Effect of titanium addition on the oxidation resistance of Fe–13Cr-5Al-0.3Ti alloy in air between 700 °C–1100 °C

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Abstract
Cyclic oxidation tests were carried out on a Fe–13Cr–5Al–0.3Ti alloy over a temperature range of 700 °C–1100 °C in air. The composition and structure of the oxide layer were characterized by SEM and XRD, and the influence of temperature and Ti on the oxidation mechanism was analyzed. The results demonstrated that a dense α-Al2O3 oxide layer was formed on the surface of the substrate at 900 °C, which inhibited the outward diffusion of Ti and made the alloy more resistant to oxidation. However, when the temperature was increased to 1000 °C, the oxide layer could not effectively inhibit the outward diffusion of the Ti. In particular, the oxide formed on alloys treated 1100 °C was divided into two layers, where the inner layer was a dense α-Al2O3 oxide layer and the outer layer was TiO2 oxide layer.

1. Introduction

FeCrAl alloys are one of the most promising high-temperature alloys used in extreme environments, due to the formation of a stable α-Al2O3 oxide surface layer at high temperatures [1–5]. Moreover, the oxidation resistance of alloys is often influenced by the density and adhesion properties of the Al2O3 layer formed during the high-temperature thermal cycles [6–8]. Generally, the addition of other elements in the alloy has an important effect on the composition and structure of the oxide layer. For example, the addition of Cr increases the outward diffusion flux of aluminum, which helps form the Al2O3 film during the initial stages of oxidation [9, 10]. Furthermore, the inner α-Al2O3 layer is thought to nucleate on either Cr2O3 or Cr2-xFexO3 during the initial oxide formation [5]. Although the synergistic effects of Cr and Al improve the oxidation resistance of FeCrAl alloys, excessive amounts of Cr or Al can also deteriorate the mechanical properties of the FeCrAl alloys [11–14]. Therefore, it is very necessary to design a stable FeCrAl alloy that has a relatively low Cr and Al content. Currently, the State Key Laboratory of Oak Ridge has found that a Cr content less than 13 wt.% can effectively avoid ‘475 brittleness’ [15]. Qiao et al further indicated that 4 wt.% Al can form a continuous aluminum oxide layer when the Cr content is 13 wt.% [16].

As a trace active element, Ti is often added to Fe–13Cr–5Al alloys to improve the oxidation resistance and mechanical properties of the materials. Huang et al [17] studied the effect of Ti on the oxide layer of an FeCrAlY-ODS alloy, and believed that the oxide layer grew outward to form an isoaxial oxidation zone even with the addition of only 0.02 wt.% Ti. Moreover, a surface coating of TiO2 on the surface of FeCrAl alloys was observed to accelerate the formation of stable α-Al2O3 [18]. Geanta et al [19] showed that the number of TiO2 particles at the surface of the FeCrAl alloy increased with increasing Ti content. In addition, Ti can form stable compounds with impurities such as C and N in the alloy and thereby to inhibit their diffusion to the interface of alumina/ alloy [20].
Although it is known that adding Ti to FeCrAl alloys produces TiO₂ particles on the surface of the alloy during high-temperature oxidation processes, the effects of Ti addition on the growth mechanism and microstructure of oxide layer are not well known. Accordingly, in this work, the effect of adding 0.3 wt.% Ti on the high-temperature oxidation resistance of Fe–13Cr–5Al alloy was studied. Based on the oxidation behavior, the role of Ti on the high-temperature oxidation process of the Fe–13Cr–5Al–0.3Ti alloy was deeply analyzed and a growth mechanism of oxide layer in Ti-containing FeCrAl alloys is proposed.

