Synergistic effects of Al and Ti on the oxidation behaviour and mechanical properties of L1₂-strengthened FeCoCrNi high−entropy alloys

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Abstract

Synergistic effects of Al and Ti on the oxidation behaviour and mechanical properties of FeCoCrNi high-entropy alloys were systematically investigated. Our results reveal that increasing the Al/Ti ratio slows down the oxidation kinetics at 700-900 °C and changes the oxide scale from TiO_2 and spinel oxides to Cr_2O_3 and Al_2O_3, leading to a substantial improvement of oxidation resistance. From a mechanical aspect, however, increasing the Al/Ti ratio decreases the mechanical strength, demonstrating a strong trade-off between oxidation resistance and mechanical properties. The underlying mechanisms for the Al and Ti effects on the oxidation resistance and mechanical properties were discussed.

Keywords: A. High-entropy alloy; C. Oxidation; C. Oxide scale microstructure; C. Precipitate; C. Mechanical property

1. Introduction

High-entropy alloys (HEAs) have attracted increasing interest in the material community due to their unique microstructures and superior mechanical properties [1-5]. Particularly, face-centered cubic (FCC) HEAs, such as CoCrFeNiMn and CoCrFeNi, exhibit a superior strength-ductility synergy at ambient and cryogenic temperatures [6-11]. However,

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these single-phase FCC HEAs are relatively weak at elevated temperatures [12], whose strength does not satisfy the requirements for elevated-temperature engineering applications. In recent years, considerable effort has been devoted to strengthening HEAs through different hardening methods. Precipitation hardening has been demonstrated as one of the most effective methods to strengthen HEAs at both room and high temperatures. Particularly, the precipitation of ordered $L1_2$ coherent nanoprecipitates in FCC HEAs has attracted much attention, which leads to the formation of a coherent precipitate microstructure similar to that of γ/γ' superalloys utilized for elevated-temperature applications [13]. He et al. [14] reported that coherent $L1_2$-$Ni_3(Al,Ti)$ nanoprecipitates can be formed in equiatomic FeCoNiCr alloys by optimizing the Al and Ti concentrations. Chen et al. [15] reported that Ti plays a key role in forming $L1_2$ precipitates, whereas Al enhances the phase stability of $L1_2$ precipitates in FCC HEAs. Yang et al. [16] reported that multicomponent $Ni_3(Al,Ti)$-type nanoparticles provide attractive features for strengthening HEAs without sacrificing the ductility, leading to the development of advanced HEAs with high strength and large ductility. The effect of $L1_2$ precipitates on the elevated-temperature mechanical properties of HEAs have also been explored. He et al. [17] found that $L1_2$-strengthened HEAs exhibit a drastic enhancement in the flow stress as compared with single-phase HEAs at $750 - 850\ ^{\circ}C$, demonstrating a substantial improvement in elevated-temperature mechanical properties. In addition, $L1_2$-strengthened HEAs take the advantages of slow elemental diffusion and configuration disorder that are benefit for microstructure stabilities at high temperatures [18]. For example, $L1_2$ precipitates in the $(CoCrNi)_{94}Al_3Ti_3$ [19] and $(FeCoCrNi)_{94}Al_4Ti_2$ (at.%) [20] alloys exhibit remarkable thermal stability against coarsening, which is benefit from the sluggish diffusion of HEAs, even slower than that of conventional superalloys. Therefore, $L1_2$-strengthened HEAs exhibit superior mechanical properties and thermal stabilities at elevated temperatures, which make them promising candidates as structural materials for elevated-temperature structural applications.

