Assessment of CrFeCoNi and AlCrFeCoNi High-Entropy Alloys as Bond Coats for Thermal Barrier Coatings

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Abstract High-entropy alloys (HEAs) represent a relatively new group of multicomponent alloys that have shown great potential for applications requiring tribological and oxidation resistant properties. Consequently, thermally sprayed coatings of different HEA chemistries have received increasing research attention. In this paper, atomized equimolar CrFeCoNi and AlCrFeCoNi feedstocks were used for high velocity air-fuel spraying (HVAF) to produce overlay coatings using two different nozzle configurations. The microstructure, phase constitution and hardness of the coatings were analyzed along with the primary aim of testing the coatings for their oxidation behavior. The performance of the two HEA chemistries was compared with two commercial MCrAlY coatings that are well-established bond coat materials for thermal barrier coatings (TBCs). An investigation was conducted to test the coatings’ performance as bond coats by applying suspension plasma sprayed yttria-stabilized zirconia top coats and evaluating the thermal cycling behavior of the TBCs.

The AlCrFeCoNi-coating was found to demonstrate a lower oxidation rate than the CrFeCoNi-coating. However, the AlCrFeCoNi-coating was found to form more rapid oxide scales compared with the commercial bond coat material that also contained reactive elements.

Keywords high velocity air-fuel · high-entropy alloys · isothermal oxidation · plasma spray · thermal barrier coatings

Introduction

Thermal barrier coatings (TBCs) are used on components within hot sections in gas-turbines and jet engines. The reason for the use of TBCs is to achieve greater engine efficiency by increasing the operating temperature according to the Brayton cycle (Ref 1). The coating system mainly consists of a mechanically compliant metallic bond coat and a thermal protective ceramic top coat. Process routes such as atmospheric plasma spray (APS), suspension plasma spray (SPS) and electron-beam physical vapor deposition (EB-PVD) are employed for depositing TBC top coats (Ref 2). Both APS and EB-PVD has been used extensively for making TBCs and are the main coating methods for top coats (Ref 3). EB-PVD can deposit columnar-structured coatings which have the advantage over APS for thermal cyclic compliance (thermal expansion and contraction), but deposition rate is lower, and cost of equipment and production is higher (Ref 4, 5). SPS is a more recent thermal spray method which can combine the advantages of both APS and EB-PVD because of its ability to produce columnar-structured coatings with a higher deposition rate and greater thermal protection at a lower cost than EB-PVD (Ref 3).
Thermal spray techniques such as high velocity oxy-fuel (HVOF) and high velocity air-fuel (HVAF) are employed to deposit metallic TBC bond coats (Ref 6, 7). The more recent introduction of HVAF is of particular interest for bond coat deposition. Coatings produced with HVAF have a denser microstructure and includes less oxides compared to HVOF (Ref 8, 9). A dense microstructure can better protect the coated component from degradation during oxidation and keep its integrity from further harmful oxide nucleation and growth that can occur around porosities (Ref 10). HVAF’s relatively low operating temperature and use of air instead of pure oxygen as oxidizing gas for combustion, also mitigates the risk of in-flight oxidation and evaporation of metallic feedstock. This ensures that the desired material composition is retained in the deposited coatings and decreases further harmful oxidation (Ref 11).

Established materials used to form TBC bond coats are the MCrAlY-alloys (M = nickel and/or cobalt) (Ref 12). These alloys are highly resistant to oxidation, mainly due to their aluminum content which forms a slow-growing oxide scale that protects the coating metal and base material from further oxidation and degradation (Ref 13). The reactive element yttrium is incorporated in minor quantities and causes columnar grains in alumina oxide scales (Ref 14). Yttrium may improve the adhesion of the oxide scale and can also inhibit aluminum outward diffusion in the bulk of the alumina TGO. By inhibiting aluminum diffusion in the TGO, the diffusion path for oxygen increases inwards through the oxide grains, which means yttrium can decrease the growth rate of alumina scales (Ref 15). Other reactive alloying elements like silicon forms SiO₂ subscales which can prevent formation of nickel or iron oxides and helping in stabilizing the Al₂O₃ formation. Hafnium can improve the adhesive properties of oxide scales but if added too much, they can lower the diffusion rates of chromium and aluminum which can have a destructive effect at elevated temperatures (Ref 13).

High-entropy alloys (HEA) is a relatively new category of alloy materials. These alloy systems consist of multiple principal elements, typically five or more, in equimolar or near equimolar ratios (Ref 16). Some HEAs have shown promising oxidation resistant properties (Ref 17, 18) and therefore it is of interest to explore their possible use as bond coats in TBC systems. Many published studies regarding HEA have a base configuration of CrFeCoNi with additional elements that may give similar properties compared with established alloy materials and are usually added in five or more equimolar composition (Ref 19). Going back to the MCrAIY material, adding Al may improve oxidation resistance in the CrFeCoNi base system. But other elements like chromium, titanium and silicon may also improve oxidation resistance (Ref 20). A few experimental studies have been made with AlCrFeCoNi-coatings deposited by plasma spray, HVOF and cold spray where the coating’s oxidation behavior was also studied (Ref 20-24). It was also reported that in-flight oxidation (IFO) for mechanically alloyed AlCrFeCoNi occurred during the hotter plasma spray process which significantly reduced the aluminum content in the coating (Ref 25). Furthermore, corrosion behavior of AlCrFeCoNi has been investigated both in the form of bulk materials (Ref 26, 27) and HVAF-sprayed coatings (Ref 9). In general, it can be said that AlCrFeCoNi-coatings show good oxidation behavior, good wear and promising corrosion properties with a high degree of hardness. A more recent study with HVOF and APS was done using Al₃₀Si₂Cr₂₃Co₂₂Ni₂₃ HEA and it was found that the coating deployed by HVOF had a lower oxidation rate compared with MCrAIY coatings when comparing the MCrAIY results to another study (Ref 28). Adding titanium to AlCrFeCoNi has shown in previous work to give favorable oxidation behavior (Ref 19). A study using Al₁₀Si₅Ti₂Cr₅Fe₂₀Co₂₀Ni and Al₁₀Si₁₀Fe₀₂₀Co₁₀Ni as bond coat was performed to make a comparison to commercial MCrAIY materials (Ref 29). The study revealed that the HEA compositions were comparable in thermal cyclic fatigue (TCF) tests but the Al₁₀Si₅Ti₂Cr₅Fe₂₀Co₁₀Ni, lasted around 70 cycles less than Al₁₀Si₁₀Fe₀₂₀Co₁₀Ni. The lifetime of the MCrAIY candidate showed to last significantly longer.

