Coupling effect of temperature and Cr content on the steam oxidation of Ni-Fe-Cr alloys

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Abstract

Excellent resistance to steam oxidation is a key required property for heat-resistant alloys used in next-generation fossil power plants. In order to clarify the degradation mechanism of Ni-Fe-Cr alloys in high temperature steam, four kinds of Ni-Fe-Cr model alloys with various Cr content were prepared and their long-term steam oxidation were investigated at 650 °C and 700 °C. The microstructure and composition of oxide scales were characterized by SEM equipped with EDS, and the oxide phases were identified by XRD. The results showed significant dependence of temperature and Cr content in alloys on the oxidation kinetics, cross-section morphology and elemental section-distribution. For Ni-Fe-Cr alloys with low Cr contents (12～16 wt.%), the increase of temperature made the oxide scale change from breakaway scale morphology (nodule-crater microstructure with external exfoliation) to protective scale morphology (uniform layer and internal oxidation). For Ni-Fe-Cr alloy with 18wt.% Cr, the effect of temperature was greatly reduced. The oxidation mechanism was discussed from the perspectives of selective oxidation and the effect of alloying elements.

1. Introduction

In recent years, the contradiction between fossil energy consumption and environmental problems has become more and more acute. Among them, the environmental problems caused by coal-fired thermal power generation are more prominent, and thermal power generation tends to be efficient, economical and reliable. In supercritical power generation plants, superheater and reheater pipes should not only have good oxidation resistance, but also have excellent tensile and creep strength in high temperature steam. The corrosion of traditional heat-resistant steel is generally enhanced to a great extent in water vapor containing environment, which cannot meet the long-term use requirements of ultra-supercritical power generation technology. However, recent research shows that nickel base alloy with high chromium content have both oxidation resistance and certain strength in high temperature steam, and are considered as candidate materials for high-temperature components of the next generation advanced ultra-supercritical generator set [1].

Oxidation resistance of heat-resistant steel is generally due to the formation of a slowly growing, continuous and dense oxide film on the surface. Such dense and uniform chromium rich oxide film can effectively slow down the oxidation of the alloy. However, it is indicated that the presence of water vapor can enhance the oxidation of chromium containing alloys and cause the breakaway behavior [2～6].

Oxidation of alloys is generally affected by the temperature, gas composition, and chromium content in the alloys. Temperature is an important factor for the critical chromium concentration required for the formation of protective oxide film. Atmosphere composition (e.g., oxygen partial pressure, water vapor content, hydrogen...
content) also has an obvious effect on the chromium concentration required to form chromium oxide [7]. Because the selective oxidation of chromium may inevitably lead to the chromium depletion near the scale/alloy interface, the chromium content at the interface is determined by the Cr consumption rate caused by the formation of oxide film and the diffusion rate of Cr through the alloy to the interface. Wagner theory [8] holds that for the system forming pure chromium oxide film, the critical chromium concentration is not only related to the molar volume of alloy and oxide, but also related to the parabolic rate constant \( k_p \) and the interdiffusion coefficient \( D_{int} \) of alloy. These two parameters are related to the experimental temperature and atmosphere compositions. The presence of water vapor significantly alters the microstructure of oxide scales, for which Cr-rich oxides are mostly formed on the surface of the alloy and/or along the grain boundary of the matrix alloy. In addition, the abnormal dependence of critical chromium concentration on temperature under medium temperature oxidation has been observed, that is, the critical chromium concentration decreases with the increase of temperature. It has been found that the oxidation rate of ferritic steel with low chromium content (9%–12% Cr) in wet gas presents an obvious ‘bell curve’ in the temperature range of 600 °C–800 °C [9], where a thin dense protective Cr-rich oxide film preferably formed at 700 °C rather than 600 °C–650 °C, and then remarkably reduced the oxidation rate. Other studies on Fe-Cr steels with chromium content up to 20 wt.% in wet gas containing 10% water vapor showed that 20 wt.%Cr steel cannot sustain the formation of protective oxide film at 650 °C, while the 16 wt.%Cr steel can be nearly passivated at 800 °C [10].

Most of the existing literatures [7, 11–14] ignore the effects of other trace alloying elements (such as Ti, and Al) on the oxidation behavior. Recently, it has been found that Ti is enriched in the gap in the matrix under the oxide film, and a thick protruding oxide film is formed above the enrichment sites [15]. Trace Al in the Ni-Cr alloy prefers forming a relatively continuous Al$_2$O$_3$ layer in the alloy matrix in wet gases, and then significantly reduces the thickness of oxide scale compared to that in dry oxygen environment [16].