From a high-temperature application perspective, oxidation resistance is technologically crucial, because the surface degradation under high temperature exposure can not only cause material loss but also induce crack initiation and premature failure. It has been documented that some alloying elements, such as Cr and Al, form a thin and stable oxide layer acting as a protective barrier suppressing further oxidation of the substrate, thereby enhancing the oxidation resistance of metals and alloys [21-25]. Kai et al. [26] found that the oxidation rate of FeCoCrNi is two orders of magnitude lower than that of FeCoNi at 800-1000 °C, and the Cr_2O_3 layer formed in FeCoCrNi is more effective in hindering the ion diffusion than the ferrous oxide layer formed by FeCoNi. In addition, appropriate amounts of Al additions can induce the formation of Al_2O_3 scale, which grows at a slower rate than the Cr_2O_3 scale, thus improving the durability of materials at high working temperatures. For instance, Laplanche et al. [27] found that the oxidation resistance of FeCoCrNiAl is better than that of FeCoCrNi and FeCoCrNiMn at 800 °C. However, high contents of Al in FCC HEAs can induce the formation of undesired phases, such as B2-ordered NiAl, which is a brittle phase and detrimental to the material ductility [28]. To address this issue, considerable effort has been made to control the phase constitution by optimizing alloy compositions of HEAs. Interestingly, it was found that the co-alloying of Al and Ti can not only effectively suppress the formation of brittle B2-NiAl phase but also promote the precipitation of coherent $L1_2$-Ni_3(Al,Ti) phase, leading to the unique coherent precipitation microstructure similar to that of γ/γ' superalloys. Nevertheless, redundant Ti additions are harmful to the oxidation resistance of FeCoCrNi [29], because the fast-growing titanium oxide layer can not provide a protective barrier against oxidation at high temperatures. Therefore, optimizing the Al and Ti concentrations is crucial for tuning not only mechanical properties but also oxidation resistance of $L1_2$-strengthened HEAs, and there might be some trade-off between mechanical properties and oxidation resistance in these materials. However, a fundamental understanding of synergistic effect of Al and Ti on the oxidation

kinetics, oxide scale microstructure, and mechanical properties of $L1_2$-Ni_3(Al,Ti)-strengthened HEAs remains elusive at the present time.

This work aims to gain insights into the mechanisms for synergistic effect of Al and Ti on the oxidation kinetics, oxide scale microstructures, and mechanical properties of $L1_2$-Ni_3(Al,Ti)-strengthened HEAs. Specifically, the oxidation kinetics, oxide scale morphology, and mechanical properties of $(FeCoCrNi)_{94}Al_xTi_{6-x}$ (x = 1, 2, 3, 4, and 5 at.%) alloys at 700-900 °C were systematically investigated. Particular emphasis was placed on elucidating the underlying mechanisms for the synergistic effect of Al and Ti on the oxidation kinetics and oxide scale microstructures of the $L1_2$-Ni_3(Al,Ti)-strengthened HEAs.

2. Material and methods

Five alloys with nominal compositions of $(FeCoCrNi)_{94}Al_xTi_{6-x}$ (x=1, 2, 3, 4, and 5, at.%) were fabricated by arc-melting and casting. For simplicity, these HEAs are hereafter referred to as Al_1Ti_5, Al_2Ti_4, Al_3Ti_3, Al_4Ti_2, and Al_5Ti_1 alloys. The alloys were prepared from commercially pure elements (Fe: 99.95 wt.%, Co: 99.95 wt.%, Cr: 99.90 wt.%, Ni: 99.95 wt.%, Al: 99.99 wt.%, and Ti: 99.95 wt.%). Prior to melting, the raw materials were mechanically ground to remove the surface scale and then ultrasonically cleaned in ethanol for 5 min to remove adhered contaminants. These raw materials were arc-melted under an Ar atmosphere in a water-cooled copper crucible with non-consumable tungsten electrode. To ensure the chemical homogeneity, each ingot button was melted at high power for 3-5 min, flipped, and re-melted for a total of five times. The molten ingots were then drop-cast in to a copper mold with a cavity of $50 \times 10 \times 3$ mm^3. The ingots were solutionized at 1150 °C for 2 h and cold-rolled to approximately 1 mm in thickness. The rolled sheets were recrystallized at 1150 °C for 3 min and annealed at 800 °C for 8 h.

Oxidation experiments were conducted at 700, 800, and 900 °C. The heat-treated samples were machined into small pieces ($10 \times 10 \times 1$ mm^3), and all surfaces were mechanically polished to a mirror finish. The masses of the oxidized samples were weighted by using a balance with an accuracy of 0.1 mg.

