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Effect of Al content on the oxidation behavior of Y/Hf-doped AlCoCrFeNi high-entropy alloy

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Abstract

In this study, three types of Y/Hf-doped AlCoCrFeNi high-entropy alloys (HEAs) with different Al content were manufactured and their oxidation behavior at 1100 °C was systematically studied. Depending on the Al content, the HEAs show two-phase or triple-phase microstructure. All HEAs exhibit extremely slow oxidation rate and meanwhile the oxidation rate gradually reduces with the increasing Al content resulting from the gradually increasing columnar grain size in the α -Al₂O₃ scale. The extremely low oxidation rate and the strong interfacial bonding make the innovative Y/Hf-doped HEAs to be promising materials for high temperature oxidation resistance.

Keywords: High-entropy alloy; Oxidation; Spallation; Alumina; Aluminum content.

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1. Introduction

Thermal barrier coatings (TBCs) are widely used in the aeroengines or gas-turbine engines to protect the engines components (made of Ni-based superalloy), which enable the engines to be serviced at the temperature of exceeding their melting points [1, 2]. The TBCs typically consist of a thermally insulating yttria-stabilized zirconia (7–8 wt% YSZ) topcoat and an intermediate metallic bond coat (e.g. Pt- or Hf-modified NiAl and NiCoCrAlY) deposited on a Ni-based superalloy substrate. A thermally grown oxide (TGO), mainly α -Al₂O₃, forms between the top coat and the bond coat during high-temperature exposure, which provides oxidation resistance and interface adherence [3, 4]. Failure of the TBCs usually occurs at or near the TGO/bond coat interface, once the interfacial toughness degrades due to the impurities segregation to interface (e.g. S segregation) and the formation of interfacial imperfections with the increasing TGO thickness [5]. Based on the analysis mentioned above, a slowly growing α -Al₂O₃ scale with well adherent interface is crucial to the durability of TBCs.

Recently, it has been clearly demonstrated that reactive elements (REs) Y/Hf doped equal atomic percent AlCoCrFeNi high-entropy alloy (HEA) exhibits a significantly lower oxidation rate compared with that of Y/Hf doped NiCoCrAl alloy [6]. Additionally, the AlCoCrFeNiYHf HEA also shows a strong resistance to oxide scale spallation (no oxide scale spallation after 1000 h oxidation at 1100 °C) [6]. In terms of the slow oxidation rate and the strong spallation resistance of oxide scale, the AlCoCrFeNiYHf HEA might be a potential bond coat material for TBCs or the protective overlay for Ni-based superalloy. It has been also reported in previous works that the different Al content in the AlCoCrFeNi-based HEA leads to the different multi-phase microstructures [7]. As for the multi-phase HEAs, they have attracted constantly increasing attention due to their adjustable mechanical properties achieving by the balance of ductility and strength [8-10].

It is well known that the oxidation behavior of alloys (e.g. Ni-based superalloy) is significantly affected by their microstructures (e.g. phase size and distribution) [11-13]. At present, only limited publications related to the effect of Al content on the oxidation

behavior of AlCoCrFeNi HEA can be found. Butler et al. [14, 15] investigated the oxidation behavior of AlCoCrFeNi HEA with various amount of Al, but the importance of REs to the oxidation performance of an oxidation resistant alloy was ignored in these works and thus these alloys exhibited an inferior oxidation performance. For the typical alumina-forming alloys (e.g. NiAlHf and FeCrAlY), the minor doping of REs (e.g. Y and Hf) in these alloys can change the growth mechanism of oxide scale and significantly improve their oxidation resistance [16, 17].

The objective of this study is to investigate the effect of Al content on the oxidation behavior of AlCoCrFeNi HEA combined with the minor doping of Y and Hf. Three types of samples with different Al content are prepared to understand the Al content effect. All the alloy microstructures (e.g. phase constitutions and distribution), the oxide scale microstructures after early oxidation and long-term oxidation and the oxidation rate are systematically investigated to understand the oxidation mechanism.

2. Materials and method

2.1. Material and sample preparation

Three types of Y/Hf-doped $Al_xCoCrFeNi$ HEAs (x represents mole number) with different Al content were designed, namely the **HEA1** ($Al_{0.7}CoCrFeNi$), **HEA2** ($AlCoCrFeNi$) and **HEA3** ($Al_{1.3}CoCrFeNi$), respectively. The chemical composition of the three as-cast alloys is given in Table 1. The AlCoCrFeNi HEAs were prepared by arc melting high purity (99.99 wt. %) Al, Co, Cr, Fe, Ni, Y and Hf metals under a high-purity argon atmosphere, which were placed on a water-cooled Cu hearth. Every alloy button ingot has a weight of 100 g with an approximate size of 65 mm (diameter) $\times$ 25 mm (height). The alloys were re-melted five times to obtain microstructural homogeneity.

