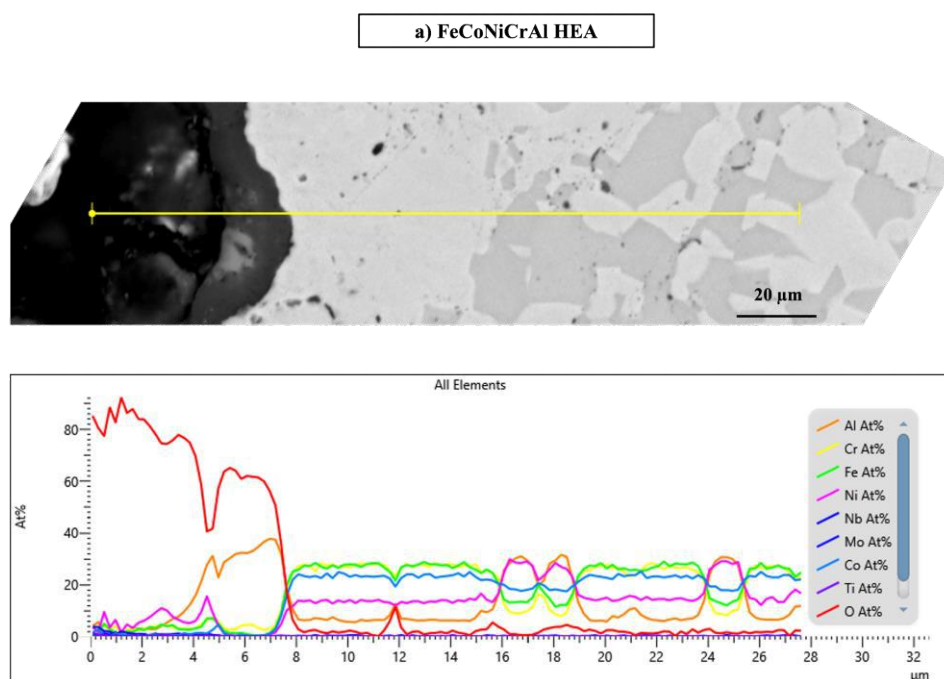
alloy bond coat deposited via HVOF. The images present microstructural characteristics, including coating morphology, elemental distribution, and oxide layer formation.

These observations can be further explained by considering the core effects of high-entropy alloys, particularly sluggish diffusion and lattice distortion. Sluggish diffusion restricts the outward migration of transition metals such as Cr, Co, and Ni and the inward diffusion of oxygen, thereby slowing the growth of the TGO. Additionally, lattice distortion influences defect concentrations and may disrupt short-circuit diffusion paths, contributing to the formation of a more stable and adherent  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> scale. The presence of reactive elements such as Hf and Y near the oxide–metal interface also plays a vital role, as these elements segregate at grain boundaries and reduce interfacial energy, enhancing oxide adhesion and minimizing void formation. These mechanistic effects collectively align with the observed suppression of spinel formation, the development of continuous alumina scales, and the improved oxidation resistance of HEA and HEA\_RE bond coats.

**Figure 6-7** illustrates the EDX line analysis performed across the TGO layer and bond coat interface for (a) HEA and (b) HEA\_RE. The figure provides insights into the elemental diffusion behavior, the formation of the alumina (Al<sub>2</sub>O<sub>3</sub>) TGO layer, and the influence of reactive elements on the oxide layer composition and uniformity. In **Figure 6-7 (a)** (HEA bond coat), a sharp and continuous oxygen (O) peak is observed near the surface, coinciding with a significant aluminum (Al) peak, which confirms the formation of a dense and stable alumina TGO layer. The other elements, such as Cr, Ni, Fe, and Co, show relatively stable and low concentrations beyond the TGO region, indicating minimal diffusion of these elements into the oxide layer. This behavior is characteristic of HEAs, where the sluggish diffusion effect suppresses elemental migration, thereby promoting the selective oxidation of Al and the formation of pure alumina. Minimal fluctuations in the profiles of Cr, Fe, and Co further highlight the uniformity and stability of the bond coat microstructure. In **Figure 6-7 (b)** (HEA\_RE bond coat), a similar oxygen (O) peak aligns with a prominent aluminum (Al) peak, again confirming the presence of an alumina TGO layer. However, the addition of Hf and Y introduces slight fluctuations in the diffusion profiles. Notably, small peaks corresponding to Hf and Y are observed near the oxide-bond coat interface. These reactive elements are known to segregate at the interface, where they act as oxide stabilizers by improving the adherence of the alumina layer and reducing the formation of interfacial defects [78,90,166,167]. Despite the presence of Hf and Y, no significant improvement in TGO

thickness was noted compared to the HEA system, as discussed earlier. This suggests that the sluggish diffusion effect remains the dominant mechanism for controlling oxidation kinetics, regardless of the addition of reactive elements.