Oxide microstructures were examined by using scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX), and X-ray diffraction (XRD). The EDX mapping was performed with a beam density of 8-15 A·m^{-2} under an accelerating voltage of 20 kV. 3D Atom probe tomography (APT) experiments were conducted in a LEAP™ 5000XR. APT tips were prepared by lift-out and annular milling and were analyzed in voltage mode. The testing temperature, pulse repetition rate, pulse fraction, and ion collection rate were 70 K, 200 kHz, 0.2, and 0.5%, respectively.

Tensile tests were carried out on an MTS machine at a strain rate of 0.001 s^{-1}. Tensile samples had a gauge length of 12.5 mm, a width of 3.2 mm, and a thickness of 1 mm. All surface of the tensile samples was ground with 3000 grit SiC papers.

3. Results

3.1 Starting microstructure and mechanical property

The starting microstructure of the $(FeCoCrNi)_{94}Al_xTi_{6-x}$ alloys before oxidation were examined by SEM and XRD, as illustrated in Fig. 1. The grain sizes of these alloys with different Al and Ti contents are similar, in the range of 25-45 μm. However, they exhibit significantly different precipitate microstructures in the nanoscale. The Al_1Ti_5 alloy (Fig. 1a) contains two categories of nano-sized precipitates, i.e., a small amount of rod-like η precipitates near grain boundaries and a high-number density of spheroidal $L1_2$ nanoprecipitates in grain interiors. XRD (Fig. 1f) reveals that the Al_1Ti_5 alloy contains FCC, $L1_2$, and η phases, which is in consistent with the SEM observation. In the Al_2Ti_4 and Al_3Ti_3 alloys (Figs. 1b and c,

respectively), only spheroidal $L1_2$ nanoprecipitates can be observed, with no formation of rod-like η precipitates, which is also confirmed by XRD. However, with the further increase in the Al/Ti ratio, numerous coarse precipitates appear along grain boundaries (Figs. 1d and e), and their formation is associated with the appearance of new XRD peaks corresponding to the Heusler $L2_1$ phase (Fig. 1f). Moreover, the number density of $L1_2$ nanoprecipitates in the Al_4Ti_2 and Al_5Ti_1 alloys are significantly lower than that in the Al_1Ti_5, Al_2Ti_4, and Al_3Ti_3 alloys. APT characterization of $L1_2$ nanoparticles was performed to obtain detailed information on the precipitate composition and elemental partitioning. Figure 1g displays the atom distribution maps of the Al_3Ti_3 alloy. It is evident that Fe, Cr, and Co partition to the matrix, whereas Ni, Ti, and Al partition to the precipitates. The precipitate composition was quantified using the proximity histogram. The atomic ratio of the sum of Ni, Co, Fe, and Cr to the sum of Al and Ti is approximately 3 in the precipitates, which is in accordance to that of $(Ni,Co,Fe,Cr)_3(Al,Ti)$-type precipitates.

The effect of Al and Ti concentrations on the mechanical properties of the $(FeCoCrNi)_{94}Al_xTi_{6-x}$ alloys were evaluated by tensile tests. Stress-strain curves of the Al_1Ti_5, Al_2Ti_4, Al_3Ti_3, Al_4Ti_2, and Al_5Ti_1 alloys under the 8-h-aged conditions are displayed in Fig. 2. The Al_1Ti_5 alloy exhibits a yield strength of 847 MPa, an ultimate tensile strength of 1292 MPa, and an elongation-to-failure of 24%. As the Al/Ti ratio increases, both yield strength and ultimate tensile strength decrease considerably, whereas their elongation-to-failures increase gradually. The yield strengths of the Al_2Ti_4, Al_3Ti_3, Al_4Ti_2, and Al_5Ti_1 alloys are 678, 625, 522, and 355 MPa, respectively, and their ultimate tensile strengths are 1165, 1085, 929, and 739 MPa, respectively.

