High temperature oxidation behavior and mechanism of FeXCr0.5Ti ferritic stainless steels

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Abstract

In order to investigate the oxidation mechanism of ferritic stainless steel during long-term oxidation at high temperature. The oxidation behavior of Fe-Cr-Ti ferritic stainless steels with 10.38 wt% Cr and 17.41 wt% Cr at 800 °C and 900 °C for 100 h was studied by a constant temperature weight gain method. The morphology and composition of the oxide film were characterized by SEM, EDS and XRD. The experimental results indicate that the oxygen element mainly diffuses inward at 800 °C for two stainless steels, and the oxide film is composed of \((\text{Cr}_{1.3}\text{Fe}_{0.7})\text{O}_3 + \text{MnCr}_2\text{O}_4\). When the temperature rises to 900 °C, metal element mainly diffuses outward, and \(\text{Fe}_2\text{O}_3\) outer oxide layer and Fe rich Fe-Cr inner oxide layer are formed in Fe11Cr0.5Ti stainless steel; \(\text{Cr}_2\text{O}_3 + \text{Cr}\text{rich Mn}_2\text{O}_4\) spinel oxide film is formed in Fe18Cr0.5Ti stainless steel, while the inner layer is composed of SiO2. The main reason for the significant decrease of oxidation resistance of Fe11Cr0.5Ti stainless steel is that the low content of Cr cannot form a Cr rich oxide layer to inhibit the outward diffusion of Fe element, and the stability of oxide film is poor to protect the matrix.

1. Introduction

In the last decades, with the rapid increase of stainless steel demand, nickel resources are becoming scarce, and the traditional austenitic stainless steel is gradually replaced by nickel-free ferritic stainless steel [1–3]. Ferritic stainless steel exhibits excellent corrosion resistance and high temperature oxidation resistance, with low cost, high thermal conductivity and small thermal expansion coefficient, and is therefore widely used in automobile, energy, home appliances and other fields. Hence, it has become an energy-saving green stainless steel material [4–8].

High temperature oxidation resistance is one of the important indexes of stainless steel in high temperature service [9, 10]. Ferritic stainless steels with different chemical compositions are distinct from oxidation products and oxide film structures, and therefore the causes of high temperature failure are also different. In recent years, material researchers have done a lot of research work on the oxidation behavior of stainless steel. Vicente et al [11] studied the oxidation kinetics of EN1.4509 ferritic stainless steel at high temperature with different time. By comparing the surface morphologies of stainless steel after oxidation for 8 min and 24 h, it is found that the oxidation products grow in an octahedral shape, and the particle size of oxidation products increases with the extension of oxidation time. Serra et al [12] studied the growth kinetics and composition of the film formed on the surface of stainless steel after short-term oxidation at different temperatures. It is proved that the oxide film is mainly composed of Cr element on the surface of stainless steel after oxidation at 850 °C for 2 h. The oxide film is mainly composed of Fe element above 900 °C, and the contents of Ti, Si and other elements are low, and the oxidation rate rises with increasing the temperature. Salgado et al [13] conducted a comparative study on the oxidation behavior of AISI441 ferritic stainless steel at high temperature and different oxygen partial pressure for 50 h, and found that the growth of oxide film on the surface of stainless steel followed the parabolic law under all test conditions. The oxidation resistance of stainless steel in synthetic air is higher than that in 1 ppm O2 + Ar atmosphere. In the synthetic air at 850 °C, there is no continuous and dense oxide film on the surface of stainless steel, and the oxidation products are mainly composed of MnCr2O4 spinel and TiO2. The content of Cr in oxide
Table 1. Chemical compositions of two stainless steels (wt.%).

| Element | C   | Si  | Mn  | Cr  | Ti  | Fe   |
|---------|-----|-----|-----|-----|-----|------|
| Fe11Cr0.5Ti | 0.022 | 0.47 | 0.21 | 10.38 | 0.46 | Bal. |
| Fe18Cr0.5Ti | 0.022 | 0.47 | 0.21 | 17.41 | 0.46 | Bal. |

film increases with the increase of temperature. Yan et al. [14] studied the oxidation behavior of 9Cr5Si ferritic heat-resistant steel after 90 h cyclic oxidation in air at high temperature, and found that the value of oxidation rate constant $K_p$ increased by an order of magnitude with the increase of temperature, and the oxidation rate increased significantly. The phase in the outer layer of the oxide film does not change and is composed of Cr$_2$MnO$_4$ + Cr$_2$O$_3$ phase.