A comparison between the two systems reveals that both HEA and HEA\_RE bond coats form a continuous and dense  $\alpha$ -alumina TGO layer with minimal evidence of mixed oxides or spinel phases. However, the addition of reactive elements (Hf and Y) in HEA\_RE introduces slight elemental fluctuations near the interface, which may contribute to improved oxide stability but do not significantly alter the overall TGO growth. The uniform profiles of Al and O, coupled with stable concentrations of other elements, further underscore the role of HEAs in suppressing diffusion and promoting selective oxidation. Although the addition of reactive elements (Hf and Y) did not significantly affect the measured TGO thickness under isothermal conditions at 1150 °C for 150 h, this observation does not necessarily imply a negligible influence on oxidation behavior. The total concentration of REs in the HEA\_RE composition (~0.6 at.%) may have been insufficient to induce strong segregation effects detectable through conventional SEM analysis. Moreover, isothermal oxidation alone may not activate the full benefits of REs, which often manifest under thermal cycling through enhanced oxide adhesion, interface stabilization, and suppression of void formation.



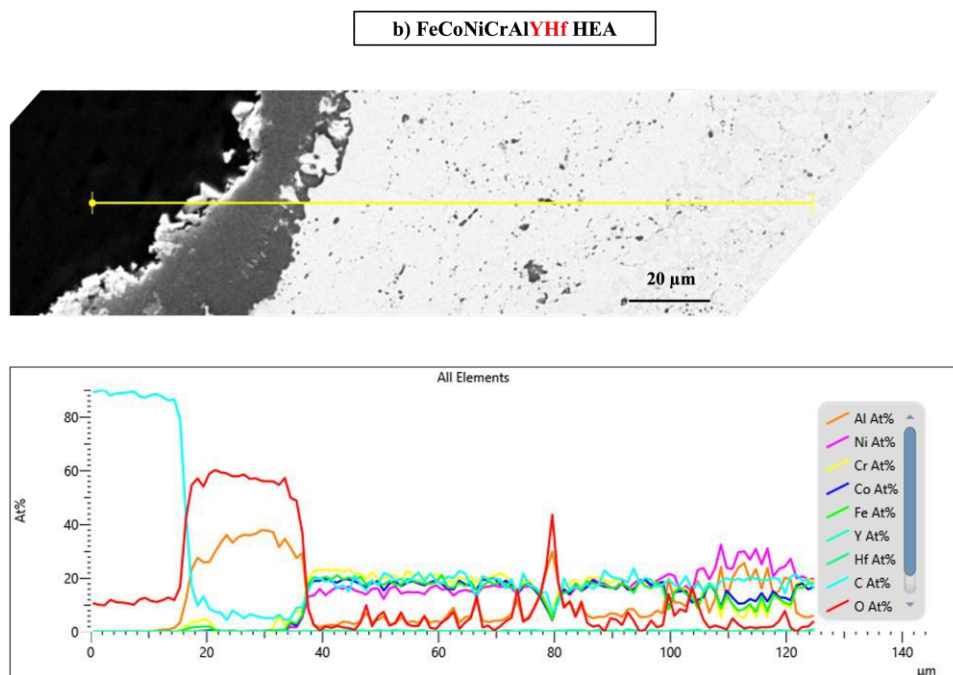


Figure 6-7EDX line analysis of elemental distribution across the TGO layer and bond coat interface for (a) FeCoNiCrAl (HEA) and (b) FeCoNiCrAlYHf (HEA\_RE) after 200 hours of isothermal oxidation at 1150°C. The profiles show a dominant Al and O peak near the surface, confirming the formation of a dense  $\alpha$ -alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) TGO layer.

### 6.3.3 Influence of Vacuum Heat Treatment

Plane sliding and recrystallization play critical roles in enhancing microstructural stability after deposition. Plane sliding alleviates residual stresses introduced during spraying, while recrystallization removes deformation-induced defects, promoting the development of a more homogeneous and equiaxed grain structure. This transformation enhances mechanical integrity and improves resistance to high-temperature oxidation. Experimental data confirmed a significant reduction in porosity following vacuum heat treatment (VHT), accompanied by an approximate 40% decrease in TGO layer growth compared to untreated samples. Despite the exposure to high temperatures, the phase stability of the bond coat was preserved [177]. This stability can be attributed to the thermodynamic favorability and kinetic barriers that suppress phase transformations. The  $\gamma$  (FCC) and  $\beta$  (B2) phases present in NiCoCrAl-based and high-entropy alloy (HEA) bond coats remain stable at 1050 °C, indicating no strong driving force for new phase formation. Additionally, the sluggish diffusion effect characteristic of multi-component HEAs further suppresses phase evolution, allowing the coating to retain its original phase composition. Overall, VHT effectively reduces porosity, enhances densification, and stabilizes the microstructure without inducing phase changes.

These improvements contribute to increased oxidation resistance and long-term durability, establishing a robust foundation for TBC systems in demanding high-temperature environments.

To evaluate the effect of vacuum heat treatment on the microstructure and oxidation resistance, the samples underwent treatment at 1050 °C for 4 hours under  $6.8 \times 10^{-4}$  mbar, and their porosity was analyzed without and with treatment using ImageJ software. As shown in **Figure 6-8**, porosity significantly decreased in all HEA and HEA\_RE bond coats deposited via HVAF and HVOF. For HVAF-sprayed coatings, the porosity reduced from 0.3% to 0.2% (HEA, HVAF-M3) and from 0.2% to 0.1% (HVAF-i7). Similarly, HEA\_RE exhibited reductions from 0.4% to 0.2%. For HVOF-sprayed coatings, HEA decreased from 3.4% to 2.2%, and HEA\_RE reduced from 2.8% to 1.7%. The benchmark NiCoCrAlYHfSi bond coat, although improved, retained higher porosity, reducing from 4.2% to 2.8%. This porosity reduction is attributed to atomic diffusion-driven pore healing, where elevated temperatures activate the migration of atoms to fill voids, while the vacuum environment prevents further oxidation and facilitates densification [32,169].