Table 1. Chemical composition (at. %) of three as-cast alloys.

Materials	Element (at. %)						
	Al	Co	Cr	Fe	Ni	Y	Hf
Al _{0.7} CoCrFeNi(HEA1)	14.85	21.28	21.28	21.28	21.28	0.02	0.02
Al _{1.0} CoCrFeNi(HEA2)	19.96	20.00	20.00	20.00	20.00	0.02	0.02
Al _{1.3} CoCrFeNi(HEA3)	24.49	18.87	18.87	18.87	18.87	0.02	0.02

2.2. Isothermal oxidation test

The three types of alloy samples were cut into $10 \times 10 \times 3 \text{ mm}^3$ square plates using a precision cut-off machine (Accutom 5, Struers) equipped with a SiC abrasive cutting blade. All the samples were prepared by grinding with SiC abrasive papers and subsequent polishing using $0.05 \mu\text{m}$ colloidal alumina. The samples were thoroughly cleaned using deionized water and acetone before oxidation. The isothermal oxidation experiment was conducted at 1100°C and the samples were placed in the center of a chamber furnace at laboratory environment for a continuous oxidation time ranging from 1 h to 1000 h. The samples were taken out from the furnace after a required oxidation time. Finally, the samples were air-cooled outside the furnace at room temperature for approximately 10 min.

2.3. Characterization

The phase constitutions of the alloys and oxide scales were collected using X-ray diffraction (XRD, Ultimo IV, Riau, Japan) at 30 kV with Cu $K\alpha$ radiation. The microstructure and chemical composition of the alloys were identified using scanning electron microscopy (SEM, FEI Nova Nano 230, Netherlands) equipped with energy dispersive X-ray spectroscopy (EDS, Oxford Instruments). To further analyze the microstructure and chemical composition of the alloys and oxide scales, thin lamellae from the alloys and the corresponding oxide scales were prepared using a focused ion beam (FIB, GAIA3, Tescan, Czech Republic) and then were analyzed in greater detail using a scanning transmission electron microscope (STEM, TALOS F200X, FEI, USA) fitted with an energy dispersive X-ray spectroscopy (EDS, XIS Ultra DLD, Kratos,

Japan) system. The details of STEM samples preparation were shown elsewhere [11]. The phase constitutions of the alumina in the early oxidation stage were characterized by the photoluminescence piezospectroscopy (PLPS) using a confocal Raman microprobe (LabRAM HR, Horiba Jobin Yvon, France) with a 532 nm Nd:YAG laser. The mixed Gaussian-Lorentzian functions (Labspec software) were employed to fit the recorded spectra and obtain the peak positions.

3. Results

3.1. Effect of Al content on microstructure of as-cast HEAs

Fig. 1 shows the XRD profiles of three types of as-cast HEAs. For the HEA1, the alloy predominantly consists of face-centered cubic (FCC) phase, body-centered cubic (BCC) A2 phase and CsCl structure B2 phase [7]. The HEA2 and HEA3, however, show two-phase structure, comprising A2 and B2 phases.

Fig. 1. XRD results of as-cast HEA1, HEA2 and HEA3.

Fig. 2 shows the surface morphology of three types of as-cast HEAs after etching. The HEA1 shows an elongated grain structure without the formation of any dendrite, suggesting negligible partition of solute elements during solidification. Inside the grains

of HEA1, a large amount of FCC-phase laths (with a width of 0.5 to 2 μm) are formed. In the inter-lath regions, a two-phase, network structure consisting of A2 and B2 phases is identified, which is a characteristic microstructure resulting from spinodal decomposition (Fig. 2d and g). In contrast, HEA2 and HEA3 both show dendritic grain structure (Figs. 2b and c), suggesting partition of solute elements during solidification of the two alloys [7]. High magnification SEM images (Figs. 2h-k) show that the microstructure of HEA2 and HEA3 is similar to that of the inter-lath regions in HEA1, consisting of alternate nanoscale A2 and B2 phases [7, 18]. The size and shape of two phases slightly vary from dendritic (DR) to interdendritic (ID) regions and are different between HEA2 and HEA3.

Fig. 2. Surface morphology of three types of as-cast HEAs: (a, b and c) optical images, giving an overview of the microstructure of the HEA1, HEA2 and HEA3, respectively; (d) low-magnification backscattered SEM image and (g) high-magnification backscattered SEM image over the area within the white rectangle in (d), showing the

grain microstructure of HEA1; (e) low-magnification backscattered SEM image and (h and i) high-magnification backscattered SEM images in (e), showing the grain microstructure in the ID and DR regions of HEA2; (f) low-magnification backscattered SEM image and (j and k) high-magnification backscattered SEM images in (f), showing the grain microstructure in the ID and DR regions of HEA3.