Exploring the high temperature oxidation behavior of ferritic stainless steel for a long time is not only of great significance for theoretical research, but also provides reliable data support for its application in the manufacturing of hot end components of exhaust system. In this work, the oxidation behavior of two Fe-Cr-Ti ferritic stainless steels with different Cr contents was studied at 800 °C and 900 °C for 100 h so as to investigate the oxidation kinetics, analyze oxidation products and oxide film structure and reveal the oxidation mechanism.

2. Experimental methods

A Fe-Cr-Ti ferritic stainless steel plate with 10.38 wt.% Cr and 17.41 wt.% Cr was used as an experimental material in this study, and the thickness of the plate was 1.2 mm and the chemical composition was given in table 1. The oxidation test sample was in a rectangular shape with the size of 60 mm $\times$ 30 mm cut by a shear plate. In order to avoid the error caused by the collapse of oxide scale on the surface of the sample during the experiment, a cylindrical corundum crucible with a diameter of 50 mm was selected to hold the sample. The data weighed before and after the experiment were the total mass of the samples and crucible. Before the oxidation experiment, the sample and corundum crucible should be pretreated to ensure that there was no oxide scale on the surface of the sample and the weight of the crucible was constant during the whole oxidation process. Firstly, the sample was polished with 600 $\#, 1000 \#, 1500 \#, 2000 \#$ SiC water sandpaper to remove the oxide scale on the surface. Then, the sample was ultrasonically cleaned in ethanol for 5 min and dried by a cold air blower. Finally, the sample was dried in a 150 °C–200 °C drying oven. After 1 h, the sample was taken out and put into a drying dish and cooled to room temperature for standby. The corundum crucible needed to be roasted repeatedly in a 1000 °C resistance heating furnace to remove the moisture and impurities until its weight was constant, and then put it into a dryer for standby. A micrometer was used to accurately measure the surface size of the cooled sample, and the surface area was calculated. The total weight of sample and corundum crucible before and after high temperature test was weighed by a BS124S electronic analytical balance. The experimental equipment was SX-4-10 box resistance furnace. The temperature difference between the furnace and digital display temperature was ±1 °C.

This experiment was a continuous constant temperature oxidation experiment, and the oxidation rate was measured by a discontinuous weighing mode. The oxidation temperature was 800 °C and 900 °C, the longest oxidation time was 100 h, and the weighing time was 5 h, 10 h, 15 h, 20 h, 30 h, 50 h, 75 h and 100 h. Three parallel samples were selected at each temperature and weighing time, and each sample was weighed three times to take the average value. After the oxidation test, the oxidation weight gain per unit area was calculated, the oxidation kinetics curve was drawn, and the oxidation kinetics model was analyzed.

The surface morphologies of the samples after high temperature oxidation were characterized by a GeminiSEM 300 field emission scanning electron microscope, and the surface element distribution was measured by EDS. An XRD-7000 X-ray diffractometer was utilized to analyze the phase of the oxide film on the surface of the sample after high temperature oxidation. The x-ray tube was irradiated by K$\alpha$ of Cu target, the tube voltage was 40 kV, the tube current was 45 mA, 2$\theta$ equaled to 20°–100°, and the step size was 4 (°)/min.