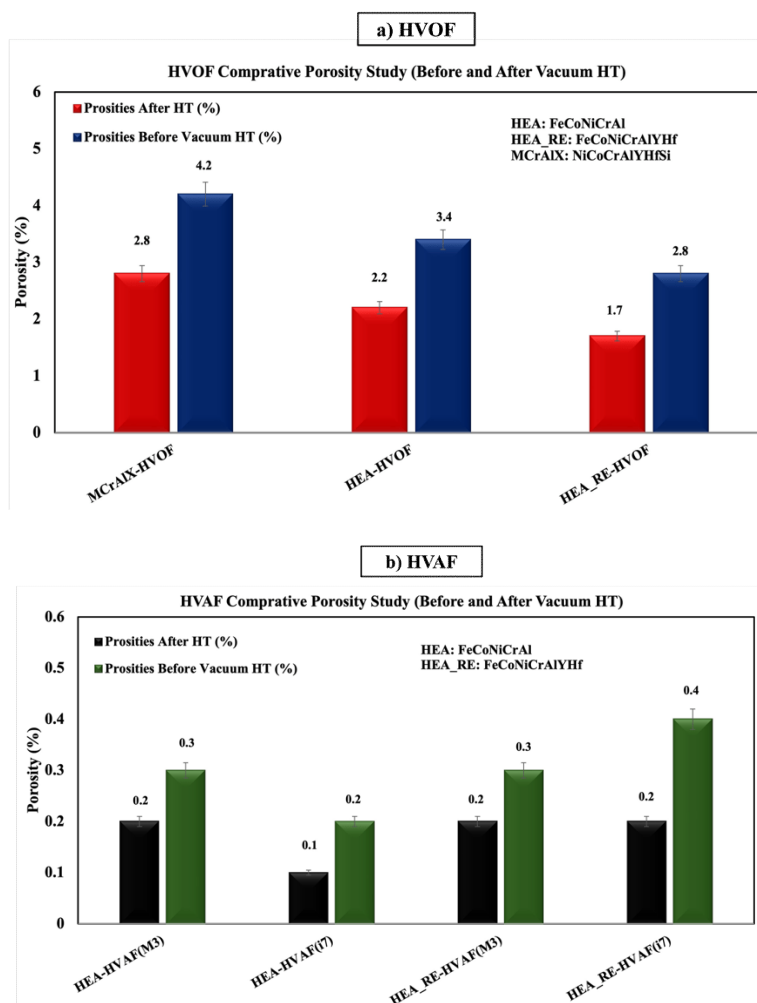


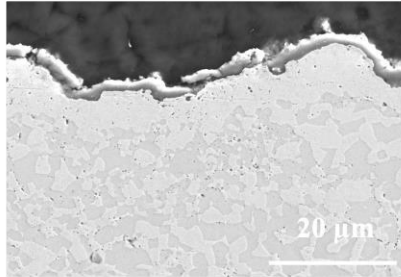
Figure 6-8 Comparative porosity analysis without and with vacuum heat treatment for (a) HVOF-sprayed bond coats and (b) HVAF-sprayed. error bars represent the standard deviation (SD) calculated from approximately one hundred measurements per coating.

Following this, isothermal oxidation tests were repeated at 1150 °C for 200 hours to examine the influence of vacuum heat treatment on TGO thickness. The results, illustrated in **Figures 6-9** and **6-10**, show a significant reduction in TGO thickness across all HEA and HEA\_RE bond coats. TGO thickness was measured from cross-sectional FESEM micrographs at 20 points per sample using image analysis software to ensure statistical reliability. For HVAF-sprayed HEA, TGO thickness decreased from 3.9  $\mu\text{m}$  to 2.1  $\mu\text{m}$  (HVAF-i7) and from 4.3  $\mu\text{m}$  to 2.9  $\mu\text{m}$  (HVAF-M3). Similarly, for FeCoNiCrAlYHf HEA\_RE, TGO thickness reduced from 4.1  $\mu\text{m}$  to 1.9  $\mu\text{m}$  (HVAF-i7) and from 4.5  $\mu\text{m}$  to 2.6  $\mu\text{m}$  (HVAF-M3). In HVOF-sprayed coatings, the TGO thickness decreased from 5.8  $\mu\text{m}$  to 3.3  $\mu\text{m}$  (HEA bond coat) and from 6.9  $\mu\text{m}$  to 3.1  $\mu\text{m}$  (HEA\_RE bond coat). The NiCoCrAlYHfSi bond coat, while improved, showed the thickest TGO layer, reducing from 9.3  $\mu\text{m}$  to 7.8  $\mu\text{m}$ , reinforcing its inferior oxidation resistance compared to HEA and HEA\_RE systems. In addition to reducing TGO thickness, vacuum heat treatment eliminated the gray  $\text{Cr}_2\text{O}_3$ -rich band observed above the alumina layer in as-sprayed coatings, leading to the formation of a stable, single-phase  $\alpha\text{-Al}_2\text{O}_3$  TGO. The significant reductions in porosity and TGO thickness in HEA and HEA\_RE coatings can be explained by the mechanism of atomic diffusion and oxidation control during vacuum heat treatment. Elevated temperatures promote the healing of micro-voids and stabilize the microstructure through elemental redistribution (e.g., Al, Cr, Hf). Simultaneously, the vacuum minimizes oxygen ingress, reducing oxidation rates and favoring the exclusive formation of thin, dense  $\alpha$ -alumina, which enhances oxidation resistance. Importantly, the addition of reactive elements (Hf, Y) in HEA\_RE did not produce a significant further reduction in TGO thickness compared to HEA. This indicates that the inherent compositional and microstructural stability of HEAs, rather than reactive-element effects, dominates oxide growth control under the tested conditions. Overall, these findings demonstrate that vacuum heat treatment effectively reduces porosity and TGO growth, significantly improving the performance of HEA and HEA\_RE bond coats compared to the NiCoCrAlYHfSi benchmark. This underscores their strong potential as advanced bond coat materials for TBC systems operating in extreme high-temperature environments.

