Cyclic Oxidation Properties of the Nanocrystalline AlCrFeCoNi High-Entropy Alloy Coatings Applied by the Atmospheric Plasma Spraying Technique

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Abstract: Microcrystalline and nanocrystalline AlCrFeCoNi high-entropy alloy (HEA) coatings were applied on Inconel 718 superalloy using the atmospheric plasma spraying (APS) process. The high-temperature oxidation behavior of the microcrystalline and nanocrystalline AlCrFeCoNi HEA-coated superalloy was examined at 1100 °C under the air atmosphere for 50 cycles under cyclic heating and cooling (1 h for each cycle). The oxidation kinetics of both nanocrystalline- and microcrystalline-coated superalloys were accordingly analyzed by weight change measurements. We noted that the uncoated and coated samples followed the parabolic rate law of the oxidation. X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray analysis (EDS), elemental mapping and X-ray photoelectron spectroscopy (XPS) were used to analyze the oxidized coated and uncoated samples. In the HEA-coated superalloy, Fe, Ni, Co and Al were oxidized in the inter-splat region, whereas the splats, which consisted mainly of Ni and Cr, remained unoxidized. Due to the formation of compact and adhesive thin NiO, CoO oxides and spinels together with the Al2O3 oxide scale on the surface of the coating during oxidation, the developed nanocrystalline HEA coating showed better oxidation resistance compared with the microcrystalline HEA coating.

Keywords: AlCrFeCoNi high-entropy alloy coating; APS deposition; cyclic oxidation

1. Introduction

High-entropy alloys (HEAs) are a new category of metallic alloys that demonstrate brilliant characteristics. These types of materials are useful candidates for the design and manufacturing of innovative engineering parts and equipment in different kinds of bulk, sintered, as-cast and coating forms to resist harsh industrial environments [1]. Despite working on advanced materials and ceramics starting in the 1990s [2–6], the development, testing and application of advanced HEAs and their coatings have been the focus of the research efforts since the mid-2010s [7–9].

Owing to the various primary metallic alloys with an equimolar or near-equimolar composition, HEAs have prominent chemical, mechanical and thermal properties, including higher mechanical strength and hardness, greater chemical stability, better corrosion and oxidation resistance and outstanding wear behavior. HEA compositions have been recently utilized as thermoelectric high-performance magnets, new generation catalysts and advanced superconductors. Among them, HEA alloys and coatings consisting of Ni, Co and Al have been shown to have excellent chemical and mechanical stabilities as well as superior high-temperature oxidation resistance in both isothermal and cyclic conditions [7,8,10–12].

Typically, AlCoCrFeNi HEA alloys and coatings show a BCC phase containing a solid solution of metallic compositions. Therefore, interesting mechanical properties, as well
as encouraging oxidation resistance, have been reported for this type of HEAs [13–16]. Most of the recent investigations indicated that the Al-Cr-Fe-Co-Ni alloying system has outstanding properties for use in the industrial sectors against mechanical, chemical and thermal attacks.

From another point of view, HEA coatings can be successfully used due to the limitations of the production of bulk or as-cast HEA parts. It was previously reported that various types of thermal spraying deposition processes (particularly plasma and high-velocity thermal spaying) are useful for the deposition of different types of HEA coatings on different kinds of substrates [17–20]. Among them, atmospheric plasma spraying (APS) is an advantageous technique for applying the HEA coatings on engineering parts and critical sections of industrial equipment [7,14]. The isothermal and cyclic oxidation resistance of AlCrFeCoNi HEA alloys and coatings is mainly related to its capability to form a dense, continuous and slow-growing oxide scale when exposed to a high-temperature environment (particularly temperatures greater than 1000 °C) [10,11,21].

Currently, the APS process is introduced for nanocrystalline coatings using micro-sized powder particles by mechanical milling. It is one of the advanced methods to produce nanocrystalline powder particles by using the ball milling process. The milled particles become fractured, resulting in the formation of the nano-crystalline structure. In addition, nanocrystalline powder particles possess excellent properties compared to conventional counterparts, such as strength, elastic modulus, microhardness, ductility, thermal conductivity, wear resistance, corrosion and oxidation resistance [7,14].

When the nanocrystalline form of the AlCrFeCoNi HEA is used as a feedstock powder, the thermal properties of the AlCrFeCoNi HEA coating were accordingly improved. The agglomerates of the HEA nanopowders formed from the conventional sized HEA powder were used for depositing nanocrystalline HEA coatings. Only limited works are available on the study of nanocrystalline HEA coatings taken from blends and milled AlCrFeCoNi HEA powder [17,22,23].