2. Materials and methods

2.1. Sample preparation

The Fe–13Cr–5Al–0.3Ti alloy used in these experiments was produced by Taiyuan Iron and Steel Company (Taiyuan Iron and Steel, Taiyuan, China). It was smelted in a vacuum induction furnace and cast into a billet to obtain an alloy ingot of about 50Kg. After removing the surface oxide scale, the ingot was hot rolled to 4mm. The chemical composition is shown in Table 1. The sample was cut into 14 mm × 14 mm × 4 mm pieces using a wire cut electric discharge machine, ground with SiC abrasive paper from No. 120 to 1000 on each surface, and then ultrasonic cleaned with alcohol.

2.2. Cyclic oxidation tests

Before the oxidation tests, the weight and size of all samples were measured. The cyclic oxidation tests at 700 °C–1100 °C were conducted in a horizontal tube furnace in ambient atmosphere. Each sample was placed in the middle of the furnace for 20 h and then removed from the furnace and cooled to room temperature in air. After
the mass was measured using an electric balance, the sample was returned to the furnace for the next cycle of oxidation exposure.

2.3. Characterization method
The samples were etched with a solution containing K$_2$S$_2$O$_5$ (0.3 g), HCl (20 ml), and H$_2$O (80 ml), and the precipitate was observed using an Optical Microscope (OM, DMRM, LEICA, Shanghai Optical instrument.)
Table 2. Parabolic oxidation rate constants (kp) and activation energy calculation of Fe–13Cr–5Al–0.3Ti alloy in air.

| Alloy    | Temperature(K) | kp (g·cm⁻²·s⁻¹) | Fitting Similarity (R) | Fitting equation | Activation energy (kJ mol⁻¹) |
|----------|----------------|-----------------|------------------------|------------------|----------------------------|
| FeCrAl   | 1173           | 2.3069 × 10⁻¹⁰  | 0.92991                | Δm = 4.80 × 10⁻²t¹/² | 206.37                     |
|          | 1273           | 1.4645 × 10⁻¹²  | 0.99146                | Δm = 1.21 × 10⁻⁶t¹/² | 206.37                     |
|          | 1373           | 4.9899 × 10⁻¹²  | 0.99686                | Δm = 2.23 × 10⁻⁶t¹/² | 206.37                     |

Factory, Shanghai, China). The surface and cross-section oxide scale morphologies and compositions were observed by Scanning Electron Microscopy (SEM, EVO18, Carl Zeiss Jen, Oberkochen, Germany) and Energy Dispersive Spectroscopy (EDS). The phase compositions of the oxide scales were identified by x-ray diffraction (XRD, RIAGKU, UltimaIV) with a Cu Kα radiation source operating at 40 kV. The spectra were collected in a 2θ range of 20–80° with a step size of 0.02°.

3. Results

3.1. Microstructure of the alloy
The optical micrograph of the Fe–13Cr–5Al–0.3Ti alloy is shown in figure 1(a). The alloy showed a fully-ferritic microstructure under optical microscopy, with dispersions of TiC (the dark contrast particles) within ferritic matrix, as shown in figures 1(b) and (c).

3.2. Oxidation kinetics
Figure 2 shows the isothermal oxidation kinetic curves and corresponding square of weight gain versus oxidation time of the Fe–13Cr–5Al–0.3Ti alloy during the oxidation tests at 700 °C–1100 °C for 120 h. The weight gain curves of the alloy followed a parabolic trend, as shown in figure 2(a), indicating that the oxidation of the alloy was controlled by elemental diffusion [21]. The oxide weight gain per unit area was enhanced with increasing oxidation temperature. The parabolic rate constant (kp) as calculated by the weight gain per unit area of a sample (ΔW/A) and oxidation time (t) according to the following equation:

\[
(\Delta W/A)^2 = k_p t
\]

