

Article

High-Temperature Oxidation Behaviors of AlCrTiSi_{0.2} High-Entropy Alloy Doped with Rare Earth La and Y

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Abstract: High-entropy alloys (HEAs) were prepared with strong antioxidant metals Al, Cr, Ti, and Si as matrix elements, and the effects of rare earth (RE) lanthanum (La) and yttrium (Y) doping on their microstructures and high-temperature oxidation resistance were explored in this study. The AlCrTiSi_{0.2}RE_{0.02} HEAs were prepared by using vacuum arc melting and were oxidized mass gain at 1000 °C. After oxidation for 53 h, AlCrTiSi_{0.2} HEA had a mass increase of 1.195 mg/cm², and it had the best oxidation resistance of three HEAs (AlCrTiSi_{0.2}, AlCrTiSi_{0.2}La_{0.02}, and AlCrTiSi_{0.2}Y_{0.02}). The surface oxide layers of three HEAs mainly consisted of Al and Ti oxides; the layered oxide film of AlCrTiSi_{0.2} alloy was mainly composed of dense Al₂O₃, and the acicular oxide films of AlCrTiSi_{0.2}La_{0.02} and AlCrTiSi_{0.2}Y_{0.02} alloys were primarily composed of loose Ti oxide. Doping La and Y decreased the oxidation resistance of AlCrTiSi_{0.2}. In the early stage of oxidation of rare earth HEAs, the surface oxide layer was loose because La and Y reacted with the matrix metal, which slowed down the diffusion of element Al or accelerated the diffusion of element Ti. In the late stage of oxidation, La and Y interacted with O and entered the matrix metal to form rare earth oxides.

Keywords: AlCrTiSi_{0.2}; rare earth; high-temperature oxidation; oxidation resistance



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1. Introduction

High-entropy alloy (HEA) is formed by a variety of metal elements with an equiatomic or near-equiatomic ratio proposed in 2004 [1,2]. HEAs have four unique core effects: high-entropy effect; severe lattice distortion; sluggish diffusion; and cocktail effect [3,4]. HEAs possess various excellent mechanical properties, such as good hardness [5,6], high strength [7,8], and exceptional oxidation resistance [9,10], which make HEAs have broad application prospects. However, due to oxidation and corrosion at high temperatures, metals are always invalid, leading to a decrease in the mechanical properties of materials and a shortened service life of the material [11,12]. Therefore, it is necessary to reduce the impact of high temperatures on materials and improve their high-temperature oxidation resistance. Recently, extensive researches have been conducted on the high-temperature mechanical properties [13], strengthening mechanisms, and deformation mechanisms of HEAs [14,15]. However, as a structural material, the oxidation-resistant behavior of HEAs also needs to be considered.

Currently, research on oxidation resistance mainly focuses on the effect of doping elements [16,17]. Adding specific elements is a conventional method to improve the oxidation resistance of materials such as Al, Cr, and Si [18,19]. Doping with a high content of Al, Cr, and Si elements is found to cause the formation of protective oxide layers (i.e., Al₂O₃, Cr₂O₃, SiO₂) [20,21]. At 700–1000 °C, Al_{1.5}CoCrFeNiTi_{0.5} alloy exhibited excellent oxidation resistance due to the continuous compact layer of (Al_{0.9}Cr_{0.1})₂O₃ oxide films formed on the alloy surface [22]. Butler et al. found that doping Al improved the continuity and internal position of the Al₂O₃ scale in Al_x(NiCoCrFe)_{100-x} (x = 8, 10, 12, 15, 20, and 30 at.%)

at 1050 °C, resulting in greater oxidation resistance [23]. In the CoCrFeNiMn system, Cr was the only element that could form a protective oxide film [24]. The CoFeNiMn alloy without Cr was oxidized quickly, and the oxide scale easily fell off. After adding Cr, MnCr_2O_4 was formed, which had the ability to prevent the internal oxidation of Mn [25]. For typical Al_2O_3 -forming alloys and coatings, many studies have been shown that adding Si changed the oxide scale growth mechanism and significantly improved their oxidation resistance and hot corrosion [26,27]. Senkov et al. reported that Ti was enriched in the area below the oxide layer of the NbCrMo_{0.5}Ta_{0.5}TiZr alloy and had a good antioxidant effect at 1000 °C [28]. When HEAs contained Ti and Cr, Ti was more inclined to act as a catalyst to enhance Cr activity and then accelerate the formation of Cr_2O_3 [29]. MCrAlY alloys (M is Ni, Co, or both) acted as protective coatings against high-temperature oxidation and corrosion of gas turbine components [30,31]. To boost the bonding strength of the oxide coating and lower the oxidation rate, a small amount of rare earth metal Y was added to some of them [32,33]. RE elements, also referred to as “industrial vitamins”, are frequently employed in many conventional alloy systems to enhance the alloy properties [34,35]. It would be fascinating to investigate how RE elements affect the ability of HEAs to withstand oxidation [36].

As a solid solution, the oxidation resistance of HEA depends on the oxidation characteristics of the constituent elements. To prevent the formation of complex, brittle phases, Al, Cr, Ti, and Si were selected as matrix elements, and the HEA design concept was adopted. The basic composition of AlCrTiSi_{0.2} (1:1:1:0.2, in molar ratio) was chosen in accordance with the pertinent theoretical calculation and prior experimental verification. Three types of HEAs, including AlCrTiSi_{0.2}, AlCrTiSi_{0.2}La_{0.02}, and AlCrTiSi_{0.2}Y_{0.02}, were designed and proposed.

In this study, the microstructures and oxidation behaviors of AlCrTiSi_{0.2} HEA were explored to confirm the oxidation resistance and investigate the effects of rare earth elements La and Y doping on the microstructures and oxidation behaviors, serving as a guide for alloy composition optimization.

2. Experimental

2.1. Materials and Methods

The HEAs were prepared from commercial-purity (all 99.9 wt.%) Al, Cr, Ti, Si, La, and Y via electric arc melting under an argon atmosphere in a water-cooled copper crucible. High-purity Ti was employed as a getter before melting to prevent contamination from lingering oxygen and nitrogen. To guarantee the homogeneity of chemical composition, HEAs were remelted at least six times. The compositions of HEA ingots were determined using an X-ray fluorescence spectrometer (XRF, ZSXPrimusIII+, Tokyo, Japan), and the results are listed in Table 1.

Table 1. Compositions of HEAs (at.%).