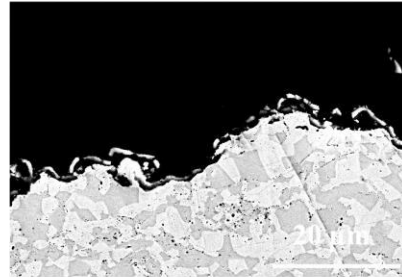
**a) HEA Bond coat**

**HVAF (M3)/ PSD 15-45μm**

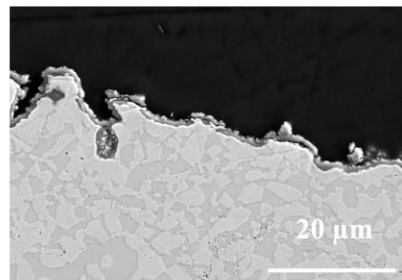
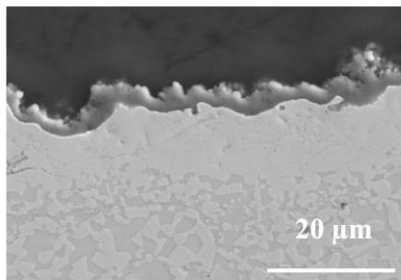
**Without VHT**



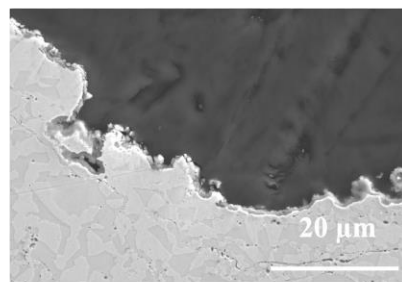
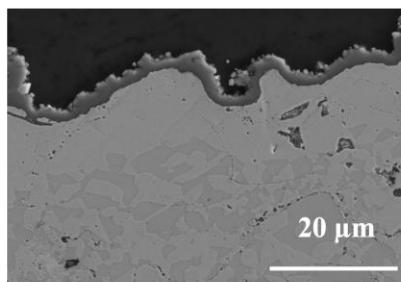
**With VHT**