Based on the above considerations, the present work was aimed to investigate the oxidation behavior of Ni-Fe-Cr alloys with various concentrations of chromium and some other trace alloying elements including Ti, Al, Mo and W, via mass gain recording, oxide phase identification, microstructure characterization, EDS mapping analysis. At last, the coupling influence of temperature and chromium content on the oxidation mechanism of Ni-Fe-Cr alloys was discussed.

### 2. Materials and methods

Four Ni-Fe-Cr model alloys were prepared to study the effect of chemical composition on their steam oxidation behavior. These alloys were prepared by vacuum induction melting furnace and melted repeatedly for 5 to 6 times to ensure uniform alloy composition. Chemical compositions of the studied alloys were determined by spark discharge atomic emission spectrometric method, and the measured chemical compositions are shown in table 1. The alloys are designated as 12Cr, 14Cr, 16Cr and 18Cr respectively according to their Cr contents. In order to obtain similar microstructure, several alloys adopt the same treatment process. Firstly, the ingot was homogenized at 1200 °C for 20 h. Secondly, the homogenized ingot was hot rolled into a plate at 1150 °C. Thirdly, the rolled plate was annealed at 1100 °C and aged at 750 °C for 10 h. Through the same heat treatment process, similar microstructures predominantly composed of simple austenite were obtained for the studied alloys. Strip specimens with dimensions of 10 × 10 × 2 mm were cut from the plates after the above heat treatment, and ground by SiC sandpaper to 1000#. After that, samples were cleaned by deionized water, acetone and absolute ethanol were subsequently, and dried with cold air.

High temperature steam oxidation experiments were carried out in a self-made experimental system as mentioned elsewhere [3]. Flowing steam was generated by pumping ultra-purified water (resistivity ≥10 MΩ·cm) into pre-heating furnace. Prior to oxidation, the reaction chamber was purged with high-purity argon to prevent the oxidation of samples during the heating process. Once the temperature reached the target temperature, closed the argon valve, continuously injected dynamic steam, and started timing the test. After reaching the predetermined test time, closed the steam valve and the heating furnace, continuously injected high-purity argon, and the sample was cooled to room temperature with the furnace under the protection of

| Alloys | Cr    | Fe | Mo  | W   | Ti | Al | C  | B  | Si   | Ni   |
|--------|-------|----|-----|-----|----|----|----|----|------|------|
| 12Cr   | 12.3  | 41.4| 1.1 | <0.2| 2.5| 1.7| <0.04| <0.003| <0.015| Bal. |
| 14Cr   | 14.2  | 41.2| 0.7 | <0.2| 2.6| 1.6| <0.04| <0.003| <0.015| Bal. |
| 16Cr   | 16.3  | 41.4| 0.9 | 0.4 | 2.2| 1.5| <0.04| <0.003| <0.015| Bal. |
| 18Cr   | 18.6  | 41.4| 0.7 | 0.4 | 2.3| 1.6| <0.04| <0.003| <0.015| Bal. |
high-purity argon. In the whole test process, steam entered from one side of the reaction tube and flowed out from the other side. The pressure in the reaction tube was slightly higher than the atmospheric pressure, so as to prevent the air outside the reaction tube from being sucked back into the reaction tube and affect the test results. During the experiment, samples were placed in the reaction tube of the horizontal tubular furnace and parallel to the flow direction of steam. In the present work, the target temperatures were set at 650 °C and 700 °C.

Weight gains of the Ni-Fe-Cr alloys were recorded by intermittent weighing, in which the sample was weighed by an electronic analytical balance with an accuracy of 0.1 mg. After oxidation tests, phase structures of oxides were identified by x-ray Diffraction (XRD) technology, the surface and cross-section morphology were investigated by Scanning Electron Microscope (SEM), and the chemical compositions was analyzed by Energy Dispersive X-ray Spectroscopy (EDS).

3. Results and discussion

3.1. Oxidation kinetics

The weight gain curves of Ni-Fe-Cr alloys in high temperature steam at 650 °C and 700 °C are shown in figure 1. It can be seen that both temperature and Cr content have a significant effect on the oxidation kinetics.