Alloys	Al	Cr	Ti	Si	La	Y
AlCrTiSi _{0.2} (nominal)	31.25	31.25	31.25	6.25	-	-
AlCrTiSi _{0.2} (measured)	31.11	31.10	30.81	6.98	-	-
AlCrTiSi _{0.2} La _{0.02} (nominal)	31.056	31.056	31.056	6.211	0.621	-
AlCrTiSi _{0.2} La _{0.02} (measured)	30.79	31.19	31.38	6.18	0.46	-
AlCrTiSi _{0.2} Y _{0.02} (nominal)	31.056	31.056	31.056	6.211	-	0.621
AlCrTiSi _{0.2} Y _{0.02} (measured)	30.91	31.42	30.95	5.87	-	0.85

2.2. Characterization

The as-cast ingot was cut into a cubic sample of 5 mm × 5 mm × 2 mm using a high-speed precision cutting machine. The sample was polished using SiC sheets with grit sizes ranging from 400 to 1500. To remove any remaining oil and grime, the sample was thoroughly cleaned with deionized water and alcohol before being dried with hot air. Discontinuous isothermal oxidation of the as-cast alloys was conducted at 1000 °C under ambient laboratory air in a box furnace (KSL 1600X, Hefei Kejing Materials Technology, Hefei City, China) and the accuracy of the temperature in the hot area was 1 K. Tests were carried out with exposure time of 6, 10, 17, 24, 40, and 53 h. The heating rate was set at 10 °C/min. The discontinuous weighing method was used to measure the quality of the sample. The sample mass was measured using an electronic balance with a precision of 0.0001 g both before and after the oxidation tests. It was used to calculate the mass gain per unit area as a function of time.

The initial sample and phase in which the content of oxidation products and crystal structures were characterized used an X-ray diffractometer (XRD, Bruker D8Advance, Cu target, $K\alpha \lambda = 1.5406 \text{ \AA}$) scanning from 20 to 100° in 2θ at a scanning rate of 8°/min. The microstructures of the cast HEAs, the morphology and composition of the oxidation products, and the cross-section of the oxide scales were investigated by a scanning electron microscope equipped with energy dispersive spectrometry (SEM/EDS, MIRA3 LKH, Tescan, Czech Republic).

3. Results and Discussion

3.1. Microstructures of Cast Alloys

The XRD patterns of $\text{AlCrTiSi}_{0.2}$, $\text{AlCrTiSi}_{0.2}\text{La}_{0.02}$, and $\text{AlCrTiSi}_{0.2}\text{Y}_{0.02}$ HEAs are shown in Figure 1, revealing that three HEAs contained both face-centered cubic (FCC) and hexagonal close-packed (HCP) phases. The basic peak type of $\text{AlCrTiSi}_{0.2}$ was unaffected by the addition of the rare earth La and Y, but the peak strength of the HCP phase was increased. This may be due to rare earth La and Y as HCP phases, which enhanced the solid solution effect of HEAs and improved the peak form of HCP phases.

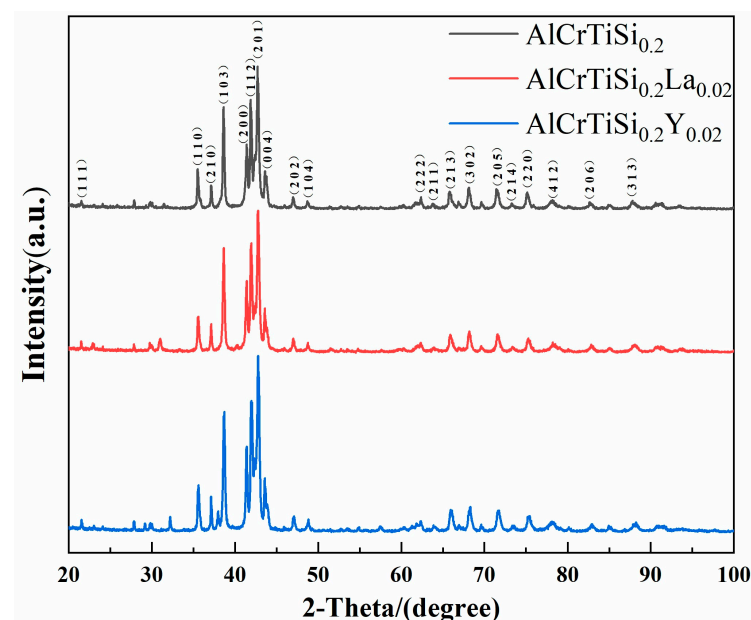


Figure 1. XRD patterns of $\text{AlCrTiSi}_{0.2}$, $\text{AlCrTiSi}_{0.2}\text{La}_{0.02}$, and $\text{AlCrTiSi}_{0.2}\text{Y}_{0.02}$ HEAs.

The backscattering electron SEM (BSE-SEM) and energy dispersive spectroscopy SEM (EDS-SEM) micrographs of all the as-cast HEAs are displayed in Figure 2. As shown in the surface scanning maps in Figure 2, the matrix metal was primarily black with some dispersed white spots. According to the EDS distribution micrographs, the white part

was mainly composed of Si, while the black part was mainly composed of Al, Cr, and Ti. Element distribution is relatively homogeneous in the HEAs, and Si elements are slightly segregated. Rare earth La and Y showed different distribution states in the AlCrTiSi_{0.2}La_{0.02} and AlCrTiSi_{0.2}Y_{0.02} HEAs; La displayed a uniform distribution in the matrix, while Y tended to combine with Al in the matrix metal. The EDS compositions of as-cast HEAs are listed in Table 2. The contents of each element were essentially the same as measured in Table 1, indicating that the HEAs had been uniformly melted.

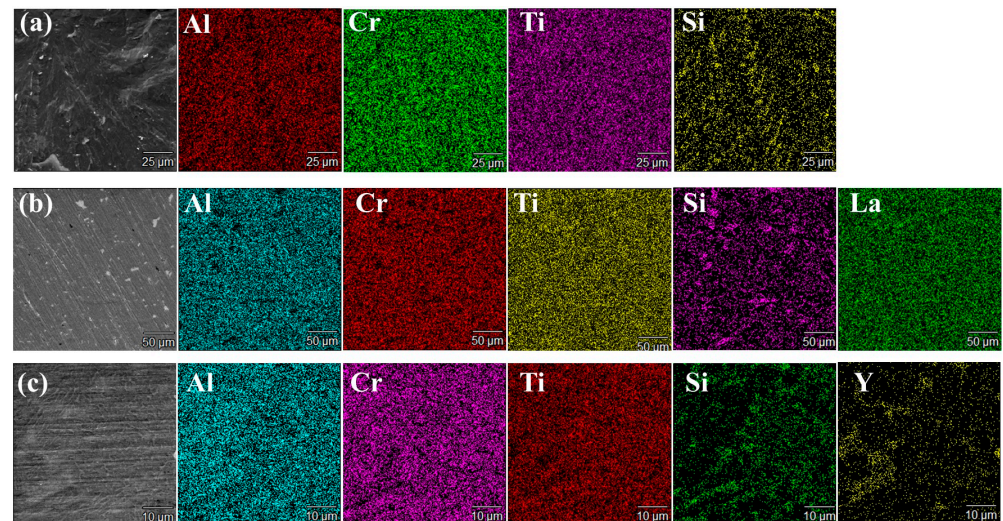


Figure 2. Microstructures and element distribution for (a) AlCrTiSi_{0.2}, (b) AlCrTiSi_{0.2}La_{0.02}, and (c) AlCrTiSi_{0.2}Y_{0.02}, as observed by SEM and EDS.