Additionally, the volume fractions of different phases from the three as-cast alloys are summarized in Table 2 based on the SEM images. The amount of B2 phases gradually increases with the increasing Al content. Due to the multi-phase structure, the composition of each phase is fixed by the strict thermodynamic equilibrium and an increased Al content in the HEA will not lead to compositional change of individual phase, but will rather increase the volume fraction of B2 phases [7, 13].

Table 2. Volume fraction of phases from the three as-cast alloys.

Materials	Phases	Volume fraction (vol. %)
HEA1	FCC	66.3
	A2	11.2
	B2	22.5
HEA2	A2	44.3
	B2	56.7
HEA3	A2	32.9
	B2	67.1

TEM analysis of HEA2 is employed as a representation to further investigate the composition and structure of A2 and B2 phases, which is presented in Fig. 3. The continuous matrix (dark contrast) and precipitates (bright contrast) are identified as B2 and A2, respectively, in conjunction with corresponding selected-area diffraction patterns (SADPs) and dark-field (DF) TEM images (Fig. 3c, d and e). These observations agree well with the XRD results presented in Fig. 1. According to the X-ray maps in Fig. 3, the A2 phase is enriched with Fe and Cr and the B2 phase is enriched with Ni and Al, while Co is uniformly distributed in the alloy. Meanwhile, the composition of A2 and B2 determined by quantitative EDS point analysis is summarized in Table 3.

Fig. 3. TEM analysis of HEA2: (a) high-angle annular dark-field (HAADF) STEM image of an ID region with corresponding elemental maps; (b) HAADF STEM image of a DR region with corresponding X-ray maps; (c) selected-area diffraction patterns (SADPs) along the $[0\ 0\ 1]$ zone axis and (d and e) corresponding dark-field (DF) TEM images taken from the diffraction spots marked by yellow and green circles in (c), respectively, showing typical A2 and B2 structure.

Table 3. Chemical composition (at. %) of A2 and B2 phases in the ID and DR regions of HEA2 determined by quantitative STEM-EDS analysis.

HEA2	Phases	Element (at. %)				
		Al	Co	Cr	Fe	Ni
ID	A2	3.9±0.7	19.7±3.1	41.2±4.3	28.1±3.6	7.1±1.7
	B2	30.6±2.4	21.4±3.7	3.7±1.1	12.8±2.5	31.5±4.3
DR	A2	3.8±0.6	18.8±2.3	43.3±4.6	27.4±3.4	6.7±1.7
	B2	30.6±3.1	22.1±4.3	4.1±1.7	11.8±2.7	31.4±4.3

3.2. Growth of oxide scale

3.2.1. Early oxidation

Fig. 4 shows the surface morphology of the oxide scales formed on the three types of HEAs after 5 min oxidation. As shown in Fig. 4a and d, a large amount of spinel develops on the HEA1 apart from Al_2O_3 . Correlation of the surface morphology before and after oxidation shows that the spinel inherits the contour of the underlying FCC phase laths in the HEA1 (Fig. 2g and 4d). This observation suggests that the spinel predominantly grows on the FCC phase. For the HEA2 and HEA3, the oxide scale is

exclusive Al_2O_3 (Fig. 4b and c). In addition, the oxide scale in the DR regions is slightly smoother than that in the ID regions (Fig. 4e, f, g and h). The finer microstructure in the DR regions leads to more uniform Al distribution and thereby the smoother surface morphology of the Al_2O_3 scale (Fig. 2).

Fig. 4. Surface morphology of three types of HEAs after isothermal oxidation at 1100 °C for 5 min: (a) low magnification SEM image of HEA1 and (d) high-magnification SEM image over the area within the white rectangle in (a), showing the microstructure of the oxide scale formed on HEA1; (b and c) low magnification SEM images of HEA2 and HEA3 respectively; (e and f) high magnification SEM images, showing the microstructure of the oxide scale formed in the ID and DR regions on HEA2; (g and h) high magnification SEM images, showing the microstructure of the oxide scale formed in the ID and DR regions on HEA3. (The oxidation experiment of 5 min was performed in a CMTM furnace at 1100 °C for 5 min in the air environment, with a quick heating rate of 200 °C/min and fan-assisted air cooling.)