Generally, one of the outstanding applications of high entropy alloys and their coatings is the protection of industrial at high-temperature service. Indeed, thermal attacks may happen in both isothermal and cyclic states. In recent years, there have been several studies on the isothermal oxidation behavior of different variations of Al-Co-Cr-Fe-Ni HEAs deposited by different methods of thermal spraying deposition [24,25]. However, there are not yet detailed studies on oxidation properties on these types of alloys and coatings under cyclic conditions.

Therefore, the present work aimed at the analysis of the structural characteristics and cyclic oxidation properties of APS sprayed microcrystalline and nanocrystalline AlCrFeCoNi HEA coatings under the air atmosphere at 1100 °C to enhance the performance and stability of the future generations of gas turbine and jet engine components. For this purpose, AlCrFeCoNi HEA feedstock powder with a nanocrystalline structure was synthesized using the high-energy ball-milling method.

In addition, conventional microcrystalline and nanocrystalline AlCrFeCoNi HEA coatings were deposited via the APS deposition process. The microstructural characteristics, phase composition porosity content, microhardness values as well as cyclic oxidation behavior of the micro- and nanocrystalline coatings at 1100 °C were evaluated. Finally, the comparative structure and composition of the oxide scale formed on both micro- and nanocrystalline coatings were also analyzed by means of FESEM, XPS, XRD and EDS tests. The oxidation kinetics under cyclic conditions for both cases of micro- and nanocrystalline coatings were accordingly investigated.

2. Materials and Methods

2.1. Base Material and Coating Powder

The raw elemental Al, Cr, Fe, Co and Ni powders (with purity of 99.5% and particle mean particle size of 10 µm) with equimolar composition (20 wt.%) were milled using a high-energy ball milling process to obtain microcrystalline and nanocrystalline AlCrFeCoNi
HEA powders. The blended powders in equimolar proportions were then processed using dry-ball milling. The milling atmosphere was controlled using an Ar gas purge into the milling cups. Hardened and chrome-plated steel bowls and balls were used.

Two durations of 5 and 25 h under 300 rpm were used to obtain homogenous microcrystalline and nanocrystalline HEA powders, respectively. All as-milled powders were then sieved individually to achieve −75 to +15 μm of particle size distribution suitable as powder feedstock for the APS deposition. Furthermore, the Inconel 718 superalloy was chosen as the base material for deposition of the micro- and nanocrystalline HEA coatings, which is the most preferred choice for the hot section of gas turbine engine components and other structural applications, as it works in high temperature, aggressive environments and has excellent mechanical properties and high-temperature phase stability. The chemical composition of Inconel 718 is listed in Table 1.

Table 1. Chemical composition of the commercial Inconel 738 used as the substrate for APS deposition of HEA coatings.

| Element | Percentage (wt.%) |
|---------|-------------------|
| Ni      | 52.3              |
| Cr      | 19.0              |
| Fe      | 18.5              |
| Ta      | 5.1               |
| Mo      | 3.1               |
| Al      | 0.5               |
| Ti      | 0.9               |
| Si      | 0.2               |
| Mn      | 0.2               |
| Cu      | 0.5               |

2.2. Development of Microcrystalline and Nanocrystalline HEA Coatings

AlCrFeCoNi HEA coating samples were deposited using a conventional air plasma spraying system that employed argon (Ar) as the primary plasma gas and hydrogen (H2) as the secondary gas to increase the overall temperature of the plasma jet. The thickness of the as-sprayed coatings was determined to be between 300 and 350 μm. Table 2 lists the details of the APS operating parameters utilized for the deposition of both types of microcrystalline and nanocrystalline AlCrFeCoNi HEA coatings.

Table 2. APS process operating parameters for the deposition of the micro- and nanocrystalline HEA AlCrFeCoNi coatings.

| Parameter                          | Value  |
|------------------------------------|--------|
| Nozzle type                        | GH     |
| Nozzle size (mm)                   | 6      |
| Primary gas flow / Argon (L/min)   | 65     |
| Secondary gas flow / Hydrogen (L/min) | 3    |
| Powder carrier gas flow / Argon (L/min) | 2    |
| Arc current (A)                    | 700    |
| Arc voltage (V)                    | 58     |
| Spraying angle (°)                 | 90     |
| Number of passes                   | 8      |
| Powder feed rate (g/min)           | 36     |
| Standoff distance (mm)             | 140    |