Table 2. EDS compositions of as-cast HEAs (at.%) (matching Figure 2).

Alloys	Al	Cr	Ti	Si	La	Y
AlCrTiSi _{0.2}	32.41 ± 0.24	29.87 ± 0.24	30.60 ± 0.21	7.12 ± 0.16	-	-
AlCrTiSi _{0.2} La _{0.02}	30.12 ± 0.20	30.76 ± 0.22	31.89 ± 0.20	6.77 ± 0.13	0.46 ± 0.07	-
AlCrTiSi _{0.2} Y _{0.02}	30.91 ± 0.23	31.00 ± 0.26	31.42 ± 0.18	5.77 ± 0.10	-	0.91 ± 0.06

3.2. Oxidation Behaviors of AlCrTiSi_{0.2}La_{0.02} and AlCrTiSi_{0.2}Y_{0.02} HEAs

Figure 3 shows the relationship between oxidation time and specific mass gain (normalized by initial surface area) of AlCrTiSi_{0.2}, AlCrTiSi_{0.2}La_{0.02}, and AlCrTiSi_{0.2}Y_{0.02} at 1000 °C. In the early stage of the oxidation reaction (0–15 h), the mass change trend of the three HEAs was basically the same, and the increase in metal mass almost linearly increased with oxidation time. It was indicated that oxygen was enriched on the substrate surface and did not form a dense oxide layer. The mass difference in the three HEAs increased with the addition of oxidation time from 15 to 53 h. While the mass gain with the addition of La and Y HEAs was depicted as a linear increase, the mass gain of the AlCrTiSi_{0.2} HEA was very modest and nearly negligible. The mass gain of AlCrTiSi_{0.2}La_{0.02} is smaller than that of AlCrTiSi_{0.2}Y_{0.02}, indicating an improvement in oxidation resistance. The increase in different masses indicated that the surface oxide layers of the three HEAs had diverse structures and compositions. It should be noted that after oxidation at 1000 °C for 53 h, the surface oxide layers of AlCrTiSi_{0.2}La_{0.02} and AlCrTiSi_{0.2}Y_{0.02} were partially exfoliated. Due to the peeling of the oxide layer, the actual mass gain was slightly larger than the measured value. After oxidation at 1000 °C for 53 h, the mass gain of AlCrTiSi_{0.2} was only 1.195 mg/cm², which was the best oxidation resistance among the three alloys.

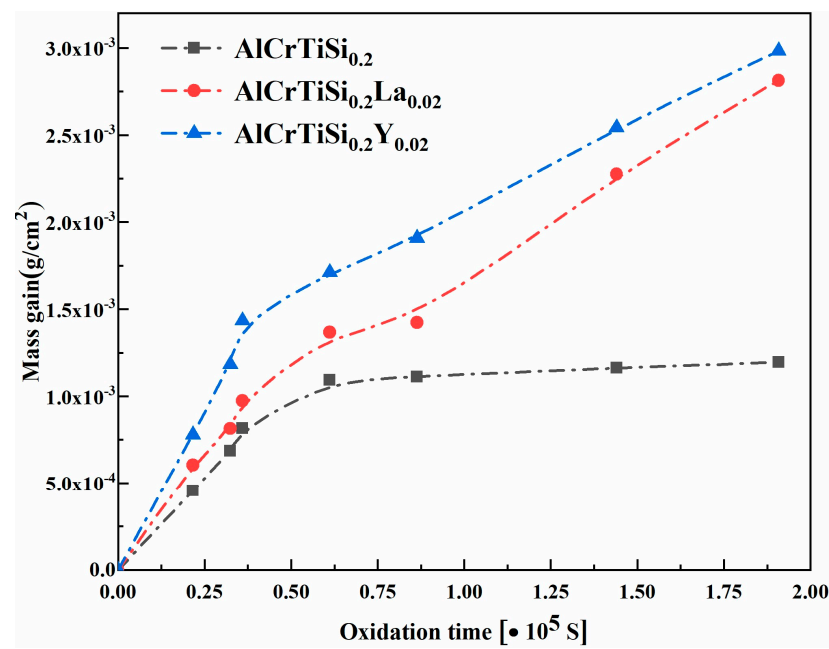


Figure 3. Mass gain per surface area versus time during oxidation of AlCrTiSi_{0.2}, AlCrTiSi_{0.2}La_{0.02}, and AlCrTiSi_{0.2}Y_{0.02} HEAs.

The results of the oxidation kinetics measurements are presented in Figure 4 using both normal and parabolic plots. As shown, the oxidation kinetics at 1000 °C for all studied alloys were approximated using a single-stage parabolic law in the form [37]:

$$\left(\frac{\Delta m}{S}\right)^2 = 2K_p t + C$$

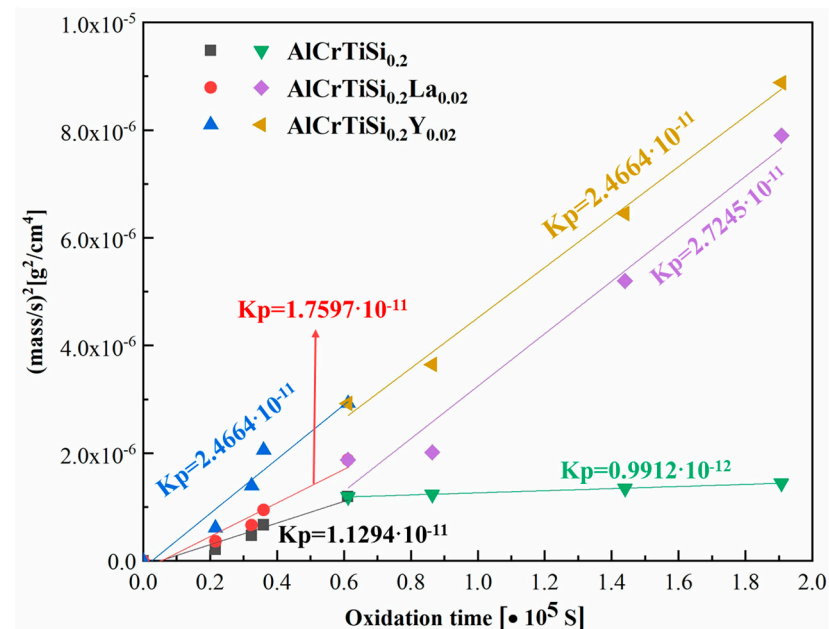


Figure 4. According to the mass gain curves of the three HEAs, the oxidation rate constant K_p value diagram is fitted.