The formation of $\theta\text{-Al}_2\text{O}_3$ is often found in the Al_2O_3 scale in the early oxidation stage, especially for the REs doped alumina-forming alloys [19-24]. The $\theta\text{-Al}_2\text{O}_3$ might be detrimental to the growth and stability of oxide scale, since the transformation of θ to $\alpha\text{-Al}_2\text{O}_3$ in the early oxidation stage will induce non-negligible volume reduction and tensile stress in the oxide scale [25]. Fig. 5 shows the PLPS spectra of the Al_2O_3 scales

formed on the three types of HEAs. As shown in Fig. 5, only characteristic α -Al₂O₃ double peaks are detected using PLPS spectra in spite of the focused positions [26]. This result indicates that the α -Al₂O₃ has been completely transformed after 5 min oxidation for all HEAs. In conclusion, the α -Al₂O₃ is rapidly established in the early oxidation stage for all HEAs.

Fig. 5. PLPS spectra of the Al₂O₃ scales formed on the three types of HEAs after isothermal oxidation at 1100 °C for 5 min. “ID” and “DR” denote that the PLPS spectra were recorded in the ID and DR regions, respectively.

3.2.2. Long-term oxidation

The XRD results presented in Fig. 6 confirm that the oxide scale formed on the HEA1 consists of α -Al₂O₃ and non-protective spinel ((Co, Ni)(Fe, Al)₂O₄), while α -Al₂O₃ is the primary phase in the oxide scales formed on the HEA2 and HEA3. It should be mentioned that minor HfO₂ and Y₃Al₅O₁₂ are also detected in the oxide scales for all HEAs.

Fig. 6. XRD results of three types of HEAs after isothermal oxidation at 1100 °C for 1000 h.

Fig. 7 shows the surface morphology of the oxide scales formed on the three types of HEAs after 1000 h oxidation. Generally, no spallation of oxide scale can be observed for any HEA after 1000 h oxidation, which indicates a good interfacial bonding at the oxide scale/HEA interface (Fig. 7a, d and g). For the HEA1, the non-protective (Co, Ni)(Fe, Al)₂O₄ with a bright contrast is seen on the surface, which is confirmed by EDS analysis (Fig. 7a, b and c) and agrees well with the XRD results in Fig. 6. For the HEA2 and HEA3, the oxide scales mainly comprise α -Al₂O₃ with uniform grain structure (Fig. 7e and h). Additionally, it is seen that the nanoscale Y/Hf-rich oxides (e.g. HfO₂ and Y₃Al₅O₁₂) are uniformly distributed at the α -Al₂O₃ grain boundaries all over the surface, which reveals a strong REs-effects [23, 24, 27].

Fig. 7. Surface morphology of the oxide scales formed on the three types of HEAs after isothermal oxidation at 1100 °C for 1000 h: (a and b) low magnification backscattered SEM images, showing the integrity of the oxide scale formed on the HEA1; (c) high magnification backscattered SEM image and corresponding X-ray maps, showing the microstructure and composition of the oxide scale; (d and g) low magnification backscattered SEM images, showing no spallation of the oxide scales for HEA2 and HEA3; (e and h) high magnification backscattered SEM images and (f and i) amplifying backscattered SEM images over the area within the white rectangle in (e and h), showing the grain microstructure of oxide scale formed on the HEA2 and HEA3.

Fig. 8 shows the evolution of cross-sectional morphology of the oxide scale as a function of oxidation time. For all the HEAs, the imperfections-free scale/substrate

interface can be still seen even after 1000 h oxidation (Fig. 8j, k and l). Additionally, a continuous and uniform Al-depletion layer develops beneath the oxide scale/substrate interface (Fig. 8a, b and c). Therefore, the stable scale/substrate interface and the strong interfacial bonding contribute to the superior spallation resistance of the oxide scale (Fig. 7). For the HEA1, even though the non-protective spinel ((Co, Ni)(Fe, Al)₂O₄) forms on top of the α -Al₂O₃ layer, the continuous α -Al₂O₃ scale is still maintained during the long-term oxidation (Fig. 8d and j). The average oxide scale thickness is merely about 5.6 ± 0.3 μ m after 1000 h oxidation (Fig. 8j). Meanwhile, the oxide scale in the spinel region is slightly thicker compared with that in the region with exclusive α -Al₂O₃ due to the faster grow rate of spinel [28, 29] (Fig. 8d and j). For the HEA2 and HEA3, the exclusive α -Al₂O₃ scale shows uniform microstructure and thickness. The thickness of scale is about 4.8 ± 0.2 μ m and 4.4 ± 0.2 μ m on HEA2 and HEA3, respectively, after 1000 h oxidation.