**HVAF (i7)/ PSD 5-30μm**



**HVOF/ PSD 15-45μm**



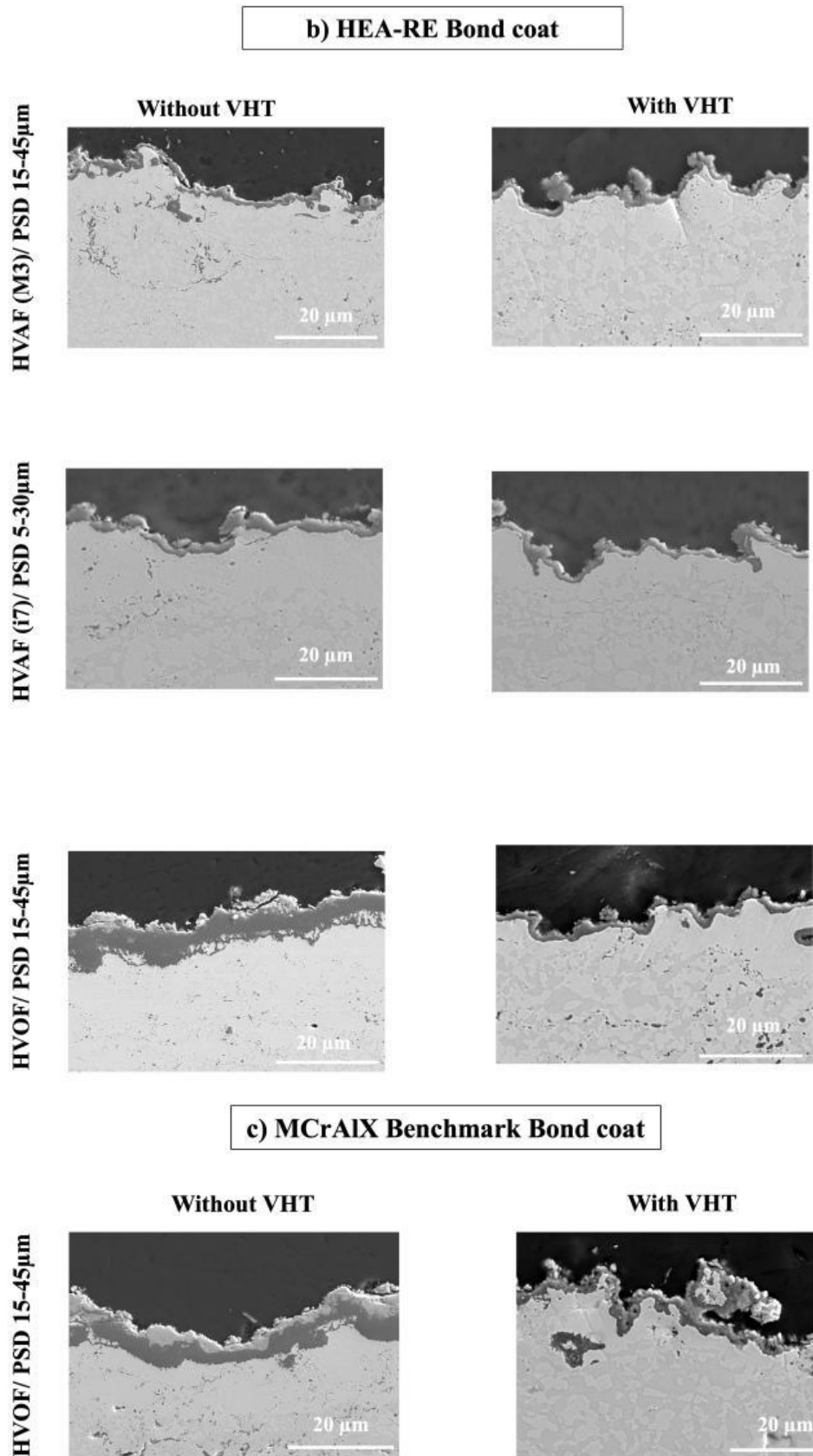


Figure 6-9 Cross-sectional FESEM micrographs of thermally grown oxide (TGO) layers in (a) FeCoNiCrAl HEA, (b) FeCoNiCrAlYHf HEA\_RE, and (c) NiCoCrAlYHfSi (MCrAlX) bond coats, shown before and after vacuum heat treatment (1050 °C, 4 h) followed by isothermal oxidation at 1150 °C for 200 h. In HEA and

HEA\_REcoatings, the as-sprayed condition displayed a thin gray  $\text{Cr}_2\text{O}_3$ -rich band above the alumina scale, which disappeared after vacuum heat treatment, leaving a continuous and dense  $\alpha\text{-Al}_2\text{O}_3$  TGO. This indicates stabilization of a single alumina oxide layer and suppression of mixed-oxide formation. In contrast, the MCrAlX coating developed a much thicker and non-uniform TGO with mixed oxides, even after vacuum heat treatment.