The 53-h oxidation at 1000 °C shown in Figure 4 was divided into two stages, the oxidation for 0–17 h and 17–53 h. Figure 4 displays the oxidation rate constants (K_p values) of the three alloys at every stage. The oxidation rate constants of AlCrTiSi_{0.2}, AlCrTiSi_{0.2}La_{0.02}, and AlCrTiSi_{0.2}Y_{0.02}

three alloys are $K_p = 1.1294 \times 10^{-11}$, $K_p = 1.7597 \times 10^{-11}$, and $K_p = 2.4664 \times 10^{-11}$, correspondingly, in the 0–17 h stage. There is not an obvious difference between the three results, which shows that oxygen is continuously infiltrating the matrix in the early stage of oxidation, where the three HEAs' effects on oxidation resistance are more consistent. The oxidation rate constant K_p values of the three HEAs vary with the extension of the oxidation duration (17–53 h), and the AlCrTiSi_{0.2} HEA has an order of magnitude lower oxidation rate constant than other two HEAs. It should be noted that the value is also lower than the previous oxidation rate constant K_p values, which shows that the AlCrTiSi_{0.2} HEA has developed an anti-oxidation layer on its surface, preventing further oxygen infiltration and lowering the oxidation rate constant.

To further investigate the high-temperature oxidation process, the samples were examined using XRD, SEM, and EDS–SEM tests for 10 and 24 h at 1000 °C. The XRD patterns of the surface layers of AlCrTiSi_{0.2}, AlCrTiSi_{0.2}La_{0.02}, and AlCrTiSi_{0.2}Y_{0.02} HEAs during isothermal exposure in air for 10 and 24 h at 1000 °C are displayed in Figure 5. The oxides on the surface of AlCrTiSi_{0.2} were Al₂O₃, TiO₂, and an unknown phase. The unknown phase may consist of different types of titanium oxides or complicated Ti–Al oxides, according to the chemical components of SEM–EDS (as mentioned in Table 3). The peak pattern after oxidation was significantly unaffected by doping La and Y. After oxidation at 1000 °C for 10 or 24 h, the peak position did not change significantly, but the peak intensity changed, indicating the formation of different oxide contents, leading to an increase in oxidation mass gain. It was consistent with the mass gain result in Figure 3.

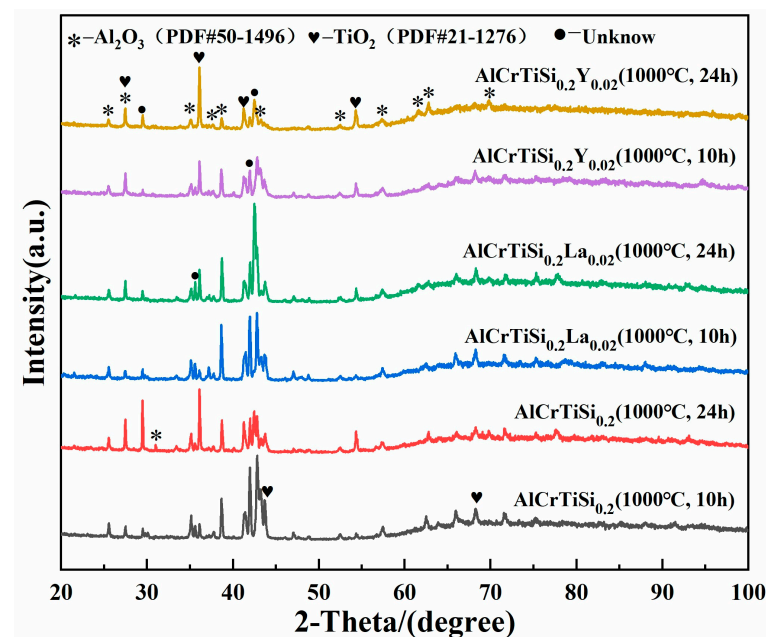


Figure 5. XRD patterns of surface layers of AlCrTiSi_{0.2}, AlCrTiSi_{0.2}La_{0.02}, and AlCrTiSi_{0.2}Y_{0.02} HEAs during isothermal exposure to air for 10 and 24 h at 1000 °C.

Table 3. Chemical compositions of oxide layers (corresponding with Figure 5).

Alloys	Oxide Layer	O	Al	Cr	Ti	Si	La	Y
AlCrTiSi _{0.2}	(a)	58.06 ± 1.17	32.26 ± 0.15	4.66 ± 0.08	4.73 ± 0.06	0.29 ± 0.05	-	-
	(d)	60.30 ± 3.61	12.26 ± 0.11	2.07 ± 0.09	23.3 ± 0.13	2.06 ± 0.05	-	-
AlCrTiSi _{0.2} La _{0.02}	(b)	58.23 ± 1.41	28.73 ± 0.14	5.35 ± 0.08	6.78 ± 0.06	0.82 ± 0.03	0.09 ± 0.03	-
	(e)	59.56 ± 2.19	20.89 ± 0.13	4.26 ± 0.06	13.32 ± 0.11	1.93 ± 0.04	0.04 ± 0.04	-
AlCrTiSi _{0.2} Y _{0.02}	(c)	58.37 ± 2.69	21.73 ± 0.14	3.48 ± 0.09	14.87 ± 0.10	1.14 ± 0.04	-	0.41 ± 0.03
	(f)	65.98 ± 0.98	3.15 ± 0.05	0.74 ± 0.07	29.43 ± 0.19	0.67 ± 0.03	-	0.03 ± 0.02

After exposure to air at 1000 °C for 10 and 24 h, the oxidation layers and corresponding chemical analysis of three HEAs were performed using EDS mappings, as shown in Figure 6. The distribution of surface oxide was stratified and acicular in shape. After oxidation at 1000 °C for 10 h, the surface oxides of all three HEAs were layered and acicular. The acicular compounds on the surface oxides of the three HEAs displayed various states with the addition of oxidation time. The acicular substances gradually increased on the surface of AlCrTiSi_{0.2}La_{0.02}, whereas they became coarse and loose on the surface of AlCrTiSi_{0.2}Y_{0.02}.