For this occasion, optimized APS operating parameters were chosen to obtain high-quality HEA coatings according to our previous investigation [26]. As in the case of the adhesion between the APS AlCrFeCoNi HEA coatings and Inconel 718 substrates, the surface morphology (or namely surface roughness) plays a remarkable role. Thus, the bonding of the APS HEA coatings appears to be entirely mechanical in nature. Therefore, before the APS coating process, the superalloy substrate surface was first roughened using manual sandblasting equipment to promote surface activation and hence the average surface roughness (Ra) of 5 μm. In due course, the blasted substrates were then cleaned for 10 min in an ultrasonic cleaning bath containing water and ethanol.
the cleaning process, all samples were accordingly dried in an open-air atmosphere. The twin air jet was utilized backward of the Inconel 718 substrate owing to the prevention of possible thermal effects during the APS spraying deposition.

2.3. Characterization of the HEA Coatings

The cross-sectioned coated and uncoated substrates were cloth polished by various grit emery sheets. Then, the polished substrates were examined by Vickers microhardness tester, X-ray diffraction analysis (XRD) and field emission scanning electron microscope (FESEM) observation equipped with energy dispersive X-ray (EDS) analysis. The porosity in the coating was measured for both microcrystalline and nanocrystalline HEA coatings by inverted transmitted-light metallurgical microscope (motorized version).

To ascertain the amount of porosity (in %), the measurement was taken at various places on the optical micrograph, which is taken from coated sample and analyzed using an image analysis software (Image-J NIMH Corporation, version 1.22, USA). On this occasion, at least five structural images with the same magnification (1000×) were captured for the image analyzing technique for all cases of microcrystalline and nanocrystalline HEA coatings.

The microhardness measurement was conducted on the coated samples via a Vickers micro-indentation hardness tester based on ASTM E92 (X’pert, Phillips, Amsterdam, The Netherlands). The test conditions are: the applied load 200 g, angle of 136° with an approach velocity of 5–60 µm/s and 15 s dwell time. The XRD profiles for the scale and powders at different milling times were conducted using the X-ray Diffractometer (Micromet-1, Buehler, USA), which was operated at an accelerating voltage 35 kV and acceleration current of 20 mA with a scan rate of 40/min and scanning range of 10 to 80 degrees (2θ) using Cu-Kα source (λ = 1.54056 Å).

The peaks of the detected phases were successfully identified by comparison of the given diffraction pattern to a known standard from the International Centre for Diffraction Data’s Powder Diffraction File (ICDD-PDF). FESEM (FESEM, MIRA3-TESCAN, Czech Republic) with EDS (EDS, INCA, Oxford Instruments, Oxfordshire, UK) was also used to characterize the cross-sectional morphology, surface morphology and X-ray mapping of the coatings. The porosity and average microhardness value of the microcrystalline and nanocrystalline HEA coating are presented in Table 3.

Table 3. Percentage of porosity (%) and microhardness (in HV) of the APS deposited HEA AlCrFe-CoNi coatings.

| Structural Mode   | Porosity (%) | Microhardness (HV 200) |
|-------------------|--------------|------------------------|
| Microcrystalline  | 1.3          | 542 ± 19               |
| Nanocrystalline   | 1.6          | 492 ± 12               |

2.4. High-Temperature Oxidation Study under Cyclic Conditions

The study of the cyclic oxidation behavior of the uncoated superalloy, as well as microcrystalline and nanocrystalline AlCrFeCoNi HEA, coated samples was conducted for 50 h/cycles at a temperature of 1100 °C in air. Each cycle includes 1 h of heating followed by 20 min of cooling at room temperature. Initially, the substrate weight was measured by an electronic scale that has an accuracy of 10^{-3} g. In the first cycle, the three samples were put within the ceramic container and placed inside the furnace, and the heating time was counted. After 1 h of heating, the samples along with crucibles were taken out from the furnace and allowed to cool for 20 min. Then, the heated samples were weighed separately and the weight gain value was accordingly noted. In the second cycle, the samples in the crucibles were again placed inside the muffle furnace, and the above-mentioned processes of 1 h heating, 20 min of cooling and weight measurement were repeated.

The same procedure was repeated for all 50 cycles. After each cycle of study, the samples were weighed and specific weight changes of the coated specimens, that is difference
3. Results and Discussion
3.1. Characterization of the Nanocrystalline HEA Powder

Figure 1 indicates the morphological structure of the micro- and nanocrystalline AlCrFeCoNi HEA powders obtained using FESEM observations, which were prepared after 5 and 25 h of the ball-milling process. According to Figure 1a, the initial milling process leads to the development of a relatively homogenous microcrystalline AlCrFeCoNi HEA powder consisting of numerous agglomerates. In this case, the average size of the fine particles was measured at about 42 \( \mu \text{m} \) using ImageJ analysis.