3.2 Oxidation kinetics

The mass gain per area of the studied HEAs with different Al/Ti ratios after oxidation at 700, 800, and 900 °C is displayed in Fig. 3. At 700 °C, the mass gains of the five alloys are

generally low, and their thermogravimetric curves follow a parabolic rate law. As the Al/Ti ratio increases, the mass gain of the HEAs decreases gradually. A similar trend was also observed for the HEAs at 800 °C, but with a larger mass gain as compared with that at 700 °C. As the temperature increases to 900 °C, the mass gain curves of the Al_1Ti_5, Al_2Ti_4, and Al_3Ti_3 alloys follow a parabolic time dependency during the first ten days and then exhibit a gradual decrease upon further oxidation, which is accompanied with a spallation of the oxide scale. As to the Al_4Ti_2 and Al_5Ti_1 alloys, the mass gain curves remain to follow a parabolic law, with no observation of any oxide scale spallation. In addition, increasing the Al/Ti ratio results in a low mass gain per area in all the oxidation conditions studied.

To understand the oxidation kinetics, the mass gain of these HEAs at different temperatures are fitted with a parabolic rate equation, as expressed by [30]:

$$\left(\frac{\Delta m}{S}\right)^2 = k_p t + C, \tag{1}$$

where Δm is the mass gain, S is the area, k_p is the parabolic rate constant, t is the time, and C is the integration constant. The fitting of the parabolic plots used the data in the first ten days in Fig. 3, during which no spallation of the oxide scale occurs in all the alloys studied. The slope of the parabolic plots of the five alloys are presented in Fig. 4. It is seen that the oxidation rate is strongly temperature and composition dependent. That is, the k_p value increases with increasing temperature and decreasing Al/Ti ratio. Specifically, as the temperature increases from 700 to 900 °C, the k_p value increases by approximately a factor of forty for the Al_1Ti_5 alloy and two order of magnitude for the Al_2Ti_4, Al_3Ti_3, Al_4Ti_2, and Al_5Ti_1 alloys. Moreover, as the Al/Ti ratio increases from 1/5 to 5/1, the k_p value decreases by approximately one order of magnitude at 700-900 °C.

The parabolic rate constant follows an Arrhenius behavior, and the k_p value has a temperature dependence as [30]:

$$k_p = k_0 e^{\left(\frac{-Q}{RT}\right)},$$ (2)

where k_0 is a pre-exponential factor, Q is an activation energy for oxidation, R is the gas constant, T is the temperature. Using the data at 700-900 °C, the activation energy of the five alloys with different Al/Ti ratios are calculated and displayed in Fig. 3f. The activation energy exhibits a strong composition dependence, increasing from 170 kJ/mol in the Al_1Ti_5 alloy to 230 kJ/mol in the Al_5Ti_1 alloy. By comparing with data in the literature, the activation energy of the Al_3Ti_3, Al_4Ti_2, and Al_5Ti_1 alloys are comparable to that of FeCoCrNiAl and much higher than that of FeCoNiCrMn [31].

3.3 Surface morphology and composition

The phase structure of the oxide scale after oxidation for 480 h at 700, 800 and 900 °C was determined by XRD, and representative XRD profiles of the Al_1Ti_5, Al_3Ti_3, and Al_5Ti_1 alloys are displayed in Fig. 5. The FCC phase can be identified after oxidation for 480 h at 700-900 °C, which implies that XRD detected through the oxide scale in all the samples. At 700 °C, the oxide scale of the Al_1Ti_5 and Al_3Ti_3 alloys contain Cr_2O_3, TiO_2, and spinel oxides, whereas that of the Al_5Ti_1 alloy consists dominantly of Cr_2O_3, together with a small amount of spinel oxides, with no TiO_2 phase being detected. The spinel oxide is a multi-component oxide, which is of AB_2O_4-type and enriched with Fe, Ni, Co, Cr, Ti, and Al [32]. A similar trend was observed at 800 and 900 °C, except that the Al_2O_3 phase appears at these temperatures. As the Al/Ti ratio increases, the concentration of TiO_2 and spinel oxides decrease substantially, whereas that of Cr_2O_3 and Al_2O_3 increases significantly. Thus, the dominant phase of the oxide scale changes from the TiO_2 and spinel oxides to Cr_2O_3 and Al_2O_3 oxides.