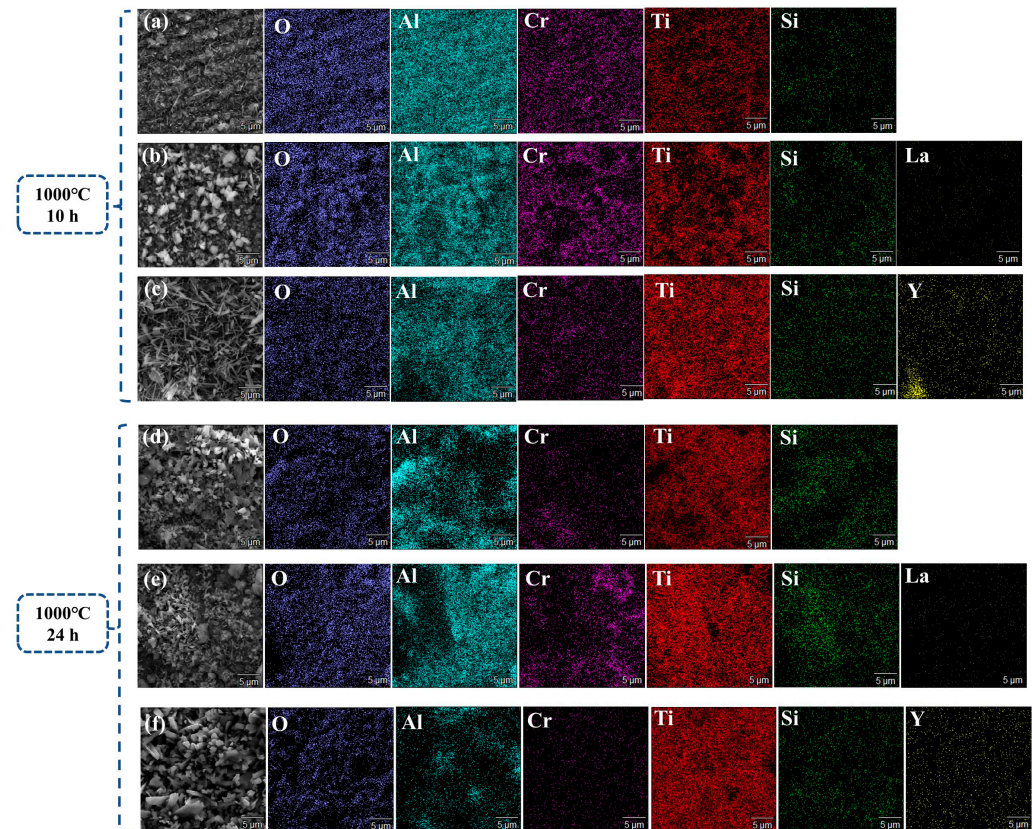


Figure 6. Oxide layers and the related chemical analyses by EDS maps for (a,d) AlCrTiSi_{0.2}, (b,e) AlCrTiSi_{0.2}La_{0.02}, and (c,f) AlCrTiSi_{0.2}Y_{0.02} following isothermal exposure to air for 10 and 24 h at 1000 °C.

Compared with AlCrTiSi_{0.2}La_{0.02} and AlCrTiSi_{0.2}Y_{0.02} HEAs, AlCrTiSi_{0.2} has the smallest mass increase after oxidation at 1000 °C for 53 h and has the best oxidation resistance. This demonstrates that the oxide layer covering the HEA's surface is a dense, layered oxide that can prevent further oxidation of the matrix by oxygen. The loose needle-like oxides found in the La and Y-doped high-entropy alloys fail to completely prevent the reaction of oxygen with the matrix and may even destroy the oxide layer, causing the oxide layer to separate.

The chemical compositions of oxide layers are listed in Table 3. Al₂O₃ and Ti oxide were the main components of layered and acicular substances, respectively. Compared with the matrix metals, the Cr and Si levels on the surface oxide layer of the three HEAs were significantly reduced. This may be due to Cr and Si being covered by Ti and Al oxide protective layers at high temperatures. On the other hand, it is possible that at high temperatures, Si and Cr elements decrease some of their content within the surface oxide layer due to inward diffusion. This phenomenon also occurred in the La and Y-doped HEAs. After oxidation at 1000 °C for 10 h, only trace rare earth elements were found in the oxide layer on the alloy surface, and these elements gradually vanished as the oxidation time extended.

3.3. Oxidation Mechanism of $\text{AlCrTiSi}_{0.2}\text{La}_{0.02}$ and $\text{AlCrTiSi}_{0.2}\text{Y}_{0.02}$ HEAs

The SEM mapping was used to gather cross-sectional images of all HEAs exposed to air at 1000 °C for 10 and 24 h to further examine the oxidation mechanism of HEAs, as shown in Figure 7. The gray portion on the right was the matrix metal, while the minor quantity of black on the left was the oxide layer. The surface oxide layer and matrix metal were securely bound, with no discernible space between them, as observed by the cross-section of $\text{AlCrTiSi}_{0.2}$ HEA (Figure 7a,b). With the addition of La and Y, the thickness of the oxide layer greatly increased, which increased the distance between the surface of the oxide layer and the matrix metal (Figure 7c,e). The doping of La and Y caused the internal erosion of the surface oxide layer, and oxygen would continue to erode the matrix metal as the oxidation duration increased (Figure 7d,f).