![Figure 1. FESEM morphology of (a) microcrystalline AlCrFeCoNi HEA powder and (b) nanocrystalline AlCrFeCoNi HEA powder.](image)

By elongating the ball milling duration to obtained powders with a finer structure, the average size of ultrafine particles in an agglomerate was substantially reduced to 185 nm (Figure 1b). For a deeper understanding, Figure 2 shows the bright-field (BF) TEM images of the nanocrystalline AlCrFeCoNi HEA powder synthesized after 25 h of the ball-milling process. As can be observed from the nanocrystalline powder (Figure 2a), each powder particle represents a fine structural morphology and also consists of numerous agglomerated and deformed micro-scaled metallic AlCrFeCoNi alloy particles.

![Figure 2. TEM morphology of the nanocrystalline AlCrFeCoNi HEA powder (a) and selected area electron diffraction pattern of diffraction spots (b).](image)
In conformity with the corresponding selective area diffraction (SAD) pattern shown in Figure 2b, the detected diffraction rings were indexed as major crystallographic planes, which represented a nanostructured solid solution phase. In another point of view, the presence of nanoparticles in the 25 h milled powder was confirmed by the bright spots coinciding with the rings, and the nano-scaled structure was proven by the sharp rings in the corresponding SAD pattern [12,22,27,28].

Figure 3 shows the elemental weight percentage of the conventional and nanocrystalline HEA AlCrFeCoNi powders obtained by atomic absorption spectroscopy (AAS) prepared by milling process. According to the AAS results, the overall percentage of oxygen in the as-milled nanocrystalline AlCrFeCoNi HEA powders was significantly increased in comparison with the microcrystalline HEA powder.

Additionally, for the examined AAS results for the nanocrystalline AlCrFeCoNi HEA powder prepared by the ball milling process, due to a slight impurity of the Ar used for the milling process, the powder mixture was partially oxidized, and therefore the oxygen content was partially increased (up to 2.5%). Additionally, the sensible amount of Fe for the nanocrystalline AlCrFeCoNi HEA powder mixture is mainly associated with its partial iron contamination during balls/powders/walls collisions. A similar alloying composition and oxygen intake were also obtained in our previous investigation [26,29].

3.2. Characterization of the Nanocrystalline HEA Coating

The cross-sectional FESEM micrograph of the microcrystalline and nanocrystalline AlCrFeCoNi HEA coating on IN718 superalloy substrate is shown in Figure 4a,b, respectively. As can be seen, Figure 4a shows the structure of the solid coating with a lamellar morphology with the presence of the structural pores, microporosities and oxide stringers formed as dark contrast spots near the boundary of the substrate and the coating layer.

The average thickness of the as-sprayed microcrystalline AlCrFeCoNi HEA coating was found at about 200 μm, which was measured from its FESEM micrograph (Figure 4a) and for the nanocrystalline AlCrFeCoNi HEA coating, the average coating thickness was measured about ~250 μm. Thus, it is clear that the coating (Figure 4b) formed from the nanocrystalline AlCrFeCoNi HEA powder has higher amounts of microporosities and oxide stringers compared with the microcrystalline one.
AlCrFeCoNi HEAs developed by the controlled atmosphere casting, spark plasma sintering (with 1.6% porosity), its microhardness was comparably higher than that of the as-sprayed powders, the BCC (B2) structure was a major detected phase. Similar phase composition powder coatings showed a diffraction pattern with similar intensities of peaks. The results particles and residual stress [32]. For this study, the as-sprayed nanocrystalline AlCrFeCoNi coating. Additionally, compared to the measured microhardness of the microcrystalline Al-CrFeCoNi HEA coating (492 ± 12 HV), according to Table 3, the average microhardness of the nanocrystalline coating was found to be higher (542 ± 19 HV). Despite higher amounts of structural pores in the as-sprayed nanocrystalline AlCrFeCoNi HEA coating (with 1.6% porosity), its microhardness was comparably higher than that of the as-sprayed microcrystalline AlCrFeCoNi HEA coating (with 1.3% porosity)—the same as reported by Jiang et al. [23] and Ghadami et al. [29–31] for similar cases of nanostructured Ni-based coatings applied by other methods of the thermal spraying process.