3. Results and analysis

3.1. Oxidation kinetics analysis

Figure 1 shows the oxidation kinetics curve of Fe11Cr0.5Ti and Fe18Cr0.5Ti stainless steels after continuous oxidation in air at 800 °C and 900 °C for 100 h. The oxidation kinetics curve of Fe11Cr0.5Ti ferritic stainless steel at 800 °C is similar to parabolic law. The oxidation kinetics curve at 900 °C is a parabola in the first 15 h, while in the last 85 h the oxidation weight gain is significantly accelerated, showing a linear characteristic. After
100 h continuous oxidation, the weight gain is 110.62 mg·cm$^{-2}$, which is 84 times of 1.12 mg·cm$^{-2}$ at 800 °C. This indicates that Fe11Cr0.5Ti stainless steel has good oxidation resistance at 800 °C, abnormal oxidation occurs at 900 °C, and oxidation weight gain increases significantly. The results show that the Fe18Cr0.5Ti stainless steel with high Cr content has no rapid oxidation phenomenon in the process of continuous oxidation at 800 °C and 900 °C, and the oxygen gain is 0.335 mg·cm$^{-2}$ and 1.31 mg·cm$^{-2}$ after oxidation for 100 h, respectively. The oxidation kinetics curve is parabolic. By comparing the oxidation kinetics curves of two ferritic stainless steels at the same temperature, it is found that the oxidation weight gain of Fe11Cr0.5Ti ferritic stainless steel at the end of oxidation is higher than that of Fe18Cr0.5Ti stainless steel, which indicates that the increase of Cr content can improve the high temperature oxidation resistance of Fe-Cr-Ti ferritic stainless steel in air.

When the oxidation kinetics curve of metal materials conforms to the parabolic law, the growth process of oxide film is related to the diffusion of elements. Metal cations generated at the metal/oxide interface diffuse outward through the oxide layer, O$_2$ is reduced to O$^-$ at the air/oxide interface, and O$^-$ ions diffuse inward through the oxide/metal interface. Oxidation is controlled by cation diffusion and/or oxygen through the oxide film. The film has good oxidation resistance [15]. According to the Kofstad [16] and Arrhenius formula, the oxidation kinetics model is established as shown in equation (1), the relationship between the oxidation rate constant and the activation energy of steel grade is shown in equation (2), and the logarithm of the left and right sides of the equal sign of equations (1)–(2) is taken as shown in equations (3)–(4).

$$\Delta m^n = K_p t$$  
$$K_p = K_0 \exp\left(-\frac{Q}{RT}\right)$$  
$$\ln \Delta m = \frac{\ln t}{n} + \frac{\ln K_p}{n}$$  
$$\ln K_p = \ln K_0 + \left(-\frac{Q}{R}\right)\frac{1}{T}$$

Where, $\Delta m$ is the oxidation weight gain per unit area (mg·cm$^{-2}$), $n$ is the oxidation rate index, $t$ is the oxidation time (h), $K_p$ is the oxidation rate constant (mg$^2$·cm$^{-4}$·h$^{-1}$), $K_0$ is the constant, $Q$ is the oxidation activation energy (kJ·mol$^{-1}$), $T$ is the oxidation temperature (K), and $R$ is the gas constant, which is 8.314 J·mol$^{-1}$·K$^{-1}$. Regression analysis was carried out on the experimental results in accordance with the parabolic law in the oxidation kinetics curve by using equations (3)–(4), and the $n$, $K_p$ and $Q$ values of two stainless steels at different temperatures were obtained. The results are shown in figures 2, 3 and table 2. It can be seen that with the increase of temperature, the oxidation rate constant $K_p$ value of two stainless steel at 900 °C is higher than that at 800 °C, and the oxidation resistance decreases; at the same temperature, the higher the Cr content of stainless steel is, the closer the oxidation rate index $n$ value approaches 2, the smaller the oxidation rate constant $K_p$ value is, the greater the oxidation activation energy $Q$ value is, and the higher the high temperature oxidation resistance is. The oxidation kinetics curve is affected by many factors, such as the porosity of the oxide layer, the adhesion between the oxide layers, the defects on the surface of the oxide layer, etc, so the parabolic law only exists under ideal conditions [17]. The closer the oxidation rate index $n$ approaches 2, the more the oxidation kinetics curve is close to parabola, and the better the oxidation resistance is.
3.2. XRD phase analysis