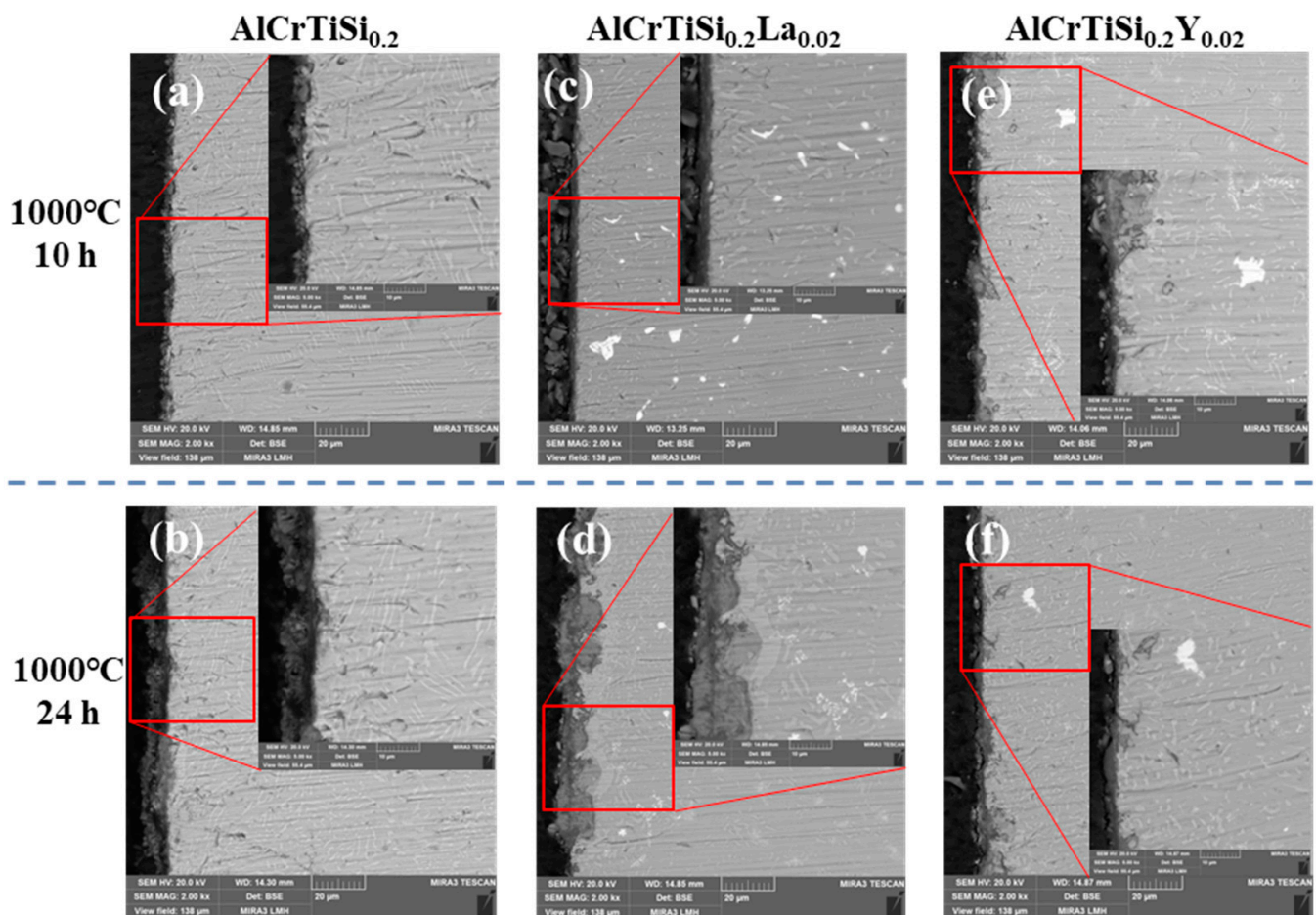


Figure 7. Cross-section images by SEM maps for (a,b) $\text{AlCrTiSi}_{0.2}$, (c,d) $\text{AlCrTiSi}_{0.2}\text{La}_{0.02}$, and (e,f) $\text{AlCrTiSi}_{0.2}\text{Y}_{0.02}$ following isothermal exposure to air after 10 and 24 h at 1000 °C.

The cross-section images by SEM mappings and chemical analyses by EDS line scan along the yellow line after isothermal exposure to air for 10 and 24 h at 1000 °C for $\text{AlCrTiSi}_{0.2}$ are given in Figure 8. As mentioned above, there was no clear pattern to the oxygen distribution in the surface oxide layer between 0–120 µm. However, it was obvious that the oxygen content near the oxide layer was higher. By observing the changes in Ti and Si contents in these three HEAs, it was found that the distribution behavior of Ti and Si in the alloy was similar. The composition analysis of surface oxides indicated that Ti and Si exhibited synergistic antioxidant corrosion resistance in the HEA system.

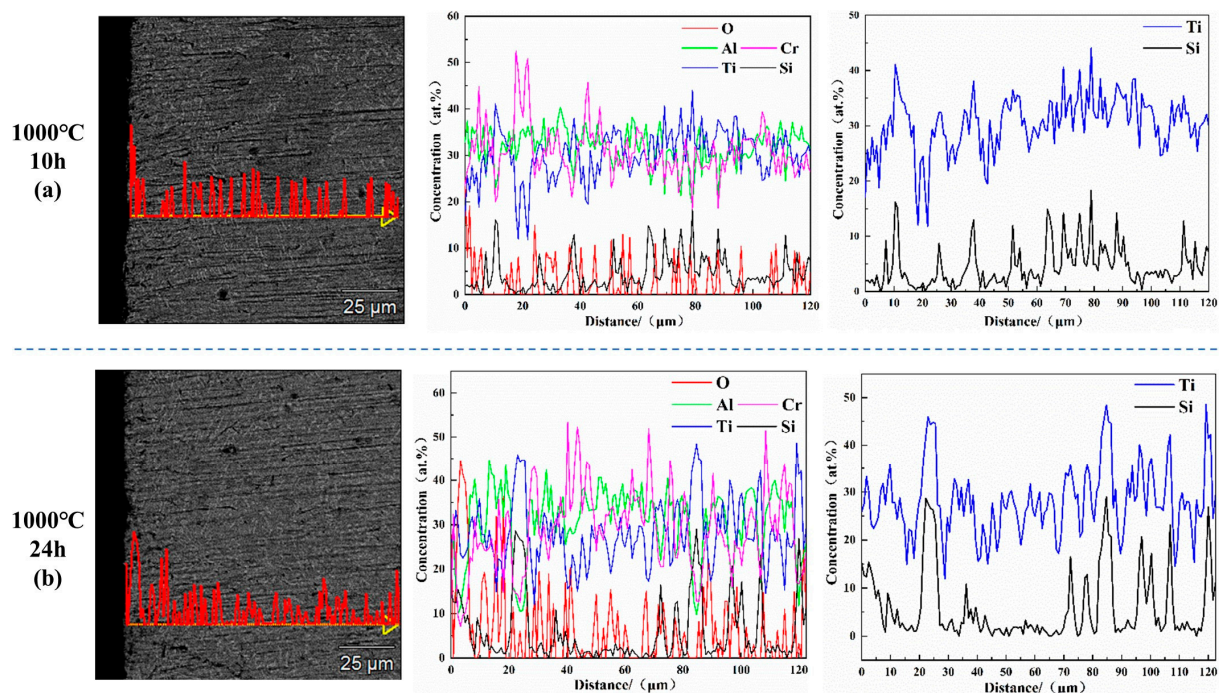


Figure 8. Cross-section images by SEM mappings and chemical analyses by EDS line scan along the yellow line (the red line is the change in oxygen content) after isothermal exposure to air for (a) 10 h at 1000 °C and (b) 24 h at 1000 °C for $\text{AlCrTiSi}_{0.2}$.