Generally, the microhardness of APS HEA coatings is mostly affected by parameters, such as the grain size, grain boundary volume fraction, porosity/oxide content, unmelted particles and residual stress [32]. For this study, the as-sprayed nanocrystalline AlCrFeCoNi HEA coating obtained from 25 h milled powder feedstock exhibited about ~10% increase in microhardness value as compared with the corresponding microcrystalline HEA coating obtained from 5 h milled powder. This increase is mainly associated with the higher volume fraction of grain boundaries and lower grain size of the nanocrystalline HEA coating [12,32].

The XRD profile of the microcrystalline and nanocrystalline AlCrFeCoNi HEA powders and their developed coatings are illustrated in Figure 5. According to the XRD results, the diffraction pattern of the as-sprayed micro- and nanocrystalline AlCrFeCoNi HEA powder coatings showed a diffraction pattern with similar intensities of peaks. The results also indicated that, for both types of the micro- and nanocrystalline HEA powders obtained from 5 and 25 h of the milling process, no major phase-transformation occurred during both the high-energy mechanical milling and APS deposition processes.

Additionally, for both cases of the micro- and nanocrystalline AlCrFeCoNi HEA powders, the BCC (B2) structure was a major detected phase. Similar phase composition also was reported in the investigation performed by Lobel et al. for different kinds of AlCrFeCoNi HEAs developed by the controlled atmosphere casting, spark plasma sintering and arc-melting process [17,18]. In addition, for both cases of as-sprayed micro- and
nanocrystalline AlCrFeCoNi HEA coatings, a major BCC (B2) phase and a minor FCC (A1) peaks were detected after the XRD test.

![XRD pattern for micro- and nanocrystalline AlCrFeCoNi HEA powder](image)

**Figure 5.** (a,b) XRD pattern for micro- and nanocrystalline AlCrFeCoNi HEA powder, (c,d) for as-sprayed micro- and nanocrystalline AlCrFeCoNi HEA coatings obtained from milled 5 and 25 h powder feedstock, respectively.

In addition, for the nanocrystalline HEA coating, it almost appeared that the relative intensity of the detected chemically ordered FCC (A1) phase was comparably lower than the as-sprayed microcrystalline coating. This is mainly associated with the partial stabilization of the BCC (B2) phase after 25 h of the high-energy ball milling process due to the increment of plastic deformation of powder particles caused by ball-particle collisions. Indeed, for the nanocrystalline AlCrFeCoNi HEA coating, Al causes to stabilize the primary solid solution BCC phase into the microstructure of HEA coatings [6].

Other individual metallic elements can effect on the major phase evolution of as-sprayed AlCrFeCoNi HEA coatings. In this regard, Ang et al. [3] indicated that metallic elements, such as Al, Cr and Fe tend to favor the progression of BCC phase growth, whereas Co and Ni tend to stabilize the secondary FCC phase in the coating. Nonetheless, regarding to the peak broadening around 46.5° and 59° of 2θ for both nanocrystalline powder (25 h milled) and nanocrystalline as-sprayed coating, the formation and development of the amorphous (or maybe an ultrafine-grained structure) phases in the APS coating structure possibly attributed to the ultra-high rate of solidification process of the partially-melted HEA particles during coating build-up on the substrate’s surface.

Similar results representing the existence of the amorphous phase on thermally-sprayed coatings were also obtained elsewhere [19,20]. In another point of view, due to an intense crash between the ball and the powder mixture during the high-energy ball milling process, the overall amount of dislocations, distortions and severe plastic deformation can increase. Subsequently, with an increment of the amount of plastic deformation, the lattice parameters and the grain size of the powders and their developed coatings were accordingly decreased [19].
3.3. Oxidation Behavior of the Nanocrystalline HEA Coating

Figure 6 depicts the XRD pattern of the oxidation test of microcrystalline and nanocrystalline AlCrFeCoNi HEA coating exposed at 1100 °C after 50 cycles. NiO (or CoO), Al₂O₃, NiAl₂O₄ oxides as well as metallic solid solution BCC phase were detected as the primary phases for the micro- and nanocrystalline coatings. Whereas, for the nanocrystalline coating, the amount of Al₂O₃ was higher than that of the microcrystalline coating. Conversely, for the nanocrystalline HEA coating, the amounts of other NiO, CoO oxides together with NiAl₂O₄ (or CoAl₂O₄) spinels were lower than for the microcrystalline coating due to the tendency of the formation of dense and adherent alumina oxide scale on the coating surface after 50 cycles [6,12].