In the formula, ΔW/A represents the weight gain per unit area (g·cm⁻²), kp is the parabolic rate constant (g²·cm⁻⁴·s⁻¹), and t is the oxidation time (s). Figure 2(b) shows the fit results of the parabolic rate constant. It can be seen that the parabolic rate increased as the oxidation temperature increased. Table 2 summarizes the fitting results. The effect of temperature on the oxidation behavior of the alloy followed by the Arrhenius equation

\[
k_p = k_0 e^{-Q/RT}
\]

and taking the logarithm of equation (2)

\[
\ln (k_p) = -Q/RT + \ln (k_0)
\]

where k₀ represents the Arrhenius constant, Q represents the activation energy (kJ/mol), T represents the absolute temperature (K), and R is the general gas constant (8.314 J·K⁻¹·mol⁻¹). The oxidation activation energy was obtained by a linear regression analysis of plot of lnkp versus the reciprocal of temperature. As shown in figure 2(a), the activation energy was calculated to be 206.37 kJ mol⁻¹. The parabolic rate constant was similar to 3.0 × 10⁻¹² g²·cm⁻⁴·s⁻¹ for Fe–12Cr–6Al–ODS at 1100 °C and the activation energy was slightly higher than 177 kJ mol⁻¹ for Fe–12Cr–6Al–ODS in air [22].

3.3. Surface morphology after oxidation
Table 3 shows the surface appearance of the alloy surface under natural light after oxidation at different temperatures, and the appearance and color have changed significantly at the different temperatures. Figure 3 shows the surface morphology after oxidation at 700 °C and 800 °C for 20 h and 120 h respectively. Different sized oxidation particles randomly distributed on the surface of the samples. Further EDS analysis showed that the oxide particles were mainly composed of three elements: Fe, Cr, and Al, with the Fe content being the highest, followed by Cr and Al, as shown in table 4. The surface oxide particles were inferred to be Fe, Cr, Al mixed oxides at 700 °C–800 °C.
Table 3. Appearance of the sample after oxidation at 700-1100 °C for 120h under natural light.

| Temperature °C | 700 | 800 | 900 | 1000 | 1100 |
|---------------|-----|-----|-----|------|------|
| 700 °C        | ![Image](image1) | ![Image](image2) | ![Image](image3) | ![Image](image4) | ![Image](image5) |
| 800 °C        | ![Image](image6) | ![Image](image7) | ![Image](image8) | ![Image](image9) | ![Image](image10) |
| 900 °C        | ![Image](image11) | ![Image](image12) | ![Image](image13) | ![Image](image14) | ![Image](image15) |
| 1000 °C       | ![Image](image16) | ![Image](image17) | ![Image](image18) | ![Image](image19) | ![Image](image20) |
| 1100 °C       | ![Image](image21) | ![Image](image22) | ![Image](image23) | ![Image](image24) | ![Image](image25) |
The surface morphologies after different oxidation times at 900 °C–1100 °C are shown in figure 4. Table 5 shows the EDS point analysis of the oxidation particles (at.%) indicated by the arrows in figure 4. The number of surface oxidized particles gradually increased with oxidation time at 900 °C. The surface of the particles had staggered plate-like features as shown in figures 4(a) and (c). Further composition analysis showed that the composition of oxidation particles was mainly Al2O3. TiO2 particles appeared on the surface of the sample after 60 h of oxidation, as shown in figure 4(b) and table 5 No.2. After 120 h of oxidation, cluster-like Al2O3 particles were observed, and the top of the particles and the top of the particles still showed a plate-like characteristics. At 1000 °C, the surface of the substrate was covered with uniformly fine oxidized particles that gradually grew over time. The larger oxidized particles exhibited completely different morphological characteristics from alumina, the surface of the particles was flat and has obvious edges and corners, as shown in figure 4(e). Further composition analysis showed that this larger oxidized particles were titanium oxide, as seen in table 5 No.5. At 1100 °C, the number of oxidized particles on the sample surface increased rapidly with increasing oxidation time. Composition analysis showed that the oxide particles were Ti and Al oxides, as presented in table 5 No.6 and No.7, and TiO2 was the predominant oxide. In addition, the titanium oxide particles on the sample surface presented a cloud-like distribution after 60 h of oxidation. The TiO2 formed on the surface causes the macroscopic appearance of the samples at 1000 °C–1100 °C to be completely different from that at 900 °C, this is consistent with the high temperature oxidation of titanium alloy [23, 24].