Fig. 8. Cross-sectional morphology of three types of HEAs after isothermal oxidation

at 1100 °C: (a, b and c) low magnification backscattered SEM images, giving an overview of the cross-section of HEA1, HEA2 and HEA3 after 250 h oxidation, respectively; (d, e and f) high magnification backscattered SEM images over the area within the white rectangle in (a, b and c), showing the microstructure of the oxide scale formed on the HEA1, HEA2 and HEA3 after 250 h oxidation, respectively; (g, h and i) low magnification backscattered SEM images, giving an overview of the cross-section of HEA1, HEA2 and HEA3 after 1000 h oxidation, respectively; (j, k and l) high magnification backscattered SEM images over the area within the white rectangle in (g, h and i), showing the microstructure of the oxide scale formed on the HEA1, HEA2 and HEA3 after 1000 h oxidation, respectively. (The Ni protective layer was fabricated using electroplated method in the solution of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (200g/L), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (50g/L) and H_3BO_3 (20g/L) with a PH ranging from 4.0 to 4.5. The current density is 100 mA/cm^2 and electroplated time is 3 min.)

Fig. 9 shows the microstructure and composition of the oxide scale formed on the HEA2 after 1000 h oxidation. The oxide scale is typically duplex in structure, consisting of outer equiaxed grains and inner columnar grains in contact with the substrate. The characteristic structure of the oxide scale results from the concurrent inward diffusion of O and outward diffusion of Al [27, 30]. According to the X-ray maps in Fig. 9, the oxide scale primarily comprises $\alpha\text{-Al}_2\text{O}_3$ with minor reactive element oxides, which is in agreement with the observations in Fig. 8. Since the inward O diffusion along the oxide grain boundaries facilitates the formation of columnar grains, the high thickness ratio of the columnar grain zone to the equiaxed grain zone (~20:1) suggests that the inward O diffusion is the dominant mechanism for the growth of the oxide scale [27, 31, 32]. Examination of the oxide scales on other alloys shows similar duplex structure as that shown in in Fig. 9.

Fig. 9. Bright-field (BF) TEM image combined with X-ray maps, showing the microstructure and composition of the oxide scale formed on the HEA2 after isothermal oxidation at 1100 °C for 1000 h.

3.3. Oxides growth kinetics

The oxidation kinetics of three types of HEAs during 1000 h oxidation at 1100 °C are presented in Fig. 10. The oxide scale thickness is determined by 50 equidistance points distributed through the cross-sectional area of the oxide scale divided by the length of interface with a step size of 20 μm. The error bar is the standard deviation of 50 equidistance points. As shown in Fig. 10a, the oxide scales formed on the three types of HEAs slowly thicken with increasing oxidation time.

Fig. 10. Oxides growth kinetics for the three types of HEAs: (a) thickness of the oxide scales formed on the HEAs as a function of oxidation time; (b) thickness of the oxide scales formed on the HEAs as a function of the square root of oxidation time, showing the parabolic law [43]. The “HEA1 Average thickness” represents the average thickness of the oxide scale including α -Al₂O₃ and spinel ((Co, Ni)(Fe, Al)₂O₄).

Based on the classical theory of oxidation, the oxides growth generally follows the parabolic law [33]. The parabolic rate constant for oxidation, k_h , is expressed by the

oxide scale thickness (h) and the oxidation time (t) [28, 34]:

$$\Delta h^2 = 2k_h t \quad (1)$$

The linear fit to oxide scale thickness versus square root of the oxidation time for three types of HEAs is presented in Fig. 10b. For the HEA1, the parabolic rate constant is about $4.9 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ in terms of the average oxide scale thickness of $\alpha\text{-Al}_2\text{O}_3$ and spinel $((\text{Co}, \text{Ni})(\text{Fe}, \text{Al})_2\text{O}_4)$. It should be mentioned that the growth of oxide scale still follows the parabolic law for the HEA1, even though the spinel develops on the top of oxide scale. This result indicates that the formation of spinel occurs in the initial oxidation period, and thus the overall growth of oxide scale is dominated by the growth of $\alpha\text{-Al}_2\text{O}_3$ after long-term oxidation. The parabolic rate constants of the $\alpha\text{-Al}_2\text{O}_3$ scale are about $4.2 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$, $3.4 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ and $2.8 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ for HEA1, HEA2 and HEA3, respectively. Taylor et al. have reported that the average parabolic rate constant of a conventional CoNiCrAlY alloy is about $9 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$, which is one order of magnitude higher than those of the three types of HEAs [28].