Figure 4 shows the XRD analysis results of surface oxidation products of Fe11Cr0.5Ti and Fe18Cr0.5Ti stainless steels after continuous oxidation at different temperatures for 100 h. The results show that the oxide film of Fe11Cr0.5Ti stainless steel is thinner at 800 °C, the diffraction peak of Fe-Cr matrix is obvious, and the main oxidation product is MnCr2O4 + (Cr1.3Fe0.7)O3. While the oxide film is thicker at 900 °C, the peak of Fe-Cr matrix disappears completely, and the oxidation product transforms into pure Fe oxide Fe2O3. This shows that the oxidation resistance of Fe11Cr0.5Ti stainless steel decreases sharply with the increase of temperature. When a thick Fe2O3 oxide layer is formed on the surface of the sample, the x-ray cannot penetrate, but it is not dense and has no ability to protect the matrix. At high temperature, the adhesion of Fe2O3 oxide layer is weak, and a
large number of oxidation holes appear on the interface between Fe₂O₃ oxide layer and matrix, which reduces the bonding strength of oxide film and matrix at the interface as well as the oxidation resistance of stainless steel. The surface oxidation product of Fe₁₈Cr₀.₅Ti stainless steel is MnCr₂O₄ + (Cr₁.₃Fe₀.₇)O₃ after continuous oxidation at 800 °C for 100 h. When the temperature rises to 900 °C, the oxidation film thickness increases, and the oxidation product is composed of MnCr₂O₄ + Mn₁₅Cr₁₃O₄ + Cr₂O₃, the diffraction intensity of the Fe-Cr matrix peak decreases, and the diffraction intensity of MnCr₂O₄ peak increases. The Mn₁₅Cr₁₃O₄ peak with lower diffraction intensity appears, and the (Cr₁.₃Fe₀.₇)O₃ peak changes to Cr₂O₃ peak, and the intensity increases. Because the radius of Cr/Fe ions is very similar, the position of (Cr₁.₃Fe₀.₇)O₃ peak in XRD pattern will coincide with Cr₂O₃ peak, and its specific composition can be determined by EDS analysis of surface oxidation products. Mn₁₅Cr₁₃O₄ and MnCr₂O₄ are close packed cubic crystals of oxygen ions, which are isomers of each other. They both belong to M₃O₄ spinel structure, which can hinder the diffusion of elements. The oxide film composed of Mn₁₅Cr₁₃O₄ and MnCr₂O₄ has good protection effect. It is found from figure 4 that the diffraction intensity of Fe-Cr matrix peak of Fe₁₁Cr₀.₅Ti stainless steel at 800 °C and Fe₁₈Cr₀.₅Ti stainless steel at both 800 °C and 900 °C has no significant change, the growth rate of oxide film is low, and the oxide layer is thin; the surface oxidation products are similar, which are mainly Cr/Mn oxide M₃O₄ + Cr rich oxide M₂O₃. The increase of Cr content does not change the element type of oxidation products, but changes the oxygen content. The ratio of the strongest peak of the product to the strongest peak of the matrix was 0.37, 0.17 and 0.76, respectively. On the other hand, the increase of Cr content will reduce the thickness of oxidized stainless steel surface and increase the oxidation resistance of stainless steel at 800 °C; Fe₁₈Cr₀.₅Ti stainless steel has better oxidation resistance at 900 °C and below, and the oxidation resistance decreases with the increase of oxidation temperature.