3.4. XRD characterization of the surface oxides
To further analyze the phase composition of the surface oxide layer formed after oxidation, the sample surface was characterized with XRD after 120 h of oxidation (all the data in the figure 5 has been normalized and the background was subtracted using jade software), as shown in figure 5. Since the oxide layer was very thin after oxidation at 700 °C–800 °C, only the matrix peak was visible in the spectrum. At 900 °C–1100 °C, the peaks in the spectrum became more and more complicated as the temperature rose. At 900 °C, the main oxide diffraction peak was α-Al2O3, and a smaller TiO2 diffraction peak with very low intensity was also present. The small peak in the XRD supported that a small amount of TiO2 oxide was present in the oxide layer at 900 °C, and was consistent with the surface SEM results in figure 4. At 1000 °C, the intensity of the diffraction peak of TiO2 increases significantly, which was basically similar to the intensity of the α-Al2O3 peak. At 1100 °C, the diffraction peak of TiO2 became the most prominent peak, indicating that the TiO2 layer was thicker and that the x-rays count not the substrate. the TiO2 PDF card was PDF #71–1167, which corresponded to Rutile structure and belonged to Tetragonal, 141/amd(141). In addition, the diffraction peak of θ-Al2O3 appeared at 1000 °C–1100 °C, and the PDF card was PDF #11–0517, which corresponded to a transition phase and belonged to Monoclinic, C2/m(12).

3.5. Cross-sectional microstructures of the oxidized FeCrAl alloy
Cross-sectional SEM images of the FeCrAl alloy oxidized at 900 °C–1100 °C for 20 h and 120 h are shown in figure 6 and were used determine the thickness and morphological characteristics of the oxide layer. A thin and uniform oxide layer was formed on the surface after being oxidized at 900 °C for 20 h. Moreover, the thickness of

### Table 4. EDS point analysis of Oxidation particles (at.%) pointed by arrows in figures 3(a) and (c).

|    | O(%) | Al(%) | Cr(%) | Fe(%) | Ti(%) |
|----|------|-------|-------|-------|-------|
| 1  | 19.07| 4.77  | 6.49  | 36.88 | 0     |
| 2  | 47.68| 4.41  | 1.45  | 15.08 | 0     |

### Table 5. EDS point analysis of Oxidation particles pointed by arrows in figure 4.

|    | O (at.%) | Al(at.%) | Cr(at.%) | Fe(at.%) | Ti(at.%) |
|----|----------|----------|----------|----------|----------|
| 1  | 67.53    | 29.55    | 0.45     | 1.46     | 0.57     |
| 2  | 79.52    | 6.09     | 0.29     | 0        | 17.12    |
| 3  | 44.48    | 28.09    | 0.12     | 0.26     | 0        |
| 4  | 61.73    | 26.72    | 0.28     | 0.52     | 1.43     |
| 5  | 75.49    | 0.79     | 0        | 0.38     | 19.53    |
| 6  | 75.09    | 9.97     | 0        | 0.37     | 10.72    |
| 7  | 60.36    | 2.37     | 0        | 0        | 27.57    |
the surface oxide layer increased after 120 h of oxidation, and the oxide layer was uniform and dense without obvious impurities as shown in figure 6(b). After 20 h and 120 h of oxidation at 1000 °C, a uniform oxide layer was formed on the surface, and the oxide layer gradually thickened with increasing oxidation time. The oxide layer structure was different between the lower and higher oxidation temperatures. The contact interface between the oxide layer and the substrate had oxide micro-pegs of different sizes and a small number of in-scale voids were seen at 1000 °C, as shown in figure 6(d). After being oxidized at 1100 °C for 20 h, a compact oxide layer with uniform texture, and uniform thickness formed on the surface, similar to the oxide layer formed after oxidation at 900 °C for 120 h, as shown in figure 6(e). Oxide pegs with a size of approximately 10 μm appeared at the interface between the oxide layer and substrate after 120 h of oxidation. Although voids and impurity oxides of different sizes were seen in the middle and upper areas of the oxide layer, there were no impurities or voids in the area connecting the oxide layer and substrate, as shown in figure 6(f). Table 6 summarizes the average thickness statistics of the oxide layer formed after oxidation at 900 °C–1100 °C for 20 h and 120 h. The data show that the thickness of the oxide layer increased with the oxidation time and temperature.