![Figure 6. XRD patterns for AlCrFeCoNi HEA coating after 50 cycles of oxidation at 1100 °C: (a) microcrystalline coating and (b) nanocrystalline coating.](image)

Figure 7 indicates the XPS spectra taken from the surface of the oxidized micro- and nanocrystalline AlCrFeCoNi HEA coatings after 50 cycles of the oxidation process at 1100 °C. According to the XPS findings, in the uppermost layer of both oxidized micro- and nanocrystalline AlCrFeCoNi HEA coatings, oxygen (O1s) and a stronger peak of carbon (C1s) caused from the residue gases, such as CO, CO₂ and O₂, in the oxidation chamber after 50 cycles. Additionally, oxygen can also be adsorbed into the coating surface to grow alumina (Al₂O₃) oxide spots. Apparently, a relatively higher amount of intensity for O1s traces for the nanocrystalline AlCrFeCoNi HEA (Figure 7b) indicated that the value of adherent oxide scale, such as alumina formed on the oxidized coating surface, was greater than that of the microcrystalline AlCrFeCoNi HEA coating (Figure 7a). Indeed, the high-energy ball milling process to develop nanocrystalline powder feedstock caused increases in C, N and O impurities in the powder mixture after 25 h.

Regarding the results of microcrystalline AlCrFeCoNi HEA coating (Figure 7a), we concluded that relatively fast-growing oxides (such as major NiO, CoO and Al₂O₃ oxides as well as minor amounts of FeO, Fe₂O₃ and Cr₂O₃, due to their instability at temperatures above 950 °C) can easily form after 50 cycles of the oxidation compared with nanocrystalline AlCrFeCoNi HEA coating. For instance, the high-resolution spectra of Ni2p for both cases types of micro- and nanocrystalline coatings mostly belong to the NiO monoxide component.
Figure 7. XPS results (survey peaks as well as high-resolution spectra of C1s, O1s, Ni2p, Cr2p and Al2p peaks) of the surface of the AlCrFeCoNi HEA coating after 50 cycles of the oxidation at 1100 °C: (a) microcrystalline coating and (b) nanocrystalline coating.

Additionally, the overall intensity of Ni-ions (referred to as Ni$^{2+}$) in the oxidized microcrystalline coating is comparably greater than the nanocrystalline one. In contrast, for
the microcrystalline AlCrFeCoNi HEA coating, the relative intensity for high-resolution spectra of Al2p (referred to as the alumina oxide component) is almost higher than that of nanocrystalline coating, which indicates a greater growth rate of the alumina oxide scale in the microcrystalline coating after 50 cycles of the oxidation at 100 °C.

Minor Al2p spectra may indicate the formation of NiAl2O4 and CoAl2O4 spinels in the oxide layer. As a consequence, after 50 cycles of the high-temperature oxidation process, a uniform and protective alumina layer can form due to its number of oxide spots on the surface (see Al2p trace for the oxidized nanocrystalline coating in Figure 7b). Among them, the alumina scale is more adherent and slow-growing due to its higher thermal stability, greater melting and lower Gibbs free energy compared to other types of oxides. The formation of a uniform and thin alumina layer can promote a lower oxide growth rate and higher cyclic oxidation resistance by controlling the oxygen interdiffusion from the surface into the coating with a nanoscaled structure [29].

Figure 8 displays the mass change per unit area against the number of cycles for the micro- and nanocrystalline AlCrFeCoNi HEA coatings subjected to the high-temperature exposure at 1100 °C up to 50 cycles. For all cases of the oxidized coatings, the cyclic oxidation process can be divided into two major stages, corresponding to stage 1 with a high-rate oxidation behavior and stage 2 with the steady-state (stable) oxidation behavior with continues to the formation of oxide scale cracking process in higher cycles of the oxidation. In the first stages, both micro- and nanocrystalline HEA coatings were directly exposed to the air atmosphere and subjected to oxidation at a relatively high rate, causing the drastic increase in their mass gain (about 2.1 and 1.0 mg/cm² for micro- and nanocrystalline coatings, respectively).