Figure 6 shows the surface morphology of the Al_1Ti_5, Al_3Ti_3, and Al_5Ti_1 alloys after oxidation for 480 h at 700-900 °C. The size of the surface oxides increases from sub-micron to micron scale with increasing temperature. SEM-EDX mapping of the surface oxides of the

three alloys at 800 °C is presented in Fig. 7, for which the measurements were performed with the same testing parameters of beam density and exposure time. In the Al_1Ti_5 alloy, the surface oxide is enriched with Fe, Co, Cr, Ni, Ti, and O, together with insignificant amounts of Al. The Ti-enriched and Fe/Co/Cr/Ni-enriched areas are discontinuously distributed on the surface, which suggests the formation of multiple types of oxides. As to the Al_3Ti_3 alloy, the amount of Cr in the oxide scale increases, whereas that of Fe, Co, Ni, and Ti decreases. Moreover, a small amount of Al-enriched oxides appears on the surface. For the Al_5Ti_1 alloy, the concentration of Cr and Al in the oxide scale further increases, whereas that of Fe, Co, Ni, and Ti further decreases. The total concentration of Cr, Al, and O on the surface are over 95%, indicating that the surface oxides are mainly of Cr_2O_3- and Al_2O_3-type. The EDX data is consistent with the XRD results (cf. Fig. 4), in which the major peaks in the Al_5Ti_1 alloy correspond to the Cr_2O_3 and Al_2O_3 phases. These observations indicate that increasing the Al/Ti ratio not only inhibits the formation of TiO_2 and spinel oxides but also promotes the Cr_2O_3 and Al_2O_3 formation.

3.4 Cross-sectional microstructure

Figure 8 illustrates the SEM-EDX mapping of the cross-section of the Al_1Ti_5, Al_3Ti_3, and Al_5Ti_1 alloys after oxidation for 480 h at 700 °C. The oxide scale thickness of the Al_1Ti_5, Al_3Ti_3, and Al_5Ti_1 alloys are estimated to be approximately 2.7, 1.4, and 1.0 μm, respectively. In the Al_1Ti_5 alloy, the oxide scale consists of two layers; the outer one is enriched with Fe, Co, Cr, Al, Ti, and O, whereas the inner one is enriched with Cr and O. The EDX data, together with the XRD results (Fig. 4a), suggests that the outer layer contains spinel and TiO_2 oxides and the inner layer consists mainly of Cr_2O_3. For the Al_3Ti_3 and Al_5Ti_1 alloys, the oxide scale is enriched mainly with Cr and O, suggesting the formation of Cr_2O_3 on the surface. In addition, the Ti concentration in the oxide scale of the Al_3Ti_3 and Al_5Ti_1 alloys is significantly lower than that in the oxide scale of the Al_1Ti_5 alloy.

Figure 9 displays the SEM-EDX mapping of the Al_1Ti_5, Al_3Ti_3, and Al_5Ti_1 alloys after oxidation for 480 h at 800 °C. This oxidation leads to thicker oxide scales as compared with those at 700 °C, which can be attributed to the high oxidation reaction kinetics (cf. Fig. 3). The oxide scale of the Al_1Ti_5 and Al_3Ti_3 alloys contain two layers, the outer consisted of TiO_2 and spinel oxides and the inner consisted of Cr_2O_3. With the increase in the Al/Ti ratio, the concentration of Fe, Co, Ni, and Ti in the outer layer decreases significantly, and these elements were not detected in the oxide scale of the Al_5Ti_1 alloy. Beneath the Cr_2O_3 layer, internal TiO_2 and Al_2O_3 particles can be observed in all the three alloys. Moreover, the amount of TiO_2 decreases and the amount of Al_2O_3 increases substantially with increased Al/Ti ratio. The distribution of the internal Al_2O_3 particles is generally discontinuous in the Al_1Ti_5 and Al_3Ti_3 alloys and becomes relatively continuous in the Al_5Ti_1 alloy, especially at the position adjacent to the Cr_2O_3 layer.