Oxidation behavior of HVAF-deposited AlCrFeCoNi and CrFeCoNi HEA coatings as bond coats for TBCs has not been reported yet. The objective of this work was to combine the HVAF’s favorable dense and low-oxide capabilities with AlCoFeCoNi promising high-temperature oxidation resistance with added comparison of the base four-component system CrFeCoNi. In this study, two pairs of HVAF-sprayed HEA overlay coatings were investigated. Intergas atomized equimolar solid solution CrFeCoNi and AlCrFeCoNi powder feedstocks were used as coating material. Each material was deposited using two different nozzle configurations for the HVAF-system. The coatings were tested for their oxidation behavior with additional hardness tests also being conducted. The results were compared with commercial MCrAIY coatings deposited by HVAF and APS. Moreover, the HEA coatings were tested as bond coats in a TBC configuration where the top coat was a columnar yttria-stabilized zirconia (YSZ) layer deposited using SPS. The aim with this research was to assess if these HEA materials have potential in high-temperature applications either as bond coats for TBCs where oxidation resistance is needed, or as stand-alone oxidation protection coatings. The assessment was done by comparing them with established commercial alternatives in various tests.
Experimental Procedure

Six sets of samples with metallic coatings were produced by HVAF spraying for isothermal oxidation and hardness tests. Additional five sets of TBC samples were produced with a columnar SPS YSZ top coat for thermal cycle fatigue (TCF) lifetime test and a thermal cycle oxidation test.

Sample Preparation

The two atomized HEA powders were supplied by Chemnitz University of Technology, Germany, with elements in equal molar ratio. The reference powders were commercial MCrAlY materials, AMDRY 386 by Oerlikon Metco, Switzerland and AMPERIT 410.860 by Höganäs AB, Sweden. The commercial powders were gas atomized and their chemical composition and particle size range can be seen in Table 1. All powders used for HVAF spraying had particles with spheroidal morphology. The top coat feedstock for the additional TBC-study was a commercial 25 wt.% solid load 8YSZ suspension from Treibacher Industrie AG, Austria, with a particle size d_{50} of around 500 nm suspended in ethanol. The solid particles in the suspension were fused and crushed and had an irregular morphology.

The coating materials were deposited on button shaped HASTELLOY® X coupons as substrates, commercially acquired from Siemens Energy AG, Sweden. The coupons were 6 mm thick and 25.4 mm in diameter. The coatings were deposited by HVAF using an M3 supersonic spray gun (Uniquecoat Technologies LLC, USA), except for AMPERIT 410.860 feedstock which was deposited by APS, see the sample nomenclature in Table 2. The coupons were cleaned with ethanol and then mounted on a rotating fixture fastened to a turntable. Prior to the coating process, the substrates were hot-grit-blasted with alumina particles to a surface roughness of Ra ≈ 3 µm. The HEA coatings were deposited with HVAF parameters that are listed in Table 3. Two different de Laval nozzles were used during HVAF spraying, designated 4L4C and 5L4C, of same divergence and with exit diameter of 22.5 and 25.8 mm, respectively. The nozzles had different lengths of 25 cm and 30 cm for 4L4C and 5L4C, respectively. The APS-410 samples were deposited using Oerlikon Metco F4 parameters for APS based on a detailed study of different F4 parameters that can be found in (Ref 30). The top coat for the TBC-study was of columnar type deposited by SPS with the Axial III spray gun (Northwest Mettech Corp., Canada) using parameters listed in Table 4. The APS-410 coating was not sprayed with a top coat.

Topography Analysis

Surface roughness of the metallic coatings in as-sprayed condition was examined using a Profilm 3D profilometer with white light interferometry (WLI) along with accompanying software (Filmetrics Inc, USA). A total of ten measurements per sample were taken at different locations. The data were post-processed using a 5 x 5 Gaussian spatial filter. Multiple top-view images were taken by scanning electron microscopy (SEM) using a Hitachi TM3000 Tabletop SEM, (Hitachi Ltd, Japan). Additionally, an inbuilt Bruker Quantax 70 electron dispersive spectroscopy (EDS) detector (Bruker Corp., USA) was used for elemental analysis.

Metallographic Preparation

All TBC samples for cross-sectional analysis went through a multi-step metallographic preparation routine based on the ASTM 1920-03 standard (Ref31). The procedure involved cold mounting prior to sample sectioning. A second cold mounting was done for handling purpose followed by a multi-step polishing procedure to a roughness of Ra ≈ 0.05 µm.

Isothermal Oxidation Test

The isothermal oxidation test was conducted in ambient air at a temperature of 1000 °C in a programmable automatic Entech ECF 14/16 furnace (Entech Energiek AB, Sweden). The coated 25 mm in diameter samples were sectioned into four pieces, ultrasonically cleaned in ethanol and dried. One of each coating was placed in cleaned ceramic crucibles, then weighed five times using a PCE AB-100 precision scale (PCE-Instruments GmbH, Germany). The samples were placed in ceramic crucibles to

Table 1 Feedstock powders used in this study.

| Powder name     | Powder size range [µm] | Chemical composition [at.%] |
|-----------------|------------------------|-----------------------------|
|                 |                        | Ni  | Co  | Cr  | Fe  | Al  | Y   | Si  | Hf  |
| CoCrFeNi        | −20 +7                 | 25  | 25  | 25  | 25  | ... | ... | ... | ... |
| AlCoCrFeNi      | −33 +15                | 20  | 20  | 20  | 20  | 20  | ... | ... | ... |
| AMDRY 386       | −63 +5                 | Bal.| 19.2| 16.9| ... | 23.2| 0.3 | 0.7 | 0.1 |
| AMPERIT-410.860 | −45 +22                | Bal.| 19.7| 16.5| ... | 23.3| 0.3 | ... | ... |
capture potentially flaked-off oxide scales during the test. After the test, the samples were allowed to cool down in ambient environment, then the samples with crucible were again weighed. The test was repeated for each duration of 10 min, 1, 10, 20 and 50 h with a new set of samples. The weight difference [mg] of each sample was then divided by the whole sample surface area (substrate + coating area) [cm²].