In addition, according to Figure 8, in the initial high-rate oxidation and the beginning of steady-state oxidation, both kinds of micro- and nanocrystalline HEA coatings indicated a parabolic rate behavior up to 20–25 cycles at 1100 °C. Regarding the fitting curves for both coatings (indicated as red dash lines), the power of equation fitting curves (n) for the oxidized micro- and nanocrystalline coatings were n = 0.52 and n = 0.47, respectively. The proximity of n to 0.5 can indicate the parabolic oxidation behavior of the coatings [33].
Nonetheless, the value of oxidation rate constant \( (K_p) \) (which can be obtained from the typical oxidation kinetics formula: \( \Delta W_A = K_p^{1/2} + C \) [29,33], where \( K_p \) is the parabolic rate constant, \( \Delta W_A \) is the weight gain per unit area and \( C \) is a constant) is minimal \( (K_p = 4.29 \times 10^{-12} \text{ g cm}^{-2} \text{s}^{-4}) \) for the nanocrystalline AlCrFeCoNi HEA coating compared with the microcrystalline AlCrFeCoNi HEA \( (K_p = 2.88 \times 10^{-11} \text{ g cm}^{-2} \text{s}^{-4}) \). The obtained finding indicated that a relatively higher cyclic oxidation resistance under air atmosphere at 1100 °C was attained for the nanocrystalline AlCrFeCoNi HEA coating deposited by the APS technique.

During the cyclic oxidation process, for both cases of the HEA coatings, a relatively thin oxide scale can be formed on the AlCrFeCoNi HEA surface and can act as an oxidative diffusion barrier, resulting in the lower mass gain and prolonging its formation. As can be observed, the higher rate oxidation stage (stage 1) for the microcrystalline HEA coating lasts for 25 cycles, which is almost longer than that of the nanocrystalline HEA coatings (20 cycles).

Moreover, the relative weight gain of the nanocrystalline coatings after 50 cycles is relatively reduced by ~58% when compared with that of the microcrystalline \( (1.81 \text{ mg/cm}^2 \) for the microcrystalline and 0.75 mg/cm² for the nanocrystalline coating). The obtained findings also revealed that the dense and adherent oxide scale (particularly the alumina oxide scale with higher thermodynamic stability) was easily formed on the surface nanocrystalline AlCrFeCoNi HEA coating and demonstrated higher cyclic oxidation resistance compared to the conventional microcrystalline AlCrFeCoNi HEA coating.

According to the cross-sectional image micrographs taken from the micro- and nanocrystalline AlCrFeCoNi HEA coatings after 50 cycles of the oxidation at 1100 °C, (Figure 9a,b, respectively), the average thickness of the oxide scale in the microcrystalline coating was relatively higher than that nanocrystalline coating (~4.1 μm for microcrystalline coating vs. ~2.6 μm for nanocrystalline coating). Moreover, as can be observed from both cases of the oxidized micro- and nanocrystalline coatings, the area percentage of internal oxidation regions for the oxidized nanostructured HEA coating as relatively greater than the as-sprayed microcrystalline HEA coating.

This finding is mainly attributed to the formation of ultra-fine (nanoscaled) structure and precipitation of higher amounts of microporosities as well as the higher volume fraction of grain boundaries for the nanocrystalline HEA coating. The localized EDS results of the oxidized coating after 50 cycles of oxidation at 1100 °C are listed in Table 4. According to the EDS results from the oxide layer (spot A), the comparative chemical composition (wt.%) of the oxide layer consisted of the Ni, Co, Al metallic oxide, consisting of NiO/CoO monoxides and NiAl₂O₄/CoAl₂O₄ spinels together with a relatively dense Al₂O₃ scale was detected in interior layers for both micro- and nanocrystalline AlCrFeCoNi HEA coatings.

Gradually, during the cyclic oxidation process at 1100 °C, Fe and Cr-based oxides and spinels (such as Cr₂O₃, Fe₂O₃ oxides together with NiCr₂O₄, CoCr₂O₄, NiFe₂O₄, CoFe₂O₄ spinels) are almost unstable, due to their tendency to decompose and evaporate at temperatures higher than 950 °C. Furthermore, despite the metallic solid solution phase in the coating structure with a bright contrast (spot B: consisting of Ni, Co, Fe, Cr and Al elements), the formation and development of internal oxidation regions (spot C) were also detected for the oxidized coatings after 50 cycles of the oxidation at 1100 °C.

### Table 4.
The localized elemental percentage (wt.%) obtained by the EDS results for the selected regions marked in the oxidized micro- and nanocrystalline coatings (indexed in Figure 9a,b).

| Indexed Region | Al   | Cr   | Fe   | Co   | Ni   | O   |
|----------------|------|------|------|------|------|-----|
| A              | 16.2 | 12.5 | 13.8 | 11.2 | 9.5  | 36.8|
| B              | 19.9 | 21.5 | 19.3 | 18.3 | 19.8 | 1.2 |
| C              | 16.2 | 16.8 | 18.2 | 15.6 | 17.3 | 15.9|

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**Note:**

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Figure 9. Cross-sectional FESEM micrographs of the oxidized (a) microcrystalline and (b) nanocrystalline AlCrFeCoNi HEA coatings after 50 cycles of the cyclic oxidation process at 1100 °C.