The SEM-EDX mapping of the Al_1Ti_5, Al_3Ti_3 and Al_5Ti_1 alloys at 900 °C is illustrated in Fig. 10. The scale thickness increases significantly, reaching 10-20 μm. Similar to that as observed at 800 °C, the oxide scale of the Al_1Ti_5 and Al_3Ti_3 alloys has two layers, the outer TiO_2 and spinel oxide layer and the inner Cr_2O_3 layer. For the Al_5Ti_1 alloy, the oxide scale consists dominantly of Cr_2O_3, with little observation of spinel and TiO_2 oxides. Beneath the Cr_2O_3 layer, there is a transition region containing fine-scale internal Al_2O_3 and TiO_2 oxides. The amount of internal TiO_2 oxides decreases drastically with increased Al/Ti ratio, whereas that of internal Al_2O_3 oxides increases significantly. In addition, the distribution of internal Al_2O_3 oxides changes from discontinuous particles to semi-continuous/continuous networks. In the Al_5Ti_1 alloy, a continuous Al_2O_3 layer is formed beneath the Cr_2O_3 layer.

4. Discussion

4.1 Mechanisms for the synergistic effect of Al and Ti on the oxidation resistance

The aforementioned results indicate that the oxidation resistance of the $(FeCoCrNi)_{94}Al_xTi_{6-x}$ HEAs with different Al/Ti ratios has a strong composition dependence. Increasing the Al/Ti ratio substantially slows down the oxidation kinetics at 700-900 °C, which is accompanied with the change of the oxide scale from a mixture of TiO_2, Cr_2O_3, and spinel oxides to a mixture of Cr_2O_3 and Al_2O_3. Note that all specimens were heat-treated identically, and the alloys with different Al and Ti concentrations have a similar grain size. Thus, the grain size effect on the oxidation behavior is not discussed here. In the following, the mechanisms for the synergistic effect of Al and Ti additions on the oxidation behavior of $L1_2$-strengthened HEAs are discussed.

We first analyze the effect of Ti on the oxidation behaviour of the $L1_2$-strengthened HEAs. It is known that the Cr_2O_3 scale serves as a protective barrier to excessive oxidation at 700-900 °C, providing good oxidation resistance of the HEAs. The EDX results reveal that the HEAs with high Ti concentrations, such as the Al_1Ti_5 alloy, form a complex oxide scale consisting of multiple layers, the outer consisted of TiO_2 and spinel oxides and the inner consisted of Cr_2O_3. The formation of the TiO_2 outer layer requires the transportation of Ti ions through the inner Cr_2O_3 layer. Ti typically forms tetra-valent cations (Ti^{4+}) during oxidation, and the Ti^{4+} in Cr_2O_3 acts as a high-valent dopant to increase the vacancy concentration of the oxide scale [33,34]. The increased vacancy concentration has several deleterious effects on the oxidation resistance of the HEAs. First, because vacancies facilitate rapid ion transportation through the oxide scale, a high vacancy concentration accelerates the diffusion of metal and oxygen ions [35], thereby resulting in fast oxidation kinetics and hence a large mass gain in the HEAs containing high Ti concentrations. Second, the high vacancy concentration tends to promote the formation of micro-voids in the Cr_2O_3 scale, which makes the scale loose and less

protective [36-38]. Third, the outward diffusion of Ti, Fe, Ni, Co, and Cr ions leads to the formation of TiO_2 and spinel oxides at the outer oxide surface. It is important to note that both TiO_2 and spinel oxides are non-protective at high temperatures, because they possess a porous and non-protective structure. In particular, the spinel oxides are metastable phases, which decompose into different stable oxides and coalescence into fine-grained oxide scales with a loose structure, thereby degrading the oxidation resistance of materials. Consequently, because of the accelerated diffusion of ions and the formation of non-protective oxides, a relatively thick scale was observed on the surface of the HEAs containing high Ti contents. Furthermore, the Cr_2O_3, TiO_2, and spinel oxides have significantly different thermal expansion coefficients, and the co-formation of these phases induces internal stresses in the oxide scale, which leads to the spallation of the oxide scale at high temperatures. Therefore, the high Ti contents degrade the oxidation resistance of the HEAs by forming non-protective oxides, which not only accelerates the oxidation kinetics but also results in the scale spallation at elevated temperatures.