### Phase Analysis

X-ray diffraction (XRD) was performed on the surface of the oxidized samples. The instrument used was a D8 Discover (Bruker Corp., USA) using Co-Kα-radiation with line focus in Bragg-Brentano geometry. A variable slit (10 mm measured length) and a LynxEye XE-T detector.

### Lifetime Test and Heat Treatment

The TCF test was conducted in the same automatic furnace as for the isothermal oxidation test. Three TBC samples of each different bond coat were placed on a platform with coating side up, giving a total of 15 samples tested. The samples were isothermally heated in air to 1100 °C in the pre-heated furnace for 1 h then cooled down by blowing compressed air for 10 min to about 100 °C, then went back in the furnace. The coating spallation is checked by a digital overview camera. The failure criteria were a 20% top coat spallation. Following the TCF test, one of each TBC samples was tested for 25 cycles to analyze how the TGO had grown in the initial stages.

### Hardness Test

A Vickers hardness test was performed on one specimen per coating according to the ASTM E384 standard (Ref 32). The indentation load applied was 200 g and the location for the indents were at the center of the coating cross section with a total of ten indents were done. The indentation device used was an HMV-2T Vickers micro hardness tester (Shimadzu Corporation, Japan).

### Results and Discussion

This study is motivated by the desire to evaluate the utility of the HVAF-sprayed HEA coatings as (1) stand-alone oxidation resistant coatings and (2) as bond coats for TBCs. Therefore, the following results and discussion reflect upon these assessments.
As-sprayed Coating Analysis: Topography

Top-view images of the as-sprayed coatings can be seen in Fig. 1. The topography has a similar microstructure comprising a combination of plastically deformed ‘splat’ and partially deformed particles on all HVAF-coatings whereas the APS-coating appears to have surface features of molten splats. Larger partially deformed particles can be seen in all coatings to a certain degree, although these are barely present on the APS-coating, indicated by the arrows. These partially deformed particles (or unmolten particles as can be said for the APS-coating), exist because they do not sufficient plastic deform or melt upon impact to form a splat (Ref 33). Since the gas temperature during HVAF spraying is significantly lower than in APS, particles may only partially melt at most and, therefore, there is a relatively greater presence of partially deformed particles (Ref 34).

According to surface roughness measurements summarized in Table 5, minor differences existed between the two parameters used for depositing the HEA coatings. The AF-386 has a notably coarser microstructure due to the larger partially deformed particles. The surface roughness is known to influence column formation during SPS deposition of ceramic coatings for which some of these coated samples were subsequently used (Ref 35). Columnar formation can occur on a polished surface provided that changes in surface peaks are significantly higher than the submicron YSZ droplet diameters which could be for example 1 μm or even less (Ref 35, 36). The APS-410 coating was not subjected to surface measurements since it was not coated with a SPS YSZ top coat.

Fig. 1 Topographic view of the coatings as-sprayed. The arrows indicate some of the undeformed particles. (a-b) H1(P1/P2), (c-d) H2(P1/P2), (e) AF-386 and (f) APS-410
As-sprayed Coating Analysis: Microstructure

The HVAF-sprayed coating microstructure cross section is seen in Fig. 2. The HVAF-coatings have a densely packed microstructure with few visible oxide inclusions. When focusing on the H1-coatings, differences between the H1P1 and H1P2 microstructures can be seen where H1P1 has undergone a greater degree of oxidation where the oxide stringers appear thicker in the microstructure marked by A. Black globular pores marked by B are present in the coatings. The variations in particle temperatures and velocities between the different nozzles were not measured but have been reported that greater thermal input and particle velocity is achieved with a longer nozzle (Ref 37, 38). It appears that a longer nozzle produced a denser coating with thinner oxide stringers. Some in-flight oxidation (IFO) may have occurred in both coatings. How readily the feedstock oxidizes is mainly dictated by the material chemistry and particle size distribution (Ref 39, 40). Traces of Al are present in the H1-coatings as confirmed by EDS, Table 6 and correlates well with the EDS analysis performed on the feedstock. This low amount

Table 5 Arithmetic mean height \([Sa]\) area roughness accompanied with the standard deviation. Values are in length unit \(\mu m\)

|     | H1P1 | H1P2 | H2P1 | H2P2 | AF-386 |
|-----|------|------|------|------|--------|
| \([Sa]\) | 4.9±0.9 | 4.1±0.8 | 5.0±1.2 | 4.7±0.7 | 6.5±0.5 |

Fig. 2 Microstructure of the metallic coatings, (a-b) H1(P1/P2), (c-d) H2(P1/P2), (e) AF-386 and (f) APS-410. A is oxide stringers at interlamellar splat regions, B is globular pores, C is Ni-rich matrix, D is Ni-Al-rich phase, E is molten region and F is partially deformed/unmolten particles.
of Al would not be enough to form any significant oxide scale of alumina and can, therefore, be ignored (Ref 13).

In the H2-coatings, a microstructure with a two-phase structure is seen as depicted in Fig. 2(c-d) where the brighter phases are marked C and darker phases are marked D. A similar microstructure is found in the literature where it was further noted that as-sprayed, the coating retained a harder bcc structure (Ref 41). Phase marked D have visual resemblance to the Ni-Al-rich \( \beta \)-phase which is found in earlier studies by Brandl et al. (Ref 42). With different parameters P1 and P2 employed for depositing the H2-coatings, no difference in microstructure was observed. Little to no oxide formation in the interlamellar regions can be found visually or by EDS. The coating chemistry is more resistant to oxidation due to the presence of Al. The average particle size in the H2 feedstock is \( d_{50} \) 24 \( \mu \)m compared with \( d_{50} \) 13 \( \mu \)m for H1. This could further affect IFO or evaporation during the spray process where larger particles are less susceptible (Ref 40).