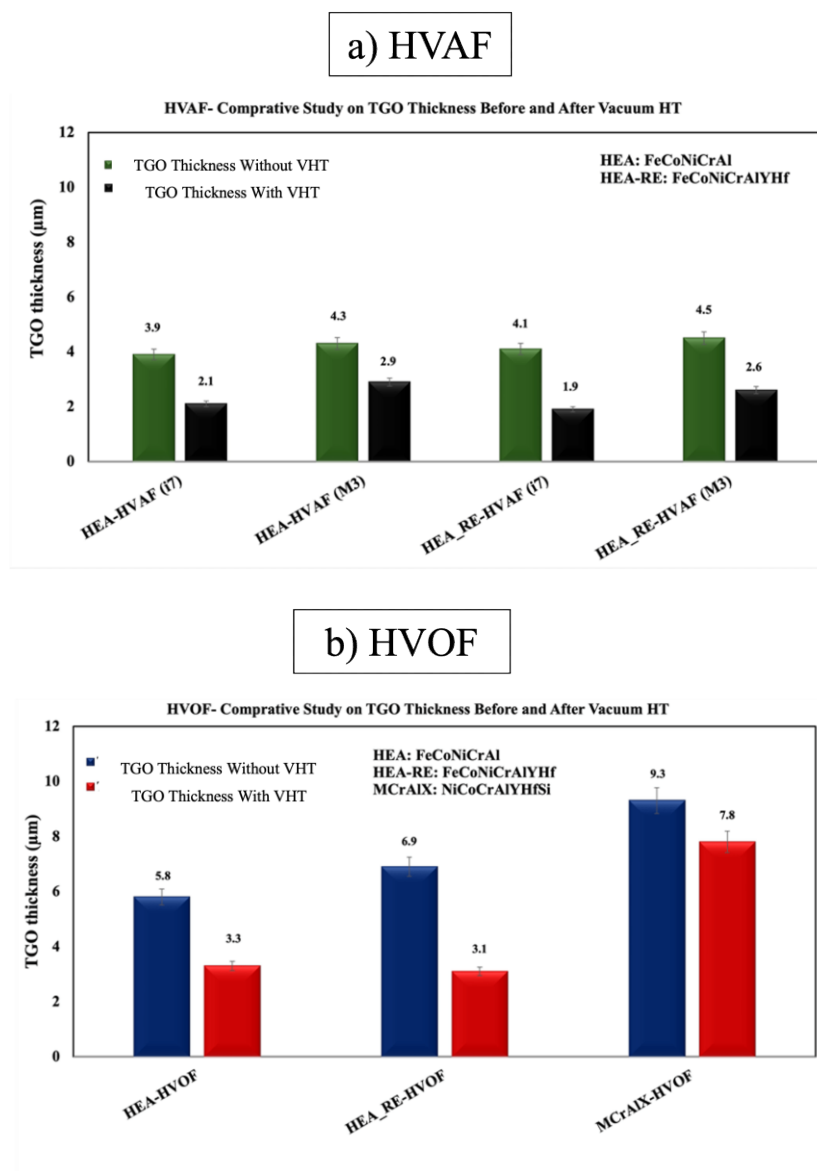


Figure 6-10 Comparative study of TGO thickness without and with vacuum heat treatment for (a) HVAF-sprayed and (b) HVOF-sprayed bond coats. The results demonstrate a 40% reduction in TGO thickness across HEA and HEA\_RE bond coats with heat treatment, with minimal reduction observed for the MCrAlX (NiCoCrAlYHfSi) bond coat. This highlights the effectiveness of vacuum heat treatment in controlling oxidation kinetics and improving the oxidation resistance of HEA and HEA\_RE systems. Error bars represent standard deviations from repeated measurements. Error bars represent the standard deviation (SD) obtained from repeated measurements at multiple cross-sectional locations.

**Figure 6-11** illustrates the mass gain evolution during isothermal oxidation testing conducted at 1150 °C for 200 hours, comparing results without and with VHT. The solid lines represent the mass gain without VHT, while the dashed lines correspond to the results after VHT. As observed, the worst-performing sample with VHT (dashed line) approaches or even outperforms the best-performing sample without VHT (solid line). This significant improvement highlights the critical role of VHT in controlling oxide growth and reducing mass gain at elevated temperatures.

The reduction in mass gain can be attributed to the dense and refined microstructure achieved through VHT, which minimizes porosity and enhances the coating's resistance to oxygen diffusion. VHT facilitates atomic diffusion and pore healing, reducing the availability of pathways for oxygen ingress and improving the cohesion of the coating structure. Consequently, the growth of the TGO layer is better controlled, leading to slower oxidation kinetics and lower mass gain.

The HEA and HEA\_RE bond coats sprayed via HVAF (M3 and i7) exhibit the lowest mass gain values with VHT, emphasizing their superior performance compared to the NiCoCrAlYHfSi bond coat sprayed via HVOF. The sluggish diffusion effect inherent to HEAs further limits the elemental mobility, which suppresses the formation of mixed oxides and promotes the preferential growth of a thin, stable  $\alpha$ -alumina TGO layer. In contrast, the NiCoCrAlYHfSi bond coat, despite benefiting from VHT, still demonstrates higher mass gain due to its less refined microstructure, higher porosity, and increased susceptibility to mixed oxide formation.

The comparison between pre-VHT and post-VHT results underscores the significant influence of vacuum heat treatment in improving oxidation resistance. By densifying the coating and reducing porosity, VHT effectively minimizes the oxidation pathways, thereby slowing TGO growth and reducing mass gain, which are critical for enhancing the long-term performance of bond coats in TBC systems operating under extreme high-temperature conditions. Additionally, oxidation kinetics analysis was conducted by fitting the mass gain data to parabolic and linear models. The resulting rate constants revealed lower oxidation kinetics for HEA and HEA\_RE coatings, consistent with their microstructural stability and resistance to mixed oxide formation. The calculated parabolic ( $k_p$ ) and linear ( $k_l$ ) rate constants for each bond coat, before and after VHT, are summarized in **Table 6-4**. These results further support the superior oxidation resistance of HEA and HEA\_RE coatings. The trend is in agreement with prior studies on high-entropy alloys' oxidation behavior [184–186].

Table 6-4 Parabolic and linear oxidation rate constants for each coating without and with vacuum heat treatment at 1150 °C for 200 h.

| Coating System   | Condition  | $k_p$ ( $\text{mg}^2 \cdot \text{cm}^{-4} \cdot \text{h}^{-1}$ ) | $k_l$ ( $\text{mg} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$ ) |
|------------------|------------|------------------------------------------------------------------|----------------------------------------------------------------|
| HEA-HVAF (M3)    | As-sprayed | 0.025                                                            | 0.031                                                          |
| HEA-HVAF (M3)    | Post-VHT   | 0.010                                                            | 0.015                                                          |
| HEA_RE-HVAF (i7) | As-sprayed | 0.020                                                            | 0.027                                                          |
| HEA_RE-HVAF (i7) | Post-VHT   | 0.008                                                            | 0.012                                                          |
| HEA-HVOF         | As-sprayed | 0.038                                                            | 0.045                                                          |
| HEA-HVOF         | Post-VHT   | 0.022                                                            | 0.028                                                          |
| HEA_RE-HVOF      | As-sprayed | 0.033                                                            | 0.040                                                          |
| HEA_RE-HVOF      | Post-VHT   | 0.018                                                            | 0.023                                                          |
| MCrAlX-HVOF      | As-sprayed | 0.042                                                            | 0.049                                                          |
| MCrAlX-HVOF      | Post-VHT   | 0.030                                                            | 0.036                                                          |