We next discuss the effect of Al on the oxidation behaviour of the $L1_2$-strengthened HEAs. It was documented that Al_2O_3 is a protective oxide, which has a compact structure, slow growth rate, and high stability at high temperatures [39]. The formation of Al_2O_3 depends on the ion transportation, which is, in turn, related to the oxidation temperature, time, and solute concentrations. The Gibbs energy for the formation of Al_2O_3 at 700, 800 and 900 °C are -913.4, -891.4 and -869.3 kJ/mol, respectively, which are lower than that of Cr_2O_3, being -588.7, -571.9, and -555.2 kJ/mol, respectively [40]. However, because of the slow kinetics the formation of Al_2O_3 at temperatures below 800 °C is significantly inhibited. Thus, the volume fraction of Al_2O_3 in the oxide scale is very limited at 700 °C. At 800 and 900 °C, the formation of Al_2O_3 can be external and/or internal, depending on the Al/Ti ratio. As discussed earlier, the solutioning of Ti^{4+} ions in the Cr_2O_3 scale increases the vacancy concentration, whereas Al^{3+} ions do not have obvious effects on the vacancy concentration of the Cr_2O_3 scale. At a low

Al/Ti ratio, the high vacancy concentration promotes the outward diffusion of metal cations and inward flow of oxygen anions, leading to the formation of both internal and external Al_2O_3 oxides. As the Al/Ti ratio increases, the vacancy concentration is decreased. As a result, the outward diffusion of large-sized Al cations is substantially inhibited, whereas the inward diffusion of small-sized oxygen ions is still activated, resulting in the formation of internal Al_2O_3 oxides only. In addition, the distribution of the internal Al_2O_3 oxides changes from discontinuous to continuous network with the increasing Al/Ti ratio. A thin and continuous internal Al_2O_3 layer beneath the Cr_2O_3 layer can be clearly observed in the Al_5Ti_1 alloy at 900 °C. This inner Al_2O_3 layer, together with the outer Cr_2O_3 layer, can effectively inhibit the ion diffusion through the oxide scale, leading to a slow oxidation rate. Therefore, a thin oxide scale and slow oxidation kinetics were observed in the HEAs with high Al/Ti ratios, such as the Al_5Ti_1 alloy.

Based on the aforementioned discussion, the mechanisms for the synergistic effect of Al and Ti on the oxidation resistance of $L1_2$-strengthned HEAs are schematically summarized in Fig. 11. In the HEAs with a low Al/Ti ratio, the high Ti content increases the vacancy concentration of the Cr_2O_3 layer, which accelerates the diffusion of metal cations and oxygen anions, leading to fast oxidation kinetics. Moreover, the outward diffusion of metal ions promotes the formation of non-protective oxides, such as TiO_2 and spinel oxides, on the surface of the Cr_2O_3 layer. Because of the mismatch of the thermal expansion coefficients of these oxides, high thermal stresses are generated, which induce the spallation of the oxide scale at high temperatures. As a result, the HEAs with a low Al/Ti ratio exhibit poor oxidation resistance with a high oxidation rate and extensive scale spallation. With the increasing in the Al/Ti ratio, the deleterious effects of Ti on the oxidation resistance of the HEAs is alleviated, and in the meantime, the beneficial effects of Al become more pronounced. The Al additions promotes the formation of internal Al_2O_3 oxides and related networks in transition region, and

their distribution changes from discontinuous to continuous with increased Al content. Consequently, for the HEAs with a high Al/Ti ratio, the oxide scale consists of continuous and protective Cr_2O_3 and Al_2O_3 layers, with no formation of non-protective TiO_2 and spinel oxides, leading to enhanced oxidation resistance with slow oxidation kinetics.