The distinct phases of C and D are equally distributed in the AF-386 microstructure. The Ni-Al-rich phases of dark and bright contrasts seem to be dominant in the unmolten or partially deformed particles/areas marked by F in Fig. 2(e), suggesting it represents the retained microstructure of the feedstock material. It can therefore be said that the feedstock material is unchanged by the HVAF-spray process. The APS-coating had lamellar splats with occasional occurrence of unmolten particles. The splats are formed by molten droplets that splash onto the surface (Ref 43). The unmolten particles result from either inadequate melting or re-solidification of material in-flight. Due to a lower spray velocity compared to HVAF, splat formation is more dependent on the thermal input by the APS-system. The APS-coating exhibits different phases in the microstructure marked by C, D and E, where E appears to be a metastable phase formed after particle melting and quenching upon impact. Due to melting of the material and its subsequent rapid solidification, the metastable phase exists because phases of equilibrium would not have the time to form (Ref 44). The microstructure of APS-410 is more porous than the other coatings with larger interlamellar splat regions, oxide stringers A and globular pores B.

Furthermore according to Table 6, no significant difference in composition between the as-sprayed coatings and the delivered feedstock is seen. The EDS data come from three scans, 2000x, 4000x and 5000x of magnification at random locations. The Al content is about 1-2 at.% less in the coating than in the powder, where H2P2 (corresponding to the ‘hotter’ spray parameters) had a lower Al content. This might be attributable to slight evaporation of Al in the spray process, although this is difficult to confirm.

In Fig. 3, the columnar microstructure of the top coat can be seen. Two observations can be noted here, (I), the column width varies due to roughness of the underlying bond coat, influenced by the presence of partially deformed particles on the bond coat surface. (II), the H2-coatings have some delamination at the splat interfaces near the top coat/bond coat interface. This delamination is most likely a metallographic artifact because it was not observed on the as-sprayed samples. Furthermore, delamination was not observed during TCF test for the as-sprayed samples by the overview camera.

### Isothermal Oxidation Test

The results from the isothermal oxidation test can be seen in Fig. 4 after exposure at 1000 °C. The oxide scales seemed to retain their adherence and no visible spallation was observed in all cases. All coatings performed well in this test when considering them as stand-alone oxidation resistant coatings because of their declined oxidation rate. The rate of oxidation is plotted as mass increase per sample area. Therefore, the plotted values give a comparison

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**Table 6** EDS analysis on the composition of the coatings compared with the feedstock

| Coating/ feedstock | EDS-measured chemical composition [at.%] |
|--------------------|------------------------------------------|
| Ni     | Co     | Cr     | Fe     | Al     | Y      | Si     | Hf     | O      |
| H1P1   | 23.7   | 25.2   | 24.6   | 24.8   | 0.6    | ...    | ...    | 1.2    |
| H1P2   | 23.6   | 25.0   | 25.2   | 25.0   | 0.5    | ...    | ...    | 0.8    |
| H1-feedstock | 24.1   | 25.9   | 24.7   | 25.2   | 0.1    | ...    | ...    | ...    |
| H2P1   | 20.1   | 21.9   | 19.9   | 21.5   | 16.0   | ...    | ...    | 0.1    |
| H2P2   | 20.7   | 22.1   | 19.9   | 21.9   | 15.3   | ...    | ...    | 0.2    |
| H2-feedstock | 20.7   | 21.8   | 19.0   | 21.1   | 17.3   | ...    | ...    | ...    |
| AF-386 | 40.5   | 19.4   | 18.0   | ...    | 20.1   | 0.8    | 1.1    | 0.1    |
| AMDRY 386.0 | 40.7   | 19.2   | 16.4   | ...    | 22.5   | 0.3    | 0.8    | 0.2    |
| APS-410 | 35.7   | 18.2   | 14.6   | ...    | 21.8   | 0.3    | ...    | 9.5    |
| AMPERIT-410.860 | 40.9   | 20.3   | 16.5   | ...    | 22.0   | 0.2    | ...    | ...    |
between the samples as a group and should not been taken as absolute values for the coatings.

After 1 h of oxidation, APS-410 showed the highest mass increase per surface area. If the coating has a lower density, then a higher degree of oxygen diffusion is possible, leading to a greater initial oxidation before a continuous protective oxide film has formed (Ref 13). When comparing the SEM images of the coating microstructure in Fig. 2, the APS-410 had a higher degree of porosity and as-sprayed oxidation compared with the HVAF samples, which can explain its higher initial oxidation. The commercial AF-386 showed the lowest rate of oxidation after 1 h which can be due to its dense and oxide-free microstructure. Moreover, the AF-386 had a refined coating chemistry containing reactive elements like Si, Y and Hf that improve scale adhesion and integrity. However, comparing the AF-386 to the H2-samples the difference is 0.02 mg/cm² at most which can be seen as a minor difference and therefore, the initial oxidation behavior is more attributed to the HVAF-process than the chemistry.

Between the HEA samples, the H2-samples showed most favorable oxidation resistance in the initial stage which can be due to the high levels of Al that may prevent rapid oxidation. The higher rate of initial mass increase for all samples could be explained by the fact that no continuous protective oxide film has been formed at this early stage, thereby enabling oxygen to diffuse into the coating more easily to interlamellar boundaries and/or interconnected pores (Ref 45, 46). It can be seen as example in Fig. 5 of H1P1 after 1 h where the TGO thickness is not uniform. In
a study by Zhang et al. (Ref 47), MCrAlY coatings sprayed with HVAF were tested for oxidation at a temperature of 1000 °C. It was observed in the study that, after 1 h of exposure, a full coverage of oxide scale had formed on the as-sprayed coating surface.