The cross-section images of $\text{AlCrTiSi}_{0.2}\text{La}_{0.02}$ and $\text{AlCrTiSi}_{0.2}\text{Y}_{0.02}$ HEAs after isothermal exposure to air for 10 and 24 h at 1000 °C by using SEM mappings and EDS line scans along the yellow line are given in Figures 9 and 10, respectively. Some white was discernible in the gray substratum of $\text{AlCrTiSi}_{0.2}\text{La}_{0.02}$ and $\text{AlCrTiSi}_{0.2}\text{Y}_{0.02}$. The primary components of the white part in $\text{AlCrTiSi}_{0.2}\text{La}_{0.02}$ were La and Al, according to the following SEM line scanning analysis (Figure 9a). As the oxidation time increased, the white portion steadily diminished, and the composition also changed. Based on a similar trend in the content of Ti and O in the white position, it was determined that the white part was titanium oxide. (Figure 9b). The main white components of $\text{AlCrTiSi}_{0.2}\text{Y}_{0.02}$ were Y and O, as shown in Figure 10a,b, indicating that oxygen penetrated into the matrix and solidly bonded with Y during the high-temperature process. The white part of the oxide layer confirmed that the oxide layer on the alloy surface was loose.

Figure 11 demonstrates the oxidation process mechanisms of the three HEAs. $\text{AlCrTiSi}_{0.2}$ HEA underwent an oxidation reaction to form an Al-rich oxide layer on the surface. Due to the dense oxide layer, it can prevent oxygen from further entering the matrix, confirming the antioxidant characteristic of HEA. During the high-temperature oxidation process, La and Y-doped $\text{AlCrTiSi}_{0.2}$ HEAs accelerated the outward diffusion of the Ti element, resulting in a partially porous oxide layer. Due to the significant affinity of rare earth metals for oxygen, rare earth metal oxides were formed when oxygen was absorbed into the metal. Rare earth metal oxides were also loose and not dense, and oxygen would continue to penetrate further into the matrix metal and form corresponding oxygen channels within the metal, as shown by the blue arrow in Figure 11. The surface oxide layer began to peel away from the metal surface due to poor adhesion leading to oxidation, indicating low oxidation resistance of HEA. The doping of La and Y will reduce the oxidation resistance of $\text{AlCrTiSi}_{0.2}$ HEA.

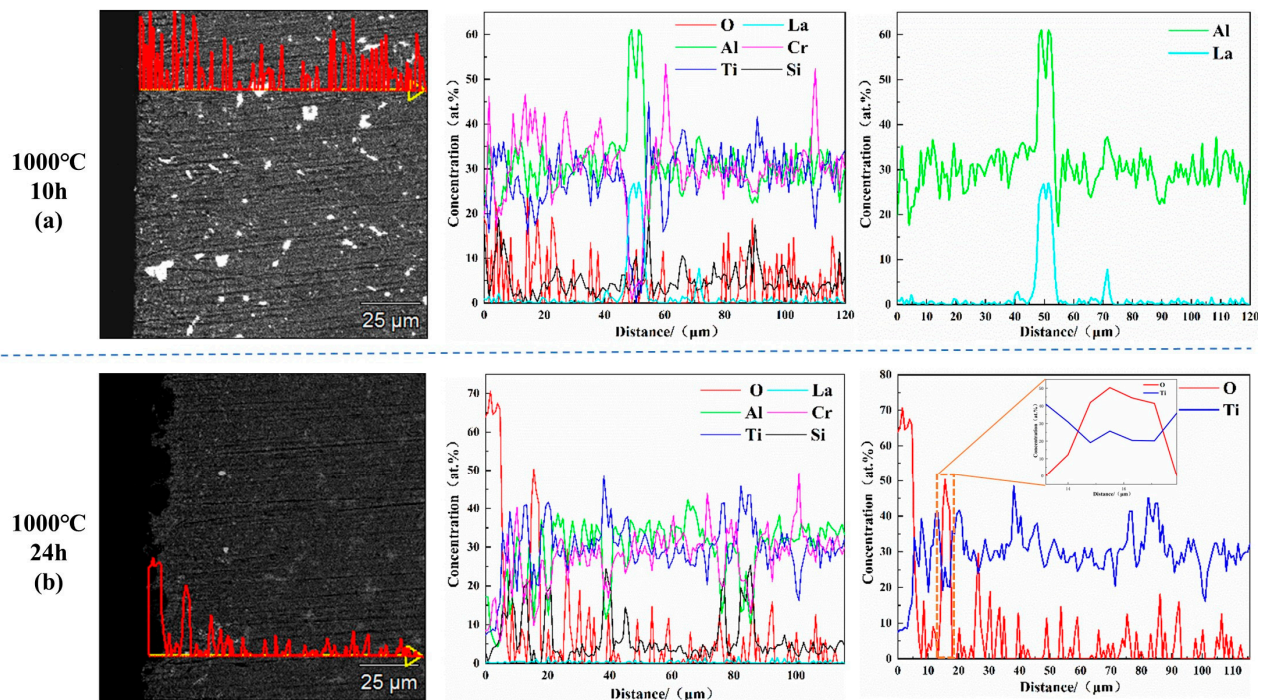


Figure 9. Cross-section images by SEM mappings and chemical analyses by EDS line scan along the yellow line (the red line is the change in oxygen content) after isothermal exposure to air for (a) 10 h at 1000°C and (b) 24 h at 1000°C for $\text{AlCrTiSi}_{0.2}\text{La}_{0.02}$.