3.3. Micro morphology analysis
Figure 5 shows the surface morphology and element distribution of Fe₁₁Cr₀.₅Ti and Fe₁₈Cr₀.₅Ti stainless steels after continuous oxidation at different temperatures for 100 h, and table 3 shows the EDS analysis results of stainless steel surface oxidation products. Figures 5(a) and (b) are the surface morphology and element distribution of Fe₁₁Cr₀.₅Ti stainless steel after oxidation at 800 °C for 100 h. There are many fine oxide particles on the surface of the sample. The energy spectrum results show that the surface oxide layer is mainly rich in Cr and Fe elements, and the oxidation products are corundum type Cr–Fe oxide and nodular Cr–Mn oxide. In addition, large white granular oxides can be observed in the grain or at the grain boundary. These oxides are rich in Ti and mainly Ti oxides. Nodular Cr–Mn oxide is composed of spinel like Cr–Mn oxide particles, which cover the surface of the matrix to isolate the metal from the air and slow down the oxidation process. Figures 5(c) and (d) are the surface morphology and element distribution of Fe₁₈Cr₀.₅Ti stainless steel after oxidation at 800 °C for 100 h. Compared with Fe₁₁Cr₀.₅Ti stainless steel, the oxide film is more compact, there are few nodular oxides with larger particles at the grain boundary, and the oxide particles in the grain boundary are smaller. The energy spectrum analysis results show that the surface of the oxide film is mainly rich in Cr and Fe elements, and the grain boundary is mainly Cr–Mn oxides. The content of Cr is higher than that of Fe₁₁Cr₀.₅Ti stainless steel. When the two stainless steels were continuously oxidized at 800 °C, the surface oxide film did not peel off, and both had good oxidation resistance. Fe₁₁Cr₀.₅Ti stainless steel was worse than Fe₁₈Cr₀.₅Ti stainless steel,
which was consistent with the change law of oxidation rate $K_p$ in table 1. Figures 5(e) and (f) show the surface morphologies and element distribution of Fe11Cr0.5Ti stainless steel after continuous oxidation at 900 °C for 100 h. The surface of the sample is sintered together to form a shell structure, and the oxide film is no longer dense. Compared with figures 5(a) and (c), the morphologies of the oxidation product get obviously changed, and the oxide film is granular with a large number of holes on the surface. The energy spectrum analysis results show that the oxide film is mainly composed of Fe elements, and the oxide film is not dense. The product is pure Fe oxide. Figures 5(g) and (h) show the surface morphologies and element distribution of Fe18Cr0.5Ti stainless steel after continuous oxidation at 900 °C for 100 h. The surface of the sample is covered by both corundum type and spinel type oxides with a small amount of nodular oxides. The oxide is evenly distributed and the oxide film is dense. The energy spectrum analysis shows that the oxide film is mainly composed of Cr and Mn, and the
content of Cr is higher than Mn. The corundum type oxides are mainly pure Cr oxides, while the spinel and nodular oxides are mainly Cr-Mn oxides. The surface of Fe11Cr0.5Ti stainless steel is composed of pure Fe oxides. With the extension of oxidation time, the pure Fe oxides grow rapidly and merge with each other, and the oxide film is almost plays no protection role. After oxidation for 15 h, the stainless steel undergoes obvious abnormal oxidation, which is the main reason for the linear oxidation weight gain curve in figure 1. After 100 h oxidation of Fe18Cr0.5Ti stainless steel, the oxide film is composed of compact Cr/Cr-Mn granular oxides, which is consistent with the results of XRD analysis, and the Fe18Cr0.5Ti stainless steel has good protection effect. It can be seen from figure 5 that with the increase of temperature, the high temperature oxidation resistance of the two stainless steels decreases, and the Cr/Mn spinel oxide formed on the surface of Fe18Cr0.5Ti stainless steel will aggregate and grow up, which will reduce the protection effect of oxide scale on the matrix, thus reducing the oxidation resistance.