Up to 10 h of oxidation, the trend seems to change for the APS-410 sample which appear to decrease in its oxidation rate compared with the H1-samples. This behavior can be explained by that the choice of thermal spray method or surface conditions can have significant impact on the initial oxidation behavior of the coating. The importance of the material choice becomes more apparent after some time when and if a protective oxide layer has formed, in this case probably after 10 h. The HEA samples seem to increase in oxidation rate at around 10 h compared to the commercial candidates. The H2-samples have a relatively low oxidation rate compared with the H1 which can only be attributed by its content of Al. The H1-samples increase in mass is becoming greater than the APS-410 despite its high Al content which must be due to the presence content of Y in APS-410. The AF-386 continues to have a relatively low oxidation rate compared with the other samples which may again be attributed to its refined chemistry.

After 20 h, all samples seem to notably decrease in oxidation rate due to formation of a thicker continuous TGO. Relatively little differences could be seen between

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**Fig. 4 Results from the isothermal oxidation test.** The error bars indicate the standard deviation.
the different parameters for the HEA samples, i.e., P1 and P2.

In Fig. 6, the EDS results from the oxidation test are plotted where the scans were done on coating surface and performed on samples for 10 min, 1 h, 10 h and 50 h of oxidation. The oxidation characteristics for HVAF parameters P1 and P2 were observed to be similar and therefore not shown here. EDS analysis reveals that the H1-coatings form a chromium-rich oxide. Cr is more apparent on the surface already after 10 min with a notably high level of oxygen, suggesting an outward diffusion of Cr that would react with O₂. A lower level of Ni is seen in all cases. Ni is suppressed in favor of Cr or Al because of its easy diffusion in γ-phase (Ref 47). The oxidation reaction becomes more stable at 10 h because of the lower inward diffusion of oxygen due to the thickening of the oxide film with time.

**XRD-Measurements**

The results from the XRD analysis of samples H1P1 (10 min, 1 h, 20 h), H1P2 (20 h), H2P1 (10 min, 1 h, 20 h), H2P2 (20 h), AF-386 (20 h) and APS-410 (20 h) are seen in Fig. 7. The diffraction patterns are on the oxide evolution from 10 min of oxidation to 1 h and 20 h. Due to similarities between the coatings, the coatings deposited with short nozzle configuration were analyzed for how the oxidation evolved and compared with the long nozzle configuration after 20 h. For all the HEA coatings, major peaks (revealing high crystallinity) were identified to be fcc, ferrite (Fe). After 10 min of oxidation, minor peaks of θ-alumina were detected along with some nickel-chromium oxides. θ-alumina were also detected after 30 min of oxidation in a previous study with HVAF-sprayed MCrAlY coatings under similar oxidation conditions (Ref 47). After 1 h, additional minor peaks of Fe(NiFe₀·₈Cr₀·₂)O₄ trevorite, chromium oxides along with spinel-(Ni, Fe, Al) and corundum chromium oxides were detected. Minor θ-alumina were present after 1 h of oxidation. After 20 h of oxidation, no traces of ferrite could be seen but instead austenitic phases and magnetite. It is difficult to tell from surface measurements if Al-oxides (α-alumina in particular) were present but most likely at a greater depth below the surface, but this could not be verified with XRD from surface measurements. No apparent differences were detected between P1 and P2 after 20 h of oxidation. The diffraction pattern observed for AF-386 after 20 h reveal similarities to the HEA coatings. Although no Fe is present in AF-386 according to EDS, peaks similar to austenitic Fe compounds could be detected however, these can also be identified as a CrNi with a slight shift from α = 3.57 Å to α = 3.59 Å. A shift in lattice parameters could be due to introduction of residual stresses with the oxide growth (Ref 50). Eskolaite chromium oxides and cobalt oxides was also detected in AF-386 after 20 h. APS-410 after 20 h had phases of CrNi present and additional Al-oxides (corundum), NiO Co₂AlO₄ and (Al₀·₇Cr₀·₃)Co.

Before a continuous TGO is eventually formed, multiple oxides may form initially including spinel oxides which were observed in Fig. 7(b). These oxides grow more rapidly compared to alumina and are the main reason for rapid increase in weight at early stage of the oxidation. Therefore, the oxidation rates determined during the early
stages may not be representative and perhaps misleading until a stable, protective TGO has fully formed (Ref 13). A rapid growth of oxides during and after initial stages is undesirable. It can be said that the H2-coatings show promising oxidation resistant behavior, but the chemistry would need further improvements like adding reactive elements to reduce TGO growth rate and possibly change its microstructure.
Thermal Cycle Fatigue Test

The results from the TCF test can be seen in Fig. 8 and mainly focuses on the coatings fit for use as bond coats in a TBC-system. The TBC’s of H1-coatings had the shortest lifetime of the tested samples. No apparent differences in lifetime can be seen between H1P1 and H1P2. The H2-coatings had a 44-65 % higher lifetime compared with the H1-coatings. Since the spray parameters were the same between the coating materials, it can be said that including Al in the chemistry was the primary reason for the longer lifetime. However, based on these results alone, it is not clear how much Al would be needed. The H2P2, had by a larger margin the longest TCF lifetime between the HEA coatings but could also have to do with greater statistical variation of failure for these coatings. The reference coating, AF-386 had the longest lifetime compared with the HEA coatings of around 50 % higher than H2P2. The feedstock used for AF-386 coating had roughly the same amount of Al as the H2, it can then be said that further increasing Al may not increase the H2-coatings TCF lifetime. AMDRY 386 has a different chemistry containing reactive elements like Si, Y and Hf. These elements can
cause different oxidation behavior as mentioned in the introduction and inhibit the diffusion of Al in the TGO along with enhancing its integrity (Ref 13).