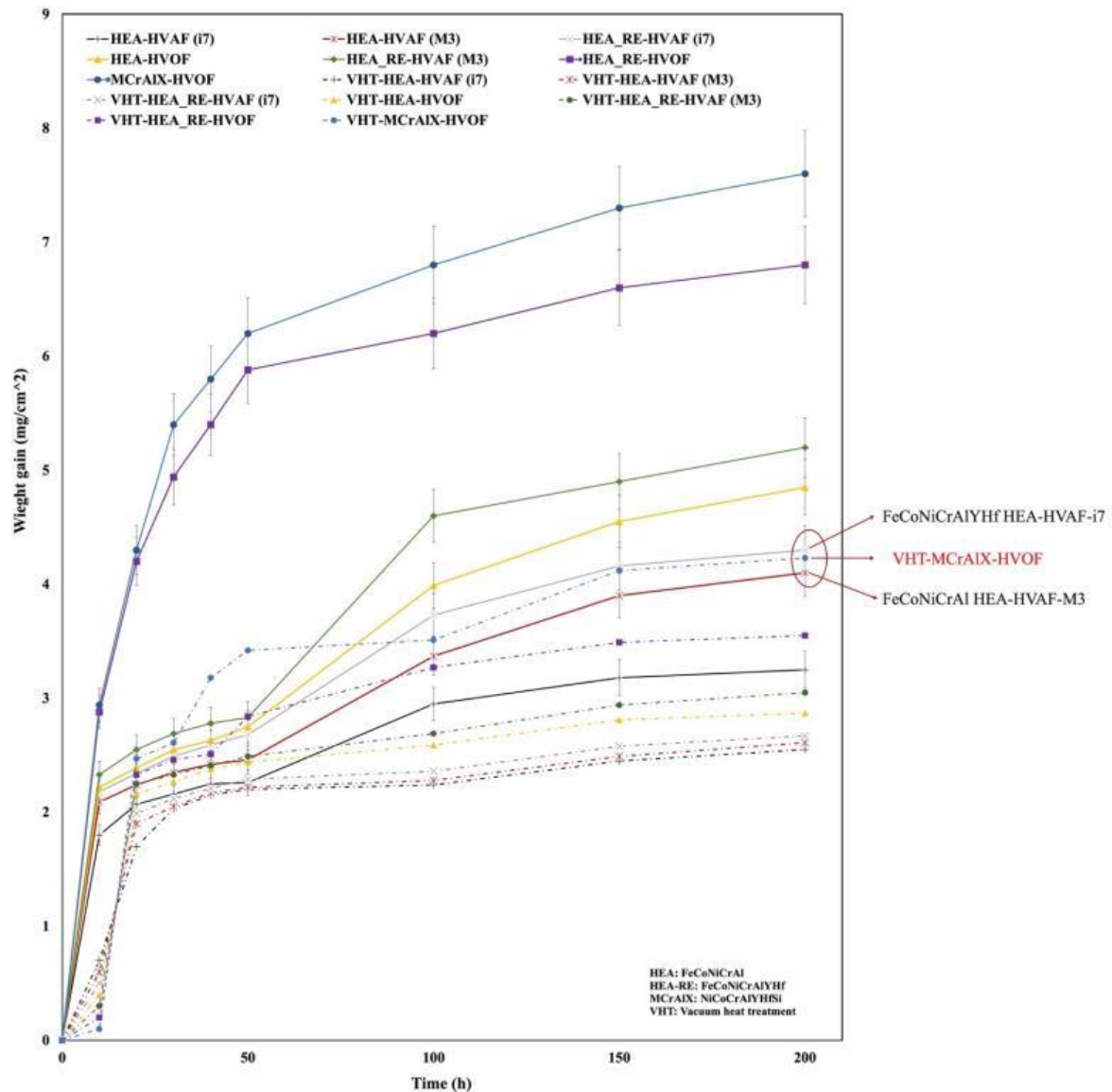


Figure 6-11 Comparative mass gain results during isothermal oxidation testing at 1150°C for 200 hours without (solid lines) and with vacuum heat treatment (dashed lines).

## 6.4 Conclusion

This study compared FeCoNiCrAl (HEA) and FeCoNiCrAlYHf (HEA\_RE) bond coats with the commercial NiCoCrAlYHfSi (MCrAlX) benchmark. Coatings were deposited by HVOF and HVOF, and their microstructure and oxidation performance were systematically evaluated, including the effect of vacuum heat treatment (VHT).

The HVAF i7 process achieved the best spraying results, with deposition efficiencies above 70% and porosity as low as 0.1–0.2% in HEA-based coatings, compared to 2.8–4.2% for HVOF-sprayed MCrAlX. The dense microstructure directly enhanced oxidation resistance. VHT at 1050 °C for 4 h further improved integrity by pore healing and stress relaxation, reduced TGO thickness by ~40%, and eliminated the gray oxide-rich layer above alumina, resulting in a more stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> interface.

Both HEA and HEA\_RE formed thinner, denser TGOs than the MCrAlX benchmark, with limited Cr<sub>2</sub>O<sub>3</sub> only in HVOF-sprayed HEA\_RE and no evidence of spallation. The addition of reactive elements (Y, Hf) did not significantly reduce TGO growth compared to the base HEA, underscoring the inherent stability of the FeCoNiCrAl system.

Overall, combining HVAF spraying with VHT produced dense, oxidation-resistant HEA coatings with robust TGO adherence, without relying heavily on costly reactive elements. These results confirm the strong potential of HEAs as next-generation bond coats for TBC systems. Future work should extend to cyclic oxidation and alternative reactive element strategies.