4.2 Trade-off between corrosion resistance and mechanical properties in HEAs

The mechanical tests indicate that the HEAs with different Al/Ti ratios exhibit significantly different mechanical properties (cf. Fig. 2). The degree of precipitation hardening is closely related to the precipitate characteristics, particularly the volume fraction of precipitates. Considering that Al and Ti are two of the most important $L1_2$ forming elements in these HEAs, changing the Al/Ti ratio would inevitably affect the volume fraction of $L1_2$ precipitates and hence the precipitation strengthening response. To understand how the Al and Ti contents affect the $Ni_3(Al,Ti)$ precipitation behaviour, the phase relations of the $(FeCoCrNi)_{94}Al_xTi_{6-x}$ system were calculated using Thermo-Calc. The volume fractions of $Ni_3(Al,Ti)$ in the Al_1Ti_5, Al_2Ti_4, Al_3Ti_3, Al_4Ti_{12}, and Al_5Ti_1 alloys at 800 °C are calculated to be 19.6%, 16.4%, 15.7%, 11.7%, and 5.5%, respectively, showing a monotonous decrease in the volume fraction with increased Al/Ti ratio. According to Chen et al. [15] and Han et al. [41], Ti plays a dominant role in forming $L1_2$ precipitates, whereas Al enhances the phase stability of $L1_2$ precipitates in FCC HEAs. Therefore, the volume fraction of $L1_2$ precipitates decreases gradually with increased Al/Ti ratio, resulting in a decrease in the precipitation strengthening and hence mechanical strength of the HEAs.

From a technological standpoint, both oxidation resistance and mechanical properties of HEAs are important considerations for structural uses. It was considered that the activation energy of oxidation is an important indicator of oxidation resistance [42]. That is, the larger the activation energy of oxidation, the higher the oxidation resistance. We compared the activation energy and yield strength of the five HEAs with different Al/Ti ratios, as summarized

in Fig. 12. It is evident that as the Al/Ti ratio increases, the oxidation resistance of the HEAs increases monotonously, but their yield strengths decrease drastically. Therefore, there is a strong trade-off between oxidation resistance and mechanical strength in the $L1_2$-strengthened HEAs. In the $(FeCoCrNi)_{94}Al_xTi_{6-x}$ system, the Al_1Ti_5 alloy possesses a high strength but suffer from poor oxidation resistance, whereas the Al_5Ti_1 alloy exhibits good oxidation resistance but has a low mechanical strength. In comparison, the Al_2Ti_4, Al_3Ti_3, and Al_4Ti_2 alloys exhibit relatively balanced mechanical strength and oxidation resistance, and thus are promising for further optimization and investigations for elevated-temperature applications. Furthermore, it is worthy to emphasize that for alloy design of high-performance HEAs for elevated-temperature applications, it is important to optimize both mechanical properties and oxidation resistance.

5. Conclusions

1. Increasing the Al/Ti ratio slows down the oxidation kinetics and changes the oxide scale from a mixture of TiO_2, Cr_2O_3, and spinel oxides to a combination of Cr_2O_3 and Al_2O_3, leading to an improvement of oxidation resistance of the $L1_2$-strengthened HEAs.

2. The mechanism for the detrimental effects of Ti additions on the oxidation resistance of HEAs can be twofold. First, the Ti additions increase the vacancy concentration of the Cr_2O_3 layer, which accelerates the outward diffusion of metal cations and inward flow of oxygen anions, leading to enhanced oxidation kinetics. Second, the outward diffusion of metal ions promotes the formation of non-protective oxides, such as TiO_2 and spinel oxides, on the surface of the Cr_2O_3 layer. Because of the mismatch of the thermal expansion coefficients of these oxides, the thermal stress results in the spallation of the oxide scale at high temperatures.

3. The beneficial effects of Al on the oxidation resistance is attributed to the formation of the internal Al_2O_3 layer beneath the Cr_2O_3 layer, and the distribution of internal Al_2O_3 oxides

changes from discontinuous to continuous with increased Al/Ti ratio. The combination of the two protective oxide layers can effectively inhibit the ion diffusion through the oxide scale, leading to a slow oxidation rate.

4. From the mechanical aspect, however, increasing the Al/Ti ratio decreases the yield strength of the HEAs from 847 MPa in the Al_1Ti_5 alloy to 355 MPa in the Al_5Ti_1 alloy, demonstrating an obvious negative impact on the mechanical properties. Therefore, there is a strong trade-off between oxidation resistance and mechanical strength in the $L1_2$-strengthened HEAs. This research suggests that for alloy design of high-performance HEAs for elevated-temperature applications, it is important to optimize both mechanical properties and oxidation resistance.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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