The distribution of cross-section elements in the oxide layer can reflect the oxidation resistance of stainless steel and explain the formation mechanism of oxide film. Figure 6 shows the cross-section morphologies and element distribution including O, Cr, Mn, Fe, Ti and Si of the oxide products of Fe11Cr0.5Ti and Fe18Cr0.5Ti ferritic stainless steels after constant temperature oxidation at different temperatures for 100 h. By comparing the color depth of each element in the picture, the distribution of each element and the change of concentration gradient can be directly analyzed, which provides a basis for determining the composition of the composite oxide film. Figure 7 shows the oxide layer thickness of two stainless steels after constant temperature oxidation at different temperatures for 100 h. It can be seen from figures 6(a), (b) and 7 that the composition of the cross-section oxide film of the two stainless steels at 800 °C is similar, the outer layer is Cr-Mn oxides, and the inner layer is Cr rich oxides. The thickness of the oxide film of Fe11Cr0.5Ti stainless steel is 2.26 ± 0.208 μm, which is greater than that of Fe18Cr0.5Ti stainless steel by 1.54 ± 0.277 μum, indicating that the stainless steel matrix with low Cr content is oxidized thicker and has low oxidation resistance. In addition, the above-mentioned results are in consistent with the kinetics curves. From figures 6(c), (d) and 7, it is found that when the temperature increases to 900 °C, the oxide layer thickness of Fe11Cr0.5Ti stainless steel is 740 ± 36.06 μm, and obvious delamination phenomenon occurs. The outer layer is pure Fe oxide layer, the inner layer is Fe rich Fe/Cr oxide layer, and a lot of cracks exist at the junction of the inner and outer oxide layers. The oxide film on the surface of Fe18Cr0.5Ti stainless steel and its interface are uneven, wedge-shaped and embedded into the matrix with a large depth. The outer layer is composed of Cr2O3 + Cr rich Cr/Mn oxides, and the inner layer is composed of SiO2 oxide. The total thickness is 2.52 ± 0.259 μm. The existence of SiO2 fills the cavity left in the matrix after Cr²⁺/Cr³⁺ and Mn²⁺/Mn³⁺ diffusing to the oxide film/air interface, prevents the aggregation of the cavity, inhibits the outward diffusion of Fe ions in the matrix, and finally reduces the oxidation rate, resulting in the formation of dense oxide film on the surface. By comparing the thickness and element distribution of oxide film cross section of stainless steel under different conditions, it is found that the oxide film of two stainless steels at 800 °C and Fe18Cr0.5Ti stainless steel at 900 °C are Cr rich oxide layers with thin thickness and less changes, which are closely combined with the matrix and have good oxidation resistance. The oxidation resistance is consistent with the results of XRD analysis. At 900 °C, the matrix of Fe11Cr0.5Ti stainless steel is seriously corroded at high temperature, and a loose Fe₂O₃ oxide film with a thickness of 370 μm is formed on the outer layer, which seriously reduces the high temperature oxidation resistance. According to the energy spectrum, the inner oxide is supposed to be Fe₂CrO₄ spinel oxide. Due to the different structures of the inner and outer oxides, the difference of linear expansion coefficient is large, which is easy to produce thermal stress and lead to the

Table 3. Corresponding chemical compositions from figure 5 for different regions.

| Region | O   | Cr  | Mn  | Fe  | Ti  | Si  |
|--------|-----|-----|-----|-----|-----|-----|
| A      | 36.04 | 34.97 | 18.43 | 8.03 | 1.83 | 0.70 |
| B      | 32.92 | 36.78 | 3.75  | 22.89 | 3.38 | 0.28 |
| C      | 30.43 | 41.68 | 3.83  | 20.54 | 3.11 | 0.42 |
| D      | 34.97 | 27.33 | 28.61 | 8.66  | 0.33 | 0.10 |
| E      | 34.06 | 38.71 | 18.35 | 5.98  | 2.42 | 0.49 |
| F      | 26.67 | 41.31 | 3.48  | 26.27 | 1.92 | 0.36 |
| G      | 6.69  | 0.00  | 0.23  | 93.03 | 0.00 | 0.05 |
| H      | 1.00  | 0.00  | 4.72  | 94.25 | 0.00 | 0.03 |
| I      | 30.33 | 44.93 | 22.74 | 1.48  | 0.44 | 0.07 |
| J      | 32.46 | 41.22 | 23.61 | 2.34  | 0.23 | 0.14 |
| K      | 29.20 | 53.42 | 6.38  | 9.22  | 0.94 | 0.84 |
| L      | 37.52 | 49.29 | 5.26  | 6.87  | 0.35 | 0.71 |
appearance of cracks. Complete and compact oxide film can be formed on the surface of Fe18Cr0.5Ti stainless steel with high content of Cr element. The existence of Cr/Cr-Mn oxide particles reduces the number of micro channels for matrix elements to diffuse through the oxide layer, reduces the oxidation rate and improves the oxidation resistance.