## **7 Chapter Seven: Conclusion and future work**

## 7.1 Conclusion

The typical operating temperature of commercial bond coats lies between 850 °C and 1050 °C, which corresponds closely to the service temperature range of Ni-based superalloy substrates ( $\approx 1000\text{--}1200$  °C) used in turbine components. At first glance, the presence of a bond coat might seem unnecessary, given the similarity in temperature capability between the coating and substrate. However, its role remains essential: the bond coat mitigates the CTE mismatch between the metallic substrate and the ceramic top coat, while simultaneously providing oxidation protection and reducing material consumption during high-temperature exposure. These functions collectively ensure the mechanical integrity and long-term durability of TBC systems.

Given the proven performance of MCrAlY-type coatings in gas turbine applications, a natural question arises: can their behavior be further enhanced using alternative materials such as HEAs? Although HEAs have demonstrated superior oxidation resistance and stability at elevated temperatures, their high production cost, complex compositional design, and limited industrial maturity remain challenges. Therefore, this research explores whether HEA-based bond coats can offer a meaningful and practical improvement over conventional MCrAlX systems.

This thesis presents a comprehensive study on the development, characterization, and performance of FeCoNiCrAl (HEA) and FeCoNiCrAlYHf (HEA\_RE) bond coats, focusing on their oxidation resistance, microstructural evolution, and deposition efficiency in comparison to conventional MCrAlX coatings. Coatings were deposited using low-temperature thermal spray techniques (HVOF and HVAF) and subsequently evaluated through oxidation testing and VHT to assess TGO growth kinetics and microstructural stability. The findings significantly contribute to advancing HEA-based bond coats as viable alternatives to commercial NiCoCrAlYHfSi (MCrAlX) coatings for high-temperature applications, particularly in TBC systems.

The results showed that HEA bond coats produced via HVOF and HVAF developed thinner and more stable alumina-based TGOs compared to the conventional MCrAlX coatings. Unlike MCrAlX, which exhibited mixed oxide formation leading to higher mass gain and accelerated oxidation, HEA coatings remained free of spinel oxides throughout the oxidation process. Among the spraying processes investigated, the HVAF i7 process demonstrated the best performance, achieving higher deposition efficiency and significantly

lower porosity (0.1–0.2%), with microstructures comparable to those produced by cold spray. The use of finer feedstock particles in the i7 gun further contributed to the production of dense microstructures, thereby improving TGO stability.

VHT at 1050 °C for four hours under a high vacuum ( $\sim 6.8 \times 10^{-4}$  mbar) proved highly effective in enhancing bond coat integrity by healing pores and reducing oxidation kinetics. Following VHT, the TGO thickness was reduced by approximately 40% across all HEA and HEA\_RE coatings, confirming the treatment's role in stabilizing the oxide layers and improving microstructural robustness. The addition of reactive elements such as Y and Hf to HEA\_RE coatings did not yield a significant reduction in TGO thickness under the present test conditions. Although reactive elements are generally expected to promote better adhesion between the TGO and the bond coat, further spallation and cyclic oxidation tests are required to more accurately assess their influence on the overall bond coat performance.

Furthermore, interdiffusion analysis revealed that HEA bond coats developed a thinner interdiffusion zone with the substrate, enhancing long-term microstructural stability. The combination of a uniform solid-solution microstructure, controlled TGO growth, and minimal interdiffusion underscores the durability of HEA-based bond coats under extreme service conditions. Overall, this work demonstrates that HEA and HEA\_RE bond coats, particularly when processed via optimized HVAF spraying and subjected to VHT, offer a cost-effective, high-performance alternative to conventional MCrAlX coatings for next-generation TBC systems.

## **7.2 Implications and Future Directions**

This research has established several key characteristics of FeCoNiCrAl (HEA) and FeCoNiCrAlYHf (HEA-RE) bond coats that demonstrate promising attributes, including superior oxidation resistance, improved deposition efficiency, and reduced porosity. The study also confirmed that the HVAF process, particularly when using the i7 gun, can produce highly dense and oxidation-resistant HEA bond coats, representing an important step toward advancing next-generation bond coat technologies for high-temperature applications.

However, while these results indicate that HEA-based bond coats hold strong potential as alternatives to conventional MCrAlY coatings, further evidence is required to fully validate

their suitability for replacing the current industry standard. In particular, additional studies should aim to:

- 1- Evaluate long-term cyclic oxidation performance under realistic service conditions to confirm durability in aerospace and power-generation environments.
- 2- Explore the role of alternative reactive elements in further optimizing TGO growth and stability.
- 3- Assess mechanical and thermo-mechanical properties, including thermal-cycling resistance, adhesion strength, and fracture toughness.
- 4- Investigate industrial scalability of optimized HVOF-HEA deposition processes for large-component applications.
- 5- Integrate high-entropy ceramics with HEA and HEA-RE bond coats, assessing adhesion performance, TGO behavior, and the overall lifespan of TBC systems.

By addressing these areas, future research will help determine whether HEA-based bond coats can reliably and economically replace MCrAlY systems in demanding high-temperature applications.

### **7.3 Final Takeaway**

Through extensive experimentation and comparative analysis, this thesis demonstrates that HEA and HEA\_RE bond coats offer transformative advantages over conventional MCrAlX coatings, particularly in terms of oxidation resistance, deposition efficiency, and long-term stability at high temperature after isothermal oxidation test. The integration of HVOF deposition and vacuum heat treatment further enhances coating durability, setting the stage for HEAs to be adopted as next-generation bond coat materials in advanced TBC systems.

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