Cross-sectional SEM-EDS mapping was used to further determine the distribution of the elements in the oxide layer. At 900 °C, the oxide was an aluminum oxide layer, and Ti was slightly enriched under the oxide layer. Moreover, Ti diffused to the surface to form discrete TiO₂ particles in individual areas, as shown in figure 7(a). At 1000 °C–1100 °C, the distribution Ti element was different from 900 °C. The oxide layer was divided into two layers: the inner layer was a uniform and dense α-Al₂O₃ layer, and the outer layer was a non-

![Figure 3. SEM images of the oxide surface morphology after oxidation at 700°C–800°C for 20 h and 120 h. (a) (b) 700 °C for 20 h and 120 h, respectively; (c) (d) 800 °C for 20 h and 120 h, respectively.](image)

| Temperature (°C) | Thickness (μm) |
|-----------------|----------------|
| 900 °C          | 1.2 2.0 2.5    |
| 1000 °C         | 2.0 4.0 7.3    |
| 1100 °C         | 2.2 4.0 7.3    |

Table 6. The average thickness of the oxide layer after oxidation at 900 °C–1100 °C for 20 h and 120 h (μm).
Figure 4. SEM images of the oxide surface morphology after oxidation at 900 °C–1100 °C for 20 h, 60 h and 120 h. (a) (b) (c) 900 °C for 20 h, 60 h and 120 h, respectively; (d) (e) (f) 1000 °C for 20 h, 60 h and 120 h, respectively; (g) (h) (i) 1100 °C for 20 h, 60 h and 120 h, respectively.

Figure 5. XRD pattern of Fe–13Cr–5Al–0.3Ti alloy after 120 h oxidation at 700 °C–1100 °C.
dense TiO₂ oxide layer because the majority of the Ti has diffused to the surface. In addition, small-scale cracks parallel to the oxide layer were seen on the upper part of the oxide pegs. These cracks may cause the outermost TiO₂ oxide layer to spall with the increasing oxidation time, but would not cause the substrate to be directly exposed to the oxidizing environment because the inner oxide layer was tightly interconnected to the substrate.

From figures 7(b) and (c), the center of the oxide micro-peg was TiO₂, and the outside was wrapped in a dense α-Al₂O₃ layer, which prevented the oxide pegs from growing rapidly and may improve the oxide scale adherence because of the pinning effect.

Figure 8 and figure 9 show the cross-section line scans of the FeCrAl alloy at 900 °C and 1100 °C for 20 h, 60 h, and 120 h, respectively, and provide further insights into the growth of the oxide layer and the element diffusion processes. Generally, the location of the greatest variation in element content could be considered as the interface. According to the position of the interface, the thickness of the oxide layers could also be seen, which is basically consistent with figure 6. The Fe and Cr content dropped rapidly while the Al content rose rapidly at the substrate/oxide layer interface, indicating that oxide layer was predominantly composed of aluminum oxide after oxidation at 900 °C for 20 h, as seen in figure 9(a). It is worth noting that a small amount of Ti was concentrated at the matrix/oxide layer interface after 60 h and 120 h oxidation. This was consistent with the results in figure 7(a), indicating that the oxide layer effectively inhibited Ti outward diffusion at 900 °C. The biggest difference between the 1100 °C line scan and the 900 °C line scan was the appearance of two interfaces. The two interfaces were caused by the Ti diffusion to the surface of the oxide layer at 1100 °C. The