3.4. Phase stability of HEAs after high temperature oxidation

Fig. 11 shows the phases evolution of three types of HEA substrates after 1000 h oxidation. The phase constitutions for HEA substrates after 1000 h oxidation are summarized in Table 4 based on the XRD results and compared with those of as-cast HEA substrates. For the HEA1 substrate, the A2 phase disappears and transforms into FCC phase. For the HEA2 and HEA3 substrates, the primary phases are still A2 and B2. However, minor FCC and σ phases ($\sigma\text{-CoCr}$ or $\sigma\text{-FeCr}$ phase) are detected in the HEA2 substrate. For the HEA3 substrate, the original phase constitutions of A2 and B2 do not change after 1000 h oxidation.

Fig. 12 shows the phase distribution of three types of HEA substrates after 1000 h oxidation. As shown in Fig. 12a and d, FCC phase (bright contrast) and B2 phase (dark contrast) are uniformly distributed in the HEA1 substrate. For the HEA2 substrate, four-phase structure consisting of A2, B2, FCC and σ phases can be found, as shown in Fig. 12b and e. The brightest phase is identified to be σ phase, which agrees well with the

observations in the HEA2 reported by Tang et al. [35]. In addition, both A2 phase and σ phase segregate from the large B2 grain, while FCC phase precipitates from the grain boundaries of HEA2 substrate. For the HEA3 substrate, only fine A2 phase precipitates from the large B2 grains and thus lead to a dispersive distribution of B2 phase (Fig. 12c and f). Meanwhile, no σ phase can be observed. These observations are well consistent with the XRD results in Fig. 11.

Fig. 11. XRD results of three types of HEA substrates after oxidation at 1100 °C for 1000 h. (To confirm the phase constitutions of HEA substrates after long-term oxidation, the samples after 1000 h oxidation were removed from furnace at high temperature and immediately water-quenched. Then, the thin oxide scales and Al-depletion layers were mechanically ground off before XRD measurement.)

Firstly, the formation of FCC phase in the HEA1 substrate and HEA2 substrate can be attributed to the decreasing Al content due to oxidation. Similar phase transformation of BCC phase to FCC phase due to Al-depletion is commonly observed in the conventional NiCoCrAlY-type alloys [36-38]. Secondly, it has been predicted by the thermodynamically calculation that two phases (FCC+B2) of HEA1, triple phases (FCC+A2+B2) of HEA2 and two phases (A2+B2) of HEA3 are possibly thermodynamically stable [39]. Therefore, the absence of A2 phase in the HEA1

substrate and the presence of FCC phase in the HEA2 substrate also probably derive from the thermodynamically stable process after 1100 °C for 1000 h, except for the contribution of Al depletion due to oxidation.

Fig. 12. Surface morphology of three types of HEA substrates after isothermal oxidation at 1100 °C for 1000 h: (a, b and c) low magnification backscattered SEM images, giving an overview of microstructure for HEA1, HEA2 and HEA3 substrates, respectively; (d, e and f) high magnification backscattered SEM images over the area within the white rectangle in (a, b and c), showing the detailed microstructure of HEA1, HEA2 and HEA3 substrates, respectively.

Table 4. Phase constitutions of as-cast HEA substrates and HEA substrates after 1000 h oxidation.

Materials	Phases (as-cast)	Phases (1000 h)
HEA1 substrate	FCC+A2+B2	FCC+B2
HEA2 substrate	A2+B2	A2+B2+FCC+ σ
HEA3 substrate	A2+B2	A2+B2

As presented in Fig. 4, the continuous oxide scale has been already formed on the HEAs and meanwhile the dendritic microstructure can be still observed after 5 min oxidation at 1100 °C. In other words, the continuous oxide scale has already developed on the HEA substrates before occurrence of microstructural evolution in the HEA substrates.

Once the continuous oxide scale and Al-depletion layer near the scale/substrate interface forms (Fig. 4 and 8), the oxygen partial pressure is much lower at scale/substrate interface compared with that at surface. At this time, the critical Al concentration required to form the α -Al₂O₃ supplied from the underlying substrate is very low in spite of microstructural evolution of HEA substrates [13]. On the other hand, the stability of overall oxide scale growth, scale/substrate interface and the continuous Al-depletion layer with the increasing oxidation time clearly indicates that the effect of microstructural evolution of HEA substrates on the oxidation behavior of HEAs is negligible (Fig. 8). The precipitation mechanism of σ phase in the HEA2 substrate is still in debate. According to the thermodynamic prediction [35, 39], σ phase is likely to occur from 500 °C to 810 °C and cannot form at 1100 °C. It is speculated by Tang et al. that a high concentration of Co (~24.7 at. %) in the σ -rich region for the HEA2 probably stabilizes the σ phase at 1283 °C (Table 5) [40].

Table 5. SEM-EDS analysis results for chemical composition (at. %) of A2, B2, FCC and σ phases in the HEA2 substrate after oxidation at 1100 °C for 1000 h.