When further studying the TBC microstructures after failure in TCF in Fig. 9, several distinct features can be seen. Starting with the reference coating AF-386, a continuous TGO layer can be seen mainly of alumina, supported by EDS analysis (Fig. 10) and similar study in the literature (Ref 51). A closer inspection of the TGO reveals multiple cracks within the oxide layer and near the top coat/bond coat interface. The continuous growth of the TGO ultimately led to spallation of the top coat. Due to the differences in thermal expansion, stresses are introduced continuously in the TGO which leads to fatigue cracks that channels further heat and oxygen to the bond coat, contributing to TGO growth (Ref 51). This form of failure is the most common and has been documented in multiple past studies (Ref 4, 35, 52). Certain widening of columnar gaps can be seen when observing the top coat which has according to previous research been attributed to either sintering of the YSZ coating or rumpling effect because of opening/closing of column gaps during thermal cycling (Ref 51, 53). The bond coat chemistry is however of greater importance (Ref 33) and in this case, the top coat is sprayed with the same parameters for all TBCs. The overview camera used for analyzing spallation did not reveal any delamination of the top coat at early stage for all samples and no significant differences of the top coat/bond coat interface could be observed despite the delamination observed of the H2-samples after metallographic preparation of the as-sprayed samples.

Fig. 9 Microstructures of TBC’s after TCF test (a) H1P1, (b) H1P2, (c) H2P1, (d) H2P2, (e) AF-386 and (f) AF-386 TGO.
In the central area of the AF-386 bond coat, the characteristic Ni-Al β-phase can be seen which is the reservoir of Al in the coating. When studying the H1-coating, using EDS, clear oxide formations of Cr-oxide scales can be seen growing at the top coat/bond coat interface. Failure most likely occurred due to a too rapid growth of the TGO and/or lack of the TGO adhesion to the top coat/bond coat which led to top coat delamination (Ref 54). The H2-coatings had a microstructure similar to AF-386. A similar Ni-Al-rich band can be seen at the central area of the bond coat just like on AF-386. The brighter areas between the darker regions contain more Cr and Fe with reduced content of Ni and Al.

While further studying the H2-coatings after the TCF test, a complex diffusion zone has been formed at the bond coat/substrate interface which can be seen in the magnified images in Fig. 11(a-c) where a second TGO has formed. Below the Ni-Al band of the bond coat, a region of dark globular Al precipitates has formed. A closer look at one of these globular precipitates can be seen in Fig. 11(d). According to EDS analysis, these precipitates mainly consist of Al with some secondary N. It is not clear if these are aluminum nitrides but a compound of Al and N. The Ni-Al band had a clear depletion or segregation from Al with a depletion zone between the band and the precipitates. A TGO layer of mainly chromium oxide has been formed. The Cr-oxide have some Mn imbedded that has probably migrated from the substrate. Further Al-oxide has been formed surrounding the Cr-oxide which can be seen by the darker regions. White carbon-rich areas, possibly a form of carbides, are formed at locations within the TGO-zone. At the interface between the different oxide scales are regions with a higher concentration of Si and W which have diffused there from the substrate. Al-oxides are also formed in the substrate which can be seen in Fig. 11(c). The Al-oxide surrounds a region of Cr-oxide with some Mn imbedded and white C-rich regions.

A closer inspection of the substrate and the interdiffusion region of H2P2 in Fig. 12 reveals black needle-like formations that are rich in Al with a notable high amount of N and seem to be located around white phases and follow their orientation. The white phases have a relatively high concentration of Mo, S and Mn. Closer to the TGO layer at the bond coat/substrate interface are some gray phases that are rich in Cr. Similar studies show that these secondary white phase regions contain a higher concentration of Mo and Si compared to the matrix (Ref 55). However, more Si in these regions was not detected by EDS. Some darker regions with similar size and morphology as the white phase regions can be seen which contains higher amount of Cr and Ni.

In recent literature by Gawel et al., this microstructure can be found in HEA with lower Al content (Ref 56). However, in that study, arc-melted bulk material of the HEA that had been cut in 1.5 mm thick plates was studied. No coating was applied onto a superalloy substrate, and these microstructure features of dark rectangular/needle-like Al precipitates were found directly under the surface layer of TGO that consisted mainly of Cr2O3. In similar studies to Gawel et al. (Ref 57, 58), these precipitates could be found but the authors declared them as AlN. Similar AlN precipitates was observed for Anupam et al. (Ref 59) in which also it was concluded that decreasing the Al content or Cr content somewhat led to a decrease in
oxidation rates. Some N were indeed found at in these precipitates according to EDS.

**Heat Treatment**

If the growth rate of the TGO was high, it could be an indicator that the coating lifetime in the TCF test was shortened by this mechanism. A cyclic heat treatment test can further reveal initial oxidation behavior and the progression of oxide growth. The heat treatment after 25-thermal cycles of oxidation showed similar oxide formation and growth rates between the H1-coatings. A continuous Cr-oxide TGO layer had formed along the top coat/bond coat interface (Fig. 13). The thickness of this layer was around 10 μm at certain places, similar to the corresponding TCF samples which means oxidation occurs rapidly in early stage at isothermal heating. The H2-coatings had a TGO layer of a thin continuous Al-oxide. The H2P1 had about 1 μm thicker layer of TGO compared to H2P2 suggesting a lower oxidation rate for H2P2. AF-386 had a thinner TGO compared with the H2-coatings of around 2-3 μm. This means that the TGO formation occurs at a lower rate for the AF-386 coating. Delamination can be seen between the top coat and bond coat for H2P1 which may again be attributed to metallographic preparation and oxide pullouts since no delamination was observed with the overview camera. The oxide scale itself may have poor adhesive properties, Y and Hf are added in commercial MCrAlY materials to improve the integrity of the oxide scale (Ref 13). The lack of these elements is most likely a major reason behind the HEA coatings earlier failure in TCF test. Both the H2 and AF-386 coatings are having some regions with Cr-oxide formations close to the top coat, indicating that these oxides form first but are later overtaken by the more thermodynamically stable, alumina oxide scale formation.
The results from the Vickers hardness test can be viewed in Fig. 14. The as-sprayed samples were here compared with the 25-heat cycle tested samples. The heat-treated samples have a lower hardness value compared to the as-sprayed. A heat treatment may cause relaxation of compressive stresses that occurs in the HVAF-coating and causing an overall softer state that could lead to a lower hardness value (Ref 60, 61). Grain boundaries may grow larger during heat treatment and that may also contribute to the softening of the material (Ref 39).