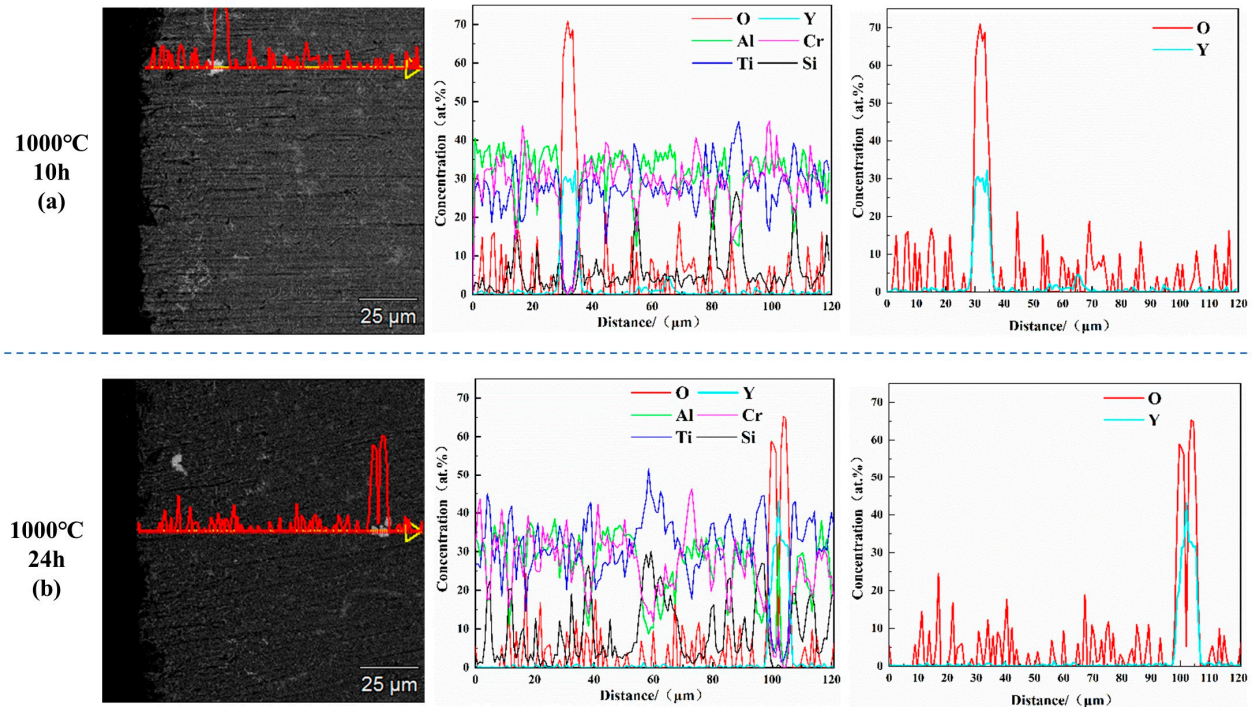


Figure 10. Cross-section images by SEM mappings and chemical analyses by EDS line scan along the yellow line (the red line is the change in oxygen content) after isothermal exposure to air for (a) 10 h at 1000°C and (b) 24 h at 1000°C for $\text{AlCrTiSi}_{0.2}\text{Y}_{0.02}$.

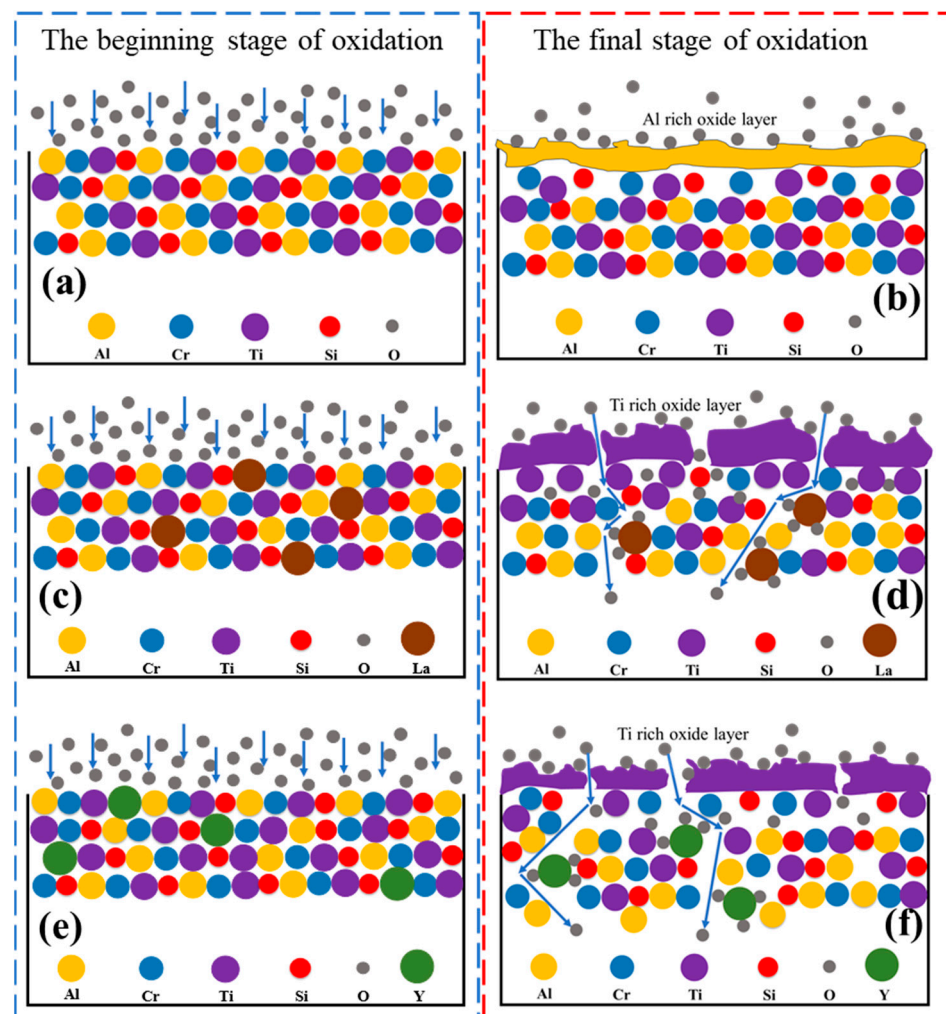


Figure 11. A schematic representation of oxide scale forming on the surface of (a,b) AlCrTiSi_{0.2}, (c,d) AlCrTiSi_{0.2}La_{0.02}, and (e,f) AlCrTiSi_{0.2}Y_{0.02} HEAs during 53 h for oxidation at 1000 °C. The left and right figures represent the beginning and final stages of oxidation, respectively.

4. Conclusions

Oxidation resistance is a critical indicator for high-temperature structural alloys. The effects of La and Y doping on the microstructure and oxidation behaviors of AlCrTiSi_{0.2} HEA were investigated in this work. All three HEAs contained FCC and HCP phases; doping La and Y boosted the peak intensity of the HCP phase but reduced the antioxidant resistance. After oxidation for 53 h at 1000 °C, AlCrTiSi_{0.2} demonstrated outstanding oxidation resistance, and its mass gain was only 1.195 mg/cm². The surface oxides of three alloys were Al₂O₃, TiO₂, and an unknown phase. The densely layered oxide component in AlCrTiSi_{0.2} HEA was mainly Al₂O₃, while the loose acicular oxide component in AlCrTiSi_{0.2}La_{0.02} and AlCrTiSi_{0.2}Y_{0.02} HEAs was mainly Ti oxide. The addition of La and Y made Ti diffuse outward, or Al diffuse inward, and the distance between the loose oxide layer and the matrix metal increased. As the oxidation time increased, oxygen would further corrode the matrix metal and produce rare earth oxides. Adding 0.621 at.% La and Y reduced the antioxidant resistance of AlCrTiSi_{0.2}.

Adding a small amount of rare earth elements to traditional alloys is usually beneficial for improving their oxidation resistance. However, this work found that the doping of La and Y reduced the antioxidant capacity of AlCrTiSi_{0.2} HEA. Reducing the amount of rare earth added or selecting suitable rare earth elements needs to be verified further.

Nevertheless, it is of great significance to study the effects of rare earths on the oxidation behavior of HEAs.

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