4. Discussion

In the early stage of high temperature oxidation, metal elements on the surface of stainless steel will react with oxygen element in the air to form corresponding oxides, but the type of oxides in the later stage of oxidation depends on the activity and content of metal elements. Cr₂O₃, Mn₂O₃, Fe₂O₃ and other oxides will be formed in the initial oxidation stage of Fe-Cr-Ti ferritic stainless steel. Because of the element diffusion rate
Cr > Mn > Fe and the high content of Cr, Cr will be selectively oxidized to form a dense Cr₂O₃ protection film, and other metal elements are mainly internally oxidized or formed in the inner layer of the external oxidation layer.

According to figures 8(a) and (b), the element depth distribution of Fe11Cr0.5Ti and Fe18Cr0.5Ti stainless steels after oxidation at 800 °C for 100 h shows that the oxidation is mainly due to the inward diffusion of oxygen anions, and Cr/Mn elements are enriched from the surface to about 0.65 μm and 0.8 μm, respectively. In the range of 0.65 μm–2.2 μm and 0.8 μm–1.8 μm, Mn element content decreases and Cr/Fe elements content increase. The results show that the outer layer of the oxide film formed at 800 °C is composed of (Cr₁.3Fe₀.₇)O₃ + MnCr₂O₄, and the inner layer is composed of (Cr₁.₁Fe₀.₉)O₃. With the increase of Cr content, the dense Cr₂O₃ protection film will be formed preferentially, the growth rate of the oxide film will be reduced, and finally a thin oxide layer will be formed, which is consistent with the results in figure 6. In the initial stage of oxidation, oxygen element diffuses inward and reacts with surface metal elements to form Cr₂O₃ thin films as well as MnO and Fe₂O₃ oxides. With the development of oxidation progress, Cr₂O₃ reacts with Fe₂O₃ and MnO to form more stable (Cr₁.₃Fe₀.₇)O₃ corundum type oxides and MnCr₂O₄ spinel type oxides. Due to different Cr contents, the oxide morphology and distribution are different. The solid state reaction between the above oxides can be expressed as follows: 13/20Cr₂O₃(s) + 7/20Fe₂O₃(s) = (Cr₁.₃Fe₀.₇)O₃(s); Cr₂O₃(s) + MnO(s) = MnCr₂O₄(s). In addition, the formation of (Cr₁.₃Fe₀.₇)O₃ + MnCr₂O₄ oxide layer blocks the internal diffusion of oxygen element and reduces the oxidation thickness, which makes the stainless steel have good oxidation resistance at this temperature.

Figures 8(c) and (d) are the results of the element depth distribution of Fe11Cr0.5Ti and Fe18Cr0.5Ti stainless steels after oxidation at 900 °C for 100 h. It is found that the oxidation of stainless steels at this temperature is dominated by the outward diffusion of metal elements. According to figure 8(c), only Fe is enriched from the surface to about 0.36 mm, while Fe and Cr are enriched in the range of 0.36 mm–0.7 mm. This indicates that Cr element diffuses outward to form Cr₂O₃ film in the initial stage of oxidation, and a certain number of small cavities are formed at the interface of matrix/oxide film. However, due to the low content of Cr element, Cr₂O₃ oxide cannot diffuse from the matrix to the surface in time to fill the cavities, and the oxide film is gradually loose, which cannot inhibit the diffusion of Fe element to the interface of oxide film/air, resulting in a large number of voids. The adhesion between the original Cr₂O₃ oxide scale and the matrix decreases and finally the oxide scale peels off. The Fe element reacts with the O element between the oxide film/air interface to form Fe/ Cr oxides and a Fe rich oxide film with poor protection. With the increase of oxidation time, the oxidation rate increases, the unstable oxidation occurs, the pure Fe oxide film is formed on the surface, and the oxygen resistance decreases significantly. Due to the significant difference in the growth rate of internal and external oxide films, the interface between oxide layer and matrix moves fast, the internal oxidation zone/matrix front cannot be established, so no SiO₂ oxide layer is formed after 100 h continuous oxidation of Fe11Cr0.5Ti stainless steel. It can be seen from figure 8(d) that the outer layer of the oxide film is rich in Cr and Mn, in which the content of Cr is greater than that of Mn; the inner layer is a Si rich oxide layer with a thickness of about 0.3 μm. The results show that due to the high Cr concentration on the surface of Fe18Cr0.5Ti stainless steel, the critical Cr concentration required to form a continuous and dense Cr₂O₃ oxide film can be met. In the initial stage of oxidation, Cr and a small amount of Mn rapidly diffuse outward to form a layer of