Phases	Elements (at. %)				
	Al	Co	Cr	Fe	Ni
A2	7.6±1.7	18.4±2.1	38.4±2.7	26.5±2.3	9.1±2.1
B2	27.9±2.1	19.3±1.9	12.3±2.3	15.1±1.7	25.8±1.8
FCC	8.3±1.9	23.4±2.1	26.2±2.4	27.9±2.5	14.2±1.9
σ	7.1±1.9	24.7±2.6	30.2±2.9	27.9±1.9	10.1±1.8

4. Discussion

4.1. Early oxidation stage

4.1.1. Fast establishment of exclusive α -Al₂O₃

For the typical alumina-forming alloys (e.g. NiAlHf and NiCoCrAlY), the non-protective θ -Al₂O₃ often forms in the early oxidation stage and the phase transformation of θ to α -Al₂O₃ occurs in the subsequent oxidation stage. The growth rate of θ -Al₂O₃ is

about one order of magnitude higher than that of α -Al₂O₃, and thereby leads to a higher oxide scale thickness [24, 25]. It has been reported that the REs (e.g. Y and Hf) in the alumina-forming alloy can inhibit the transformation of θ to α -Al₂O₃ by entering the relatively open θ -Al₂O₃, which will further promote thickening of the oxide scale [22]. Our previous work has shown that the Al₂O₃ scale on a NiCoCrAlY alloy has 7% θ -Al₂O₃ after 10 min oxidation at 1100 °C [23]. However, for the three types of REs-doped HEAs used in this study, no θ -Al₂O₃ can be detected even after 5 min oxidation at 1100 °C. The unique nanostructure of A2 and B2 phases in ID/DR coherent structure might be a cause. The crystallographic defects (e.g. phase boundary) can provide nucleation sites for the heterogeneous formation of α -Al₂O₃ [11]. The featured nanostructure resulting from the spinodal decomposition will introduce large number of A2/B2 phase boundaries, which significantly increases the nucleation sites for the formation of α -Al₂O₃ and thus facilitates the earlier establishment of α -Al₂O₃.

4.1.2. Maintaining the formation of exclusive α -Al₂O₃ scale

It has been demonstrated by Wang et al. that nano-sized, and uniformly distributed Al-rich phase (e.g. B2 phase) is more favorable for the formation of exclusive α -Al₂O₃ scale for the two-phase alloy (e.g. HEA2 and HEA3) [13]. As presented in Fig. 2 and 3, the B2 phase is nano-sized with a width of ~100 nm and randomly distributed in the HEA2 and HEA3. Therefore, the exclusive α -Al₂O₃ scale develops on the HEA2 and HEA3. Additionally, a higher amount of B2 phase in the HEA3 (Table 2) can also facilitate the formation of α -Al₂O₃ [13]. However, for the HEA1, spinel predominantly grows on the FCC phase (Fig. 4a and d). First, the overall Al content in the HEA1 is lower compared with other two types of HEAs (Table 1). Second, the FCC phase is Al-poor and meanwhile relatively large phase size will lead to a high minimum Al concentration required to nucleate α -Al₂O₃ [12, 13]. These two reasons can cause a relatively long transition oxidation stage and thereby promote the formation of spinel. Once a continuous oxide scale is developed, the oxygen partial pressure will be significantly lower at the scale/alloy interface than that at surface. According to classic

theory for selective oxidation of α -Al₂O₃, the minimum Al concentration for the formation of exclusive α -Al₂O₃ can be decreased at lower oxygen pressure. Thus, the formation of α -Al₂O₃ can be still maintained underneath the spinel for the long-term oxidation for the HEA1 (Fig. 8d and j).

4.2. Long-term oxidation stage

The effect of REs doping on the oxidation behavior for the alumina-forming alloys can be elaborated as follows: (1) REs ions can segregate to scale/substrate interface from the underlying alloy, which can inhibit the formation of interfacial pores and thus enhance the interfacial adherence [16, 41]. (2) REs ions can block outward Al diffusion by diffusing along the α -Al₂O₃ scale grain boundaries and thereby the overall growth of oxide scale is dominated by the inward O diffusion for the long-term oxidation [27, 41]. The uniform distribution of REs in the form of Y/Hf-rich oxides at the α -Al₂O₃ scale grain boundaries clearly indicates that the strong REs-effects occur in the all HEAs (Fig. 7).