The hardness values between the coating pairs of different spray parameters are similar. The hardness values of
H2 are higher compared with H1 due to harder Ni-Al-rich bcc-phase and seem to coincide well with the literature (Ref 41). The hardness values for the HVAF-sprayed coatings seem to have increased compared to the arc-melted bulk material that was 160HV0.5 for H1 and 540HV0.5 for H2 according to measurements conducted at Chemnitz University of Technology. But due to different loads for these tests, it is not an accurate comparison. Typically, lower load will give higher hardness results. The differences in hardness compared to bulk material could be due to two main reasons; (I) the inert gas atomization process that produces the powder where the atomized droplets experience a rapid cooling rate (Ref 62). A rapid cooling rate would lead to relatively small grains in the feedstock microstructure and therefore increase material hardness (Ref 39). (II), the HVAF does not completely melt the feedstock but soften it then as the particles hits the substrate, plastic deformation is introducing a work hardening effect followed by rapid cooling (Ref 39, 62). This suggests that partial oxide formation, work hardening due to plastic deformation and compressive stresses are causing significant changes in hardness.

The AF-386 had a hardness value of around 550 HV0.2 which was slightly lower than the H2-coatings. Finally, the APS-coating had the lowest hardness value which can be attributed to its higher level of porosity due to lower particle velocity and lower compressive residual stresses. In general, a higher hardness of the bond coat could be disadvantageous for TBC lifetime since it is less effective in absorbing stresses that occurs during thermal expansions, a more ductile material is desired. The hardness of the H2-coatings was the highest however, it may not be an issue since it was shown to drop at a comparable level of AF-386 after heat treatment.

Conclusions

In this study, HEA materials comprising equimolar compositions of CrFeCoNi and AlCrFeCoNi were HVAF-sprayed employing two distinct nozzle configurations. The resulting coatings were comprehensively investigated to assess their utility as stand-alone oxidation resistant layers and as bond coats for TBCs.

HVAF spraying can successfully deposit the HEA powder feedstocks with little to no element loss of the chemical composition or IFO. No significant differences between the coatings produced by different nozzles were observed. The HVAF produced coatings with more favorable oxidation behavior compared with APS. The HVAF-coatings had a lower initial oxide formation compared to the APS-coating.

The CrFeCoNi HEA may not be suitable as bond coat material for TBCs due to its relatively high oxidation rate compared with commercial material. However, the AlCrFeCoNi HEA used in this study show great promise of being able to be used as a bond coat material for TBCs but only with alloying modifications. The authors believe that by fine tuning with reactive elements like Y, Hf and Si, oxidation behavior at elevated temperatures can be significantly improved and perhaps surpass the performance of established MCrAlY materials. Further research in alloy composition is therefore recommended for the AlCrFeCoNi HEA.

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References

1. N.P. Padture, M. Gell and E.H. Jordan, Thermal Barrier Coatings for Gas-Turbine Engine Applications, Science, 2002, 296(5566), p 280-284.
2. R.A. Miller, Thermal Barrier Coatings for Aircraft Engines: History and Directions, JTST, 1997, 6(1), p 35-42.
3. S. Mahade, R. Li, N. Curry, S. Björklund, N. Markocsan and P. Nylén, Isothermal Oxidation Behavior of Gd 2 Zr 2 O 7 /YSZ Multilayered Thermal Barrier Coatings, Int. J. Appl. Ceram. Technol., 2016, 13(3), p 443-450.
4. N. Curry, K. VanEvery, T. Snyder and N. Markocsan, Thermal Conductivity Analysis and Lifetime Testing of Suspension Plasma-Sprayed Thermal Barrier Coatings, Coatings, 2014, 4(3), p 630-650.
5. A. Feuerstein, J. Knapp, T. Taylor, A. Ashary, A. Bolcavage and N. Hitchman, Technical and Economical Aspects of Current Thermal Barrier Coating Systems for Gas Turbine Engines by Thermal Spray and EBPVD: A Review, J Therm Spray Tech, 2008, 17(2), p 199-213.
6. H.-J. Jang, D.-H. Park, Y.-G. Jung, J.-C. Jang, S.-C. Choi and U. Paik, Mechanical Characterization and Thermal Behavior of HVOF-Sprayed Bond Coat in Thermal Barrier Coatings (TBCs), Surf. Coat. Technol., 2006, 200(14-15), p 4355-4362.
7. G.-J. Yang, X.-D. Xiang, L.-K. Xing, D.-J. Li, C.-J. Li and C.-X. Li, Isothermal Oxidation Behavior of NiCoCrAlTaY Coating
Deposited by High Velocity Air-Fuel Spraying, *J Therm Spray Tech*, 2012, **21**(3-4), p 391-399.

8. D.L.-M. Berger and D.S. Matthews, Potential von HVAF-Spritzprozessen Potential of HVAF Spray Processes, n.d., p 5.

9. M. Löbel, T. Lindner, T. Mehner, L.-M. Rymer, T. Lampke, S. Björklund, and S. Joshi, Microstructure and Corrosion Properties of AlCrFeCoNi High-Entropy Alloy Coatings Prepared by HVAF and HVOF, n.d., p 6.

10. J. Lu, H. Zhang, Y. Chen, X. Zhao, F. Guo and P. Xiao, Effect of Microstructure of a NiCoCrAlY Coating Fabricated by High-Velocity Air Fuel on the Isothermal Oxidation, *Corros. Sci.*, 2019, **159**, p 108126.

11. F. Tang, L. Ajdelsztajn, G.E. Kim, V. Provenzano and J.M. Schoenung, Effects of Surface Oxidation during HVOF Processing on the Primary Stage Oxidation of a CoNiCrAlY Coating, *Surf. Coat. Technol.*, 2004, **185**(2-3), p 228-233.