![Figure 6. SEM images of the cross-section oxide scale morphology after oxidation at 900 °C–1100 °C for 20 h and 120 h.](image)
oxide layer was still dominated by alumina after 20 h oxidation, which was consistent with the surface morphology in figure 4(g). However, an oxide layer dominated by TiO₂ appeared on the outermost layer after oxidation for 60 h, which was also consistent with figure 4(h). With oxidation times greater than 60 h, the TiO₂ layer gradually thickened with increasing oxidation time, but the thickness of the internal Al₂O₃ layer did not change significantly, indicating that the oxidation weight gain was primarily from the TiO₂ formed on the surface after being oxidized at 1100 °C for 60 h.

4. Discussion

4.1. Growth mechanisms at different temperatures based on the microstructure and composition analysis of the formed oxide layers

From the experimental results, the oxidation of Fe-13Cr-5Al-0.3Ti at 700 °C–1100 °C can be divided into three temperature stages: 700 °C–800 °C, 900 °C and 1000 °C–1100 °C. In the first stage from 700 °C–800 °C, the sample surface still had a metallic luster after 120 h oxidation, as shown in figure 2(a). With increasing oxidation times, the oxidation weight gain did not change significantly, as can be seen in figure 2(a), indicating that the
oxide layer formed on the surface could effectively protect the substrate. Similarly, Suzue Yoneda et al. studied the initial oxide layer formed on Fe–Cr–Al ternary alloys, and showed that first a transient (Fe, Cr)2O3 oxide layer was formed during the initial stages of oxidation and, an Al-or (Al, Cr)-amorphous oxide film was formed under the transient oxide layer. In addition, in conjunction with Figure 4(d), there were smaller oxidized particles on the surface of the samples, which may be the initial alumina particles.

Figure 10 shows the mechanism of the oxide layer at 900 °C and 1100 °C. Within 20 h of the initial oxidation, the oxygen in the air rapidly reacts with the metal elements. It is worth noting that because the Cr addition increased the outward diffusion flux of aluminum in the alloy [9, 10] and the concentration of Al in the matrix was higher than that of Ti, a dense α-Al2O3 oxide layer was formed at both temperatures. In addition, because the alloy matrix originally contained a large number of TiC precipitates of different sizes, and TiO2 particles appeared in the positions of the precipitates. As shown in Figure 10(a), Al and Ti gradually diffused outward with increasing oxidation time at 900 °C, but the aggregation of Ti at the oxide layer/matrix interface indicated that the α-Al2O3 oxide layer could effectively inhibit the outward diffusion of Ti, as shown in Figure 7(a) and Figures 8(b) and (c). In addition, there were plate-like Al2O3 particles on the surface of the oxide layer. The number of particles increased with an increase in oxidation time, and the particles grew into clusters.

The oxidation growth mechanism of FeCrAl at 1100 °C is summarized in Figure 10(b). There were more TiO2 particles on the surface at the initial stage of oxidation compared to 900 °C, as shown in Figure 4(g). Subsequently, with the outward diffusion of Al element, TiO2 particles formed at the initial TiC position are
wrapped by Al₂O₃, as shown in figure 7 and figure 10(b). The TiO₂ growth rate on the surface accelerated with an increase in temperature and gradually formed a cloud-like distribution, until a layer of TiO₂ oxide layer finally formed on the surface, as shown in figures 4(h) and (i). As a result, the oxide layer was divided into two layers at 1100 °C, the inner layer was the α-Al₂O₃ oxide layer that grew first and the outer layer was the TiO₂ oxide layer that gradually grew with increasing oxidation time. It is worth noting that a large number of voids appeared in the TiO₂ oxide layer and small-scale cracks appeared at the position of the larger oxide pegs, indicating that the excessive size of the TiC precipitates on the surface had a negative effect on the oxidation resistance of the alloy.