Fig. 13 shows the fractured cross-sectional structure of oxide scale formed on the three types of HEAs after 250 h and 1000 h oxidation. On one hand, the typical duplex α -Al₂O₃ scale structure on the either HEA demonstrates the concurrent inward diffusion of O and outward diffusion of Al during long-term oxidation. On the other hand, the predominant columnar grain structure in the α -Al₂O₃ scale suggests that the growth of oxide scale is controlled by the inward diffusion of O and thus leads to a slow oxidation rate for the all HEAs [27, 32]. In summary, the extremely low oxidation rate for the three types of HEAs can be attributed to both the fast establishment of exclusive α -Al₂O₃ and the strong REs-effects.

Fig. 13. The fractured cross-sectional morphologies of: (a, b and c) oxide scale formed on the HEA1, HEA2 and HEA3 at 1100 °C for 250 h, respectively; (d, e and f) oxide scale formed on the HEA1, HEA2 and HEA3 at 1100 °C for 1000 h, respectively.

Another interesting result should be specially noted that the growth rate of α -Al₂O₃ is gradually reduced with the increasing Al content in the HEAs (Fig. 10b). Based on the foregoing discussion, the transformation rate of α -Al₂O₃ in the early oxidation stage and the beneficial REs-effects are basically similar for the three types of HEAs. On the other hand, the dominant growth mechanism of α -Al₂O₃ scale is the inward O diffusion for the three types of HEAs. Therefore, the difference in the growth rate of α -Al₂O₃ scale might derive from the different amount of inward O diffusion paths, which is determined by the columnar grain size in the oxide scale [42]. It can be clearly seen in Fig. 13 that the columnar grain size gradually increases with the increasing Al content after a same oxidation time. Meanwhile, the average columnar grain sizes are summarized in Table 6. The average columnar grain size increases from 0.7 ± 0.2 μm to 1.2 ± 0.3 μm after 250 h oxidation with the increasing Al content, while the average columnar grain size increases from 0.9 ± 0.2 μm to 1.5 ± 0.3 μm after 1000 h oxidation.

Moreover, the average columnar grain size also increases due to grains growth for either HEA with the increasing oxidation time. The lower amount of inward O diffusion paths due to the increasing columnar grain size, which might be the predominant reason for the lower growth rate of α -Al₂O₃ scale with the increasing Al content in the HEAs. However, the mechanism for the increasing columnar grain size with the increasing Al content in the HEAs is still unclear. Further works should be made to understand this point, which can contribute to design a high-performance oxidation resistant alloy.

Table 6. The columnar grain size in the oxide scales for the three types of HEAs after 250 h and 1000 h oxidation. (The columnar grain size is determined by the SEM image width divided the overall numbers of columnar grains in a single SEM image. Five SEM images with a magnification of 20000 $\times$ are employed to measure the average columnar grain size using Image J software and meanwhile the error bar is the standard deviation of measured widths).

Samples	Columnar grain size after 250 h oxidation (μm)	Columnar grain size after 1000 h oxidation (μm)
HEA1	0.7 $\pm$ 0.2	0.9 $\pm$ 0.2
HEA2	0.9 $\pm$ 0.2	1.2 $\pm$ 0.3
HEA3	1.2 $\pm$ 0.3	1.5 $\pm$ 0.3

5. Conclusions

In this work, three types of Y/Hf-doped Al_{0.7}CoCrFeNi (HEA1), AlCoCrFeNi (HEA2) and Al_{1.3}CoCrFeNi (HEA3) high-entropy alloys (HEAs) with different Al content were fabricated and their oxidation behavior was investigated. HEA1 consists of face-centred cubic (FCC) phase, disordered body-centered cubic (BCC) A2 phase and ordered BCC B2 phase. With the increasing Al content, FCC phase disappears and only nano-sized A2 and B2 phases exist in the HEA2 and HEA3. In the early oxidation stage, the fast establishment of α -Al₂O₃ scale for the all HEAs is related to the featured nanostructure in the HEAs. After the long-term oxidation, the oxide scale on the HEA1 consists of an outer spinel layer and an inner α -Al₂O₃ layer, but the oxide scales on the HEA2 and HEA3 show a single-layer structure with exclusive α -Al₂O₃ grains. Meanwhile, nanoscale Y/Hf-rich oxides uniformly distribute at the α -Al₂O₃ grain boundaries for all

HEAs, which reveals the strong REs-effects. All HEAs exhibit the extremely slow oxidation rate with low k_p values ($4.9 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ for HEA1, $3.4 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ for HEA2 and $2.8 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ for HEA3). Additionally, the oxidation rate gradually reduces with the increasing Al content resulting from the gradually increasing columnar grain size in the $\alpha\text{-Al}_2\text{O}_3$ scale. In summary, the innovative Y/Hf-doped HEAs are expected to be promising materials for high temperature oxidation resistance due to the extremely low oxidation rate and strong interfacial bonding.

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