\[ \text{Cr}_2\text{O}_3 + 0.5\text{Mn} \rightarrow \text{MnCr}_2\text{O}_4 \]
Cr$_2$O$_3$ + MnCr$_2$O$_4$ + Mn$_{1.5}$Cr$_{1.5}$O$_4$ oxide film and improve the adhesion between the oxide film and the matrix. The growth mode of the oxide film is an embedded mode. With the increase of oxidation time, SiO$_2$ enters into the cavities caused by the outward diffusion of metal cations, which not only increases the adhesion between the matrix and the oxide film but also improves the oxidation resistance.

The high temperature oxidation resistance of stainless steel is still related to the critical strain $\varepsilon_0$ of oxide film during its fracture, as shown in equations (5)–(7) [17]:

$$
\varepsilon_0 = \frac{K_{IC}}{f \sqrt{\pi C}} \times \frac{1 + \frac{r}{\xi}}{m}
$$

(5)

$$
m = \frac{2E_{ox}}{1 + \mu_{ox}}
$$

(6)

$$
\varepsilon_0 = \frac{K_{IC}}{2E_{ox} f \sqrt{\pi C}} \left(1 + \frac{r}{\xi}(1 + \mu_{ox})\right)
$$

(7)

Where $K_{IC}$ is the fracture strength, $C$ is the radius of the physical defects at the maximum strain of the interface, $r$ is the interface undulation height, and $f$ is the geometric factor. From equation (7), we can get that the critical
strain $\varepsilon_f$ of oxide film is directly proportional to the interface undulation height $r$ and inversely proportional to the radius $C_0$ of the physical defects at the interface maximum strain. That is to say, the thinner the oxide film thickness or the smaller the radius of physical defects at the interface, the less the prone to fracture and the better the oxidation resistance.

According to the test results, the oxide film of Fe11Cr0.5Ti stainless steel is the thickest in the early oxidation stage at 900 °C, and many cavities and microcracks exist in the oxide film, so the critical strain value of oxide film during its fracture is the smallest. Moreover, the phenomena of oxide scale peeling and abnormal oxidation occur in the continuous oxidation process. When Fe18Cr0.5Ti stainless steel is continuously oxidized at 800 °C for 100 h, the thickness of the oxide film is the smallest, and the physical defects at the interface are the least, so the critical strain of the oxide film is the largest and the stability of the oxide film is the highest.

5. Conclusion

1. The results show that the oxidation kinetics curves of Fe11Cr0.5Ti and Fe18Cr0.5Ti stainless steels follow the parabolic law at 800 °C. The oxidation product is $(Cr_{1.3}Fe_{0.7})O_3 + MnCr_2O_4$, and the oxidation rate decreases with the increase of Cr content.

2. At 900 °C, the oxidation of the two stainless steels is dominated by the outward diffusion of metal elements. When the oxidation time of Fe11Cr0.5Ti stainless steel exceeds 15 h, the oxidation kinetics curve changes from parabola to linearity with the increase of oxidation time. The outer layer is pure Fe oxide layer, and the inner layer is Fe rich Fe/Cr oxide layer. However, the oxide film of Fe18Cr0.5Ti stainless steel grows in a wedge-shaped pattern, the outer layer is composed of $Cr_2O_3 + MnCr_2O_4 + Mn_{1.5}Cr_{1.5}O_4$, and the inner layer is mainly composed of $SiO_2$.

3. At high temperature, Fe18Cr0.5Ti stainless steel has better oxidation resistance than Fe11Cr0.5Ti stainless steel, which is attributed to two main reasons. The first is the formation of Cr rich oxide film, which hinders the diffusion of Fe in the matrix; the second is the formation of thin oxide film and less physical defects on the interface, which improves the critical strain required for the fracture of the oxide film and increases the stability of the oxide film.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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