In contrast to 900 °C, at 1100 °C, the α-Al₂O₃ oxide layer initially formed cannot inhibit the outward diffusion of Ti element, which may be related to the increase in oxidation temperature.

4.2. Effects of adding Ti on the growth of the Fe-13Cr-5Al-0.3Ti alloy oxide layer

It can be seen from the cross-sectional line scans in figure 9 that a small amount of Ti aggregated at the oxide layer/alloy interface, and Ti did not exist as TiO₂ oxide particles after 60 h oxidation at 900 °C. Conversely, TiO₂ exhibited cloud-like accumulation after oxidation at 1100 °C for 60 h, as shown in figure 4(h). This indicates that Ti diffusion is a process, which is reflected in that Ti first diffuses from the matrix to the oxide layer/matrix interface, and then diffuses to the surface. This process takes a certain amount of time. In Fe-13Cr-5Al-0.3Ti alloy, this process needs about 60 h. In addition, a large number of Ti diffuse to the surface of the oxide layer at 1100 °C, indicating that the diffusion coefficient of Ti is greater than Al, in combination with the results of Ni-based superalloy [26].

Transition state Al₂O₃ particles with a plate-like structure appeared on the surface at 900 °C [18], as shown in figures 4(a) and (c), indicating that the oxide layer grew outwardly. The morphology of the α-Al₂O₃ oxide layer formed after being oxidized at 1100 °C for 20 h was very similar to the layer formed at 900 °C which can be seen in conjunction with figure 6(e). The difference was that there were more defects at 1100 °C than 900 °C, and there was no accumulation of Ti at the substrate/oxide layer interface, indicating that the oxide layer can no longer inhibit the outward diffusion of Ti at 1100 °C. It can be seen from the XRD analysis in figure 5 that the θ
- $\text{Al}_2\text{O}_3$ peak appeared at 1100 °C, which also supported that the oxide layer grew outwards. This result is contrary to the conclusion that the oxide layer grows inward in some works, [27, 28] but similar with results by Huang et al [17]. Who studied FeCrAl-ODS with added Ti. In addition, the connection between the TiO$_2$ outer layer and the Al$_2$O$_3$ inner layer was not dense, which was not conducive to maintaining a stable outer oxide layer long-term. Fortunately, the inner $\alpha$-Al$_2$O$_3$ oxide layer was closely connected to the metal substrate, which could effectively protect the substrate.

5. Conclusions

After oxidizing the Fe-13Cr-5Al-0.3Ti alloy at 700 °C-1100 °C for 120 h in an atmospheric environment, using SEM-EDS, XRD analysis and testing, combined with the cross-section morphology, composition, surface morphology, and composition analysis, the following conclusions can be drawn:

(1) During the oxidation process, the oxide layer did not fall off, indicating that the alloy can be used normally within the scope of the experiment. But after oxidation at 1100 °C, the oxide layer was divided into two layers, with an outer TiO$_2$ oxide layer, and an inner $\alpha$-Al$_2$O$_3$ layer. The connection between the outer and inner layers was not dense, which was not conducive to maintaining a long-term, stable outer layer.
(2) At 900 °C, the inner $\alpha$-$Al_2O_3$ oxide layer could inhibit the outward diffusion of Ti to some extent, but had no such effect at 1100 °C. Ti diffusion is a process, which is reflected in that Ti first diffuses from the matrix to the oxide layer/matrix interface, and thendiffuses to the surface. This process takes a certain amount of time. In Fe-13Cr-5Al-0.3Ti alloy, this process needs about 60 h.

(3) Addition of 0.3wt.% Ti changed the growth mechanism of the oxide layer and caused the oxide layer to grow outward, forming transition state $Al_2O_3$ particles and $TiO_2$ particles.

(4) The oxide pegs may be related to the precipitation of TiC in the alloy matrix. TiC precipitates too large in size are not conducive to improving the oxidation resistance of the alloy.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

Conflict of interest

The authors declare no financial or commercial conflict of interest.