12. C.T. Sims, N.S. Stoloff and W.C. Hagel, *Protective Coatings, Superalloys II*, Wiley, New York, 1987.

13. C.T. Sims, N.S. Stoloff and W.C. Hagel, *High-Temperature Oxidation, Superalloys II*, Wiley, New York, 1987.

14. B.A. Pint, Experimental Observations in Support of the Dynamic-Segregation Theory to Explain the Reactive-Element Effect, *Oxid Met*, 1996, **45**(1-2), p 1-37.

15. F.A. Golightly, F.H. Stott and G.C. Wood, The Influence of Yttrium Additions on the Oxide-Scale Adhesion to an Iron-Chromium-Aluminium Alloy, *Oxid Met*, 1976, **10**(3), p 163-187.

16. J.-W. Yeh, Alloy Design Strategies and Future Trends in High-Entropy Alloys, *JOM*, 2013, **65**(12), p 1759-1771.

17. J.-W. Yeh, S.-K. Chen, S.-J. Lin, J.-Y. Gan, T.-S. Chin, T.-T. Shun, C.-H. Tsau and S.-Y. Chang, Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes, *Adv. Eng. Mater.*, 2004, **6**(5), p 299-303.

18. P.-K. Huang, J.-W. Yeh, T.-T. Shun and S.-K. Chen, Multi-Principal-Element Alloys with Improved Oxidation and Wear Resistance for Thermal Spray Coating, *Adv. Eng. Mater.*, 2004, **6**(12), p 74-78.

19. A. Meghwal, A. Anupam, B.S. Murty, C.C. Berndt, R.S. Kottada and A.S.M. Ang, Thermal Spray High-Entropy Alloy Coatings: A Review, *J. Therm. Spray Tech.*., 2020, **29**(5), p 857-893.

20. D. Lin, N. Zhang, B. He, B. Jin, Y. Zhang, D. Li and F. Dong, Influence of Laser Re-Melting and Vacuum Heat Treatment on Plasma-Sprayed FeCoCrAlY Alloy Coatings, *J. Iron Steel Res.*, 2017, **24**(12), p 1199-1205.

21. K.-C. Cheng, J.-H. Chen, S. Stadler and S.-H. Chen, Properties of Atomized AlCoCrFeNi High-Entropy Alloy Powders and Their Phase-Adjustable Coatings Prepared via Plasma Spray Process, *Appl. Surf. Sci.*, 2019, **478**, p 478-486.

22. M. Srivastava, M. Jadhav, R.P.S. Chethan, C.M. Muniraksh and S. Singh, Synthesis and Properties of High Velocity Oxy-Fuel Sprayed FeCoCrNi2Al High Entropy Alloy Coating, *Surf. Coat. Technol.*, 2019, **378**, p 124950.

23. L. Wang, F. Zhang, S. Yan, G. Yu, J. Chen, J. He and F. Yin, Microstructure Evolution and Mechanical Properties of Atmosphere Plasma Sprayed AlCoCrFeNi High-Entropy Alloy Coatings Under Post-Annealing, *J. Alloys Compd.*, 2021, **827**, p 159607.

24. A. Meghwal, A. Anupam, V. Luzin, C. Schulz, C. Hall, B.S. Murty, R.S. Kottada, C.C. Berndt and A.S.M. Ang, Multiscale Mechanical Performance and Corrosion Behaviour of Plasma Sprayed AlCoCrFeNi High-Entropy Alloy Coatings, *J. Alloys Compd.*, 2021, **854**, p 151740.

25. A.S.M. Ang, C.C. Berndt, M.L. Sesso, A. Anupam, P.S.R.S. Kottada and B.S. Murty, Plasma-Sprayed High Entropy Alloys: Microstructure and Properties of AlCoCrFeNi and MnCoCrFeNi, *Metall. Mat. Trans. A*, 2015, **46**(2), p 791-800.
44. J.R. Davis & Associates and ASM International, Eds., Splat, Handbook of thermal spray technology, (Materials Park, OH), ASM International, 2004, p 47-48.

45. P. Niranatlumpong, C.B. Ponton, and H.E. Evans, The Failure of Protective Oxides on Plasma-Sprayed NiCrAlY Overlay Coatings, n.d., p 18.

46. H. Choi, B. Yoon, H. Kim and C. Lee, Isothermal Oxidation of Air Plasma Spray NiCrAlY Bond Coatings, Surf. Coat. Technol., 2002, 150(2-3), p 297-308.

47. W. Kai, W.L. Jang, R.T. Huang, C.C. Lee, H.H. Hsieh and C.F. Du, Air Oxidation of FeCrNi-Base Equi-Molar Alloys at 800 and 1000°C, Oxid Met, 2005, 63(3-4), p 169-192.

48. X.-X. Yu, M.A. Taylor, J.H. Perepezko and L.D. Marks, Competition between Thermodynamics, Kinetics and Growth Mode in the Early-Stage Oxidation of an Equimolar CoCrFeNi Alloy, Acta Mater., 2020, 196, p 651-659.

49. A. Ganvir, V. Vaidhyanathan, N. Markocsan, M. Gupta, Z. Pala and F. Lukac, Failure Analysis of Thermally Cycled Columnar Thermal Barrier Coatings Produced by High-Velocity-Air Fuel and Axial-Suspension-Plasma Spraying: A Design Perspective, Ceram. Int., 2018, 44(3), p 3161-3172.

50. N. Curry, N. Markocsan, L. Östergren, X.-H. Li and M. Dorfman, Evaluation of the Lifetime and Thermal Conductivity of Dysprosia-Stabilized Thermal Barrier Coating Systems, J Therm Spray Tech, 2013, 22(6), p 864-872.

51. B. Bernard, A. Quet, L. Bianchi, V. Schick, A. Joulia, A. Malié and B. Rémy, Effect of Suspension Plasma-Sprayed YSZ Columnar Microstructure and Bond Coat Surface Preparation on Thermal Barrier Coating Properties, J Therm Spray Tech, 2017, 26(6), p 1025-1037.

52. A.G. Evans, D.R. Clarke and C.G. Levi, The Influence of Oxides on the Performance of Advanced Gas Turbines, J. Eur. Ceram. Soc., 2008, 28(7), p 1405-1419.

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