As mentioned elsewhere [34], the high-energy mechanical milling process can synthesize AlCrFeCoNi HEA powder feedstock suitable for APS deposition with an agglomerated morphology composed of numerous fine particles with a nanocrystalline structure. The nanocrystalline HEA powder is susceptible to absorbing a higher volume of oxygen from the atmosphere during the in-flight situation in the APS process compared to the conventional HEA powder with a microcrystalline structure. In fact, the higher amounts of atomic oxygen were maintained in the metallic solid solution BCC phase for the nanocrystalline AlCrFeCoNi HEA coating [35,36].

Therefore, a higher volume fraction of the internal oxides was detected for the oxidized nanocrystalline coating after 50 cycles owing to the reaction of soluble O and metallic Al, Cr, Fe, Co and Ni into the coating cyclic exposure at 1100 °C [37,38]. Among these, the volume fraction of the structural porosity is an important factor in the formation and development of the internal oxidation and oxide scale growth for the AlCrFeCoNi HEA coatings [16,32,39].

For the case of the nanocrystalline coating, under cyclic oxidation, the structural porosity (1.6%) can promote the oxygen interdiffusion into the coating structure to form internal oxidation at the first stage of cyclic oxidation. Conversely, the higher volume fraction of structural grain boundaries in the nanocrystalline HEA coating together with the formation of internal oxidation regions may prevent metallic diffusion and metallic ion consumption to the layers adjacent to the surface [34]. Therefore, the cyclic oxidation resistance of the nanocrystalline AlCrFeCoNi HEA coating increases by the formation of adherent and slow-growing alumina oxide layer after 50 cycles at 1100 °C.
4. Summary and Conclusions

In this study, micro- and nanocrystalline AlCrFeCoNi HEA powders and coatings were successfully prepared using high-energy mechanical milling and APS spraying techniques. The microstructural properties and high-temperature cyclic oxidation behavior of the micro- and nanocrystalline AlCrFeCoNi HEA coatings were then studied in detail. Both as-sprayed micro- and nanocrystalline coatings indicated a typical lamellar microstructure, including interlamellar microporosities and scattered oxide phases. For cases of micro- and nanocrystalline HEA coatings, major BCC (B2) and minor FCC (A1) phases were detected in their microstructure.

Nonetheless, the amount of the FCC (A1) phase was lower for the nanocrystalline coatings due to the partial stabilization of BCC (B2) caused by plastic deformation during the milling process. With respect to the obtained results, we concluded that the nanocrystalline AlCrFeCoNi HEA coating had a higher cyclic oxidation resistance at 1100 °C after 50 cycles in comparison with the microcrystalline coating. The main causes of this outstanding oxidation enhancement could be associated with the formation of thin, protective and slow-growing alumina oxide scale on the surface of the nanocrystalline coating during the initial cycles at 1100 °C.

The lifecycle of the next generations of high-temperature turbine and aero-engine components mainly depends on the quality and development of a protective oxide scale formed on HEA coatings in the air at an elevated temperature. In this case, the Al₂O₃, NiO and CoO oxides as well as their spinels phase were thermodynamically stable at high temperatures under isothermal or cyclic conditions. Among these, the alumina scale was more adherent and slow-growing due to its higher thermal stability, greater melting and lower Gibbs free energy compared to other types of oxides.

The formation of solid scale for nanocrystalline AlCrFeCoNi HEA acts as a diffusion barrier that increases the high-temperature oxidation resistance. The rate of reaction is faster at an early stage because the oxygen and the metallic elements are close to each other. However, after a while, the scale becomes thicker, continuous and more stable; therefore, the diffusion of these elements becomes difficult, and the mass gain of the specimen decreases in high thermal cycles.

The development of oxide scale generally shows a parabolic dependence with time, and its durability depends on the concentration of the scale-forming element in the coating material, temperature, oxidizing conditions and alloy microstructure. Therefore, the AlCrFeCoNi HEA nanocrystalline coating may apply against high-temperature corrosion and oxidation attacks in harsh environments for the hot section in the next generation of gas turbine and aero-engines in the future.

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