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References

[1] Rebak R B, Gupta V K and Larsen M 2018 JOM 70 1484
[2] Park D J, Kim H G, Park J Y, Jung Y I, Park J H and Koo Y H 2015 Corr. Sci. 94 459
[3] Unocic K A, Esuaman E, Dryepondt S and Pint B A 2012 Mater High Temp. 29 171
[4] McCarron F E, Le Fontaine A, Nguyen T D, Smith A F, Zhang J, Young D J and Cairney J M 2018 Corr. Sci. 139 267
[5] Liu F, Götlinger H, Svensson J E, Johansson L G and Halvarsson M 2018 Corr. Sci. 50 2272
[6] Hou P Y and Am J 2003 Ceram. Soc. 86 660
[7] Matéchel L, Lesage B, Huntz A M and Molins R 2003 Oxid. Met. 60 1
[8] Stott F H and Hiramatsu N 2000 Mater High Temp. 17 93
[9] Yoneda S, Hayashi S, Saeki I and Ukiy S 2016 Oxid. Met. 86 557
[10] Yoneda S, Hayashi S, Saeki I and Ukiy S 2018 Oxid. Met. 89 81
[11] Yamamoto Y, Gussev M N, Kim B K and Byun T S 2015 ORNL. https://info.ornl.gov/sites/publications/files/Pub38117.pdf ORNL/ TM-2015/414
[12] Yamamoto Y, Pint B A, Terrani K A, Field K G, Yang Y and Sneed L L 2015 J. Nucl. Mater. 467 703
[13] Gussev M N, Field K G and Yamamoto Y 2017 Mater. Des. 129 227
[14] Vicente A D A, Moreno J R S, Espinosa D C R, Santos T F D A and Tenório J A S 2019 J. Mater Res Technol. 8 1636
[15] Yamamoto Y, Pint B A, Terrani K A, Field K G, Yang Y and Sneed L L 2015 J. Nucl. Mater. 467 703
[16] Qiao Y et al 2020 J. Alloys Compd. 828 154310
[17] Huang T, Naumenko D, Song P, Lu J and Quadakers W J 2018 Oxid. Met. 90 671
[18] Galerie A, N'Dah E, Wouters Y and Roussel-Dherbey F 2008 Mater. Corros. 59 423
[19] Geanta V, Voiculescu I and Stanciu E M 2016 IOP Conf. Series: Mat. Sci. Eng. A-Struct. 133, 1
[20] Gray T H 1997 Proc. of Int. Conf. on Metal Supported Automotive Catalytic Converters (MACC’97) ed H Bode (Frankfurt-am-Main: Werkstoff-Informations gesellschaft mbH) p 47 https://www.osti.gov/etdeweb/biblio/349639
[21] Hou X M, Chou K C and Eur J 2009 Ceram. Soc. 59 17–23
[22] Lipkina K, Hallatt D, Geiger E, Fitzpatrick B W N, Sakamoto K, Shibata H and Piro M H A 2020 J. Nucl. Mater. 541 152305
[23] Liang X M, Chen M H, Su N and Luo F 2019 Titanium Industry Progress. 36 2
[24] Xiang W Y, Jiang H T and Tian S W 2020 Metallic Functional Materials. 27 3
[25] Chen H, Kim S H, Long C, Kim C and Jang C 2018 Prog. Nat. Sci.- Mater. 28 731
[26] Zhu Y X, Li C, Liu Y C, Ma Z Q and Yu H Y 2020 J. Iron Steel Res. Int. 27 1179–89
[27] Yang Z, Pan J, Wang Z, Wu Y, Jia G, Li J and Xiao X 2020 Corr. Sci. 172 108728
[28] Li J, Cao G, Wang H, Zhang W, Li C, Wang G and Liu Z 2020 Corr. Sci. 174 108796