At 650 °C, the oxidation kinetics curves of 12Cr, 14Cr and 16Cr alloys do not show clear functional laws (such as linear law, parabolic law, etc), and obvious weight loss can be found, indicating that there is obvious peeling of oxide film. However, 18Cr alloy basically follows the parabolic law shown in equation (1), where, \( \Delta w \) is the mass gain (mg), \( A \) is the exposed surface area (cm²), \( k_w \) is the rate constant, and \( t \) is exposed time (h). This shows that at the same temperature, with the increase of Cr content, the oxidation rate of the alloy decreases, but the anti-spalling ability of the oxide film increases obviously.

\[
\left( \frac{\Delta w}{A} \right)^2 = 2k_w t
\]

At 700 °C, the oxidation kinetics of the four alloys basically follows the parabolic law shown in equation (1), and no obvious weight loss caused by oxide film peeling can be found. With the increase of Cr content, the oxidation rate of the alloy decreases significantly.

Comparing the oxidation kinetics at two temperatures, it can be seen that the oxidation rate is inversely correlated with temperature for 12Cr, 14Cr, and 16Cr alloys, while the oxidation rate is positively correlated with temperature for 18Cr alloy.

3.2. Normal temperature dependent oxidation of 18Cr alloy

Figure 2 shows the surface morphology of 18Cr alloy oxidized at 650 °C for 500 h. At low magnification, the surface of oxide film is relatively flat without cracking, falling off and bulge. At high magnification, the surface of oxide film presents two morphologies: one is reticular oxide film, there are many voids and the surface accounts for a large proportion; the other is the granular oxide film with small grain size and tight combination (figure 2b), which accounts for less surface and is distributed between the network oxide films. EDS analysis indicates that the reticular oxide film is rich in Fe and the granular oxide film is rich in Cr. XRD patterns as shown in figure 3 reveals that the oxide film is composed of Fe₃O₄, (Fe, Cr)₂O₄ and Cr₂O₃.
Figure 4 shows the cross-sectional morphology of 18Cr alloy after 500 h oxidation at 650 °C. The oxide scale is similar to the nodule-crater scales of stainless steel in steam environment reported in literatures [17–19]. The outer layer is mainly composed of Fe and O, which should correspond to the Fe₃O₄ phase detected by XRD. The interface layer between the inner and outer layers is composed of Cr, Fe, Ni and O, which should be caused by the gradual degradation of the initially formed protective Cr rich oxide film. For the crater region, the thin, continuous and dark contrast oxide on the boundary is mainly composed of Cr, O and a small amount of Fe, which should be (Fe, Cr)ₓO₄ and/or Cr₂O₃ with good protection, while the black-and-white oxidation area in the pit like area is mainly composed of Ni, Cr, Fe, O and a small amount of Ti and Al, in which the darker area should be (Fe, Cr)ₓO₄ and/or Cr₂O₃, and a small amount of oxide particles such as Al₂O₃ and TiO₂, and the bright grid like material on the periphery should be Ni. This is due to the large oxygen affinity of Cr, Al and Ti, which reacts preferentially to the inward diffused oxygen, while the more inert Ni remains in the metal state [19].
Figure 5 presents the surface morphology of 18Cr alloy after 500 h steam exposure at 700 °C. It is evident that the surface of the oxide film is still flat without cracking and falling off, which is consistent with the oxidation kinetics. At high magnifications, the oxide film surface presents two morphologies: one is granular oxide with large grain size, the other is the oxide with small grain size and tight binding, and its surface is inlaid with flake oxide. Combined with EDS analysis and XRD identification (shown in figure 3), the granular oxide with large grain size in the outermost layer is Fe₃O₄, the oxide with small grain size and tight binding is Cr-rich (Fe,Cr)₃O₄ and/or Cr₂O₃ with good protection, and the flake oxide is Fe and Cr rich oxide. Different from the network Fe₃O₄ oxide formed by oxidation at 650 °C, the granular Fe₃O₄ formed at 700 °C does not cover the surface widely, but is evenly scattered on the surface.

Figures 6(a), (b) shows the cross-section morphology of 18Cr alloy after 500 h steam exposure at 700 °C. There are several obvious characteristics for the oxide scale: first, the outermost oxide protrudes outward; second, the oxide thickness of the intermediate layer accounts for about 80% of the overall oxide film thickness; and third, internal oxides are formed along the alloy grain boundaries. From the EDS mapping analysis as shown in figure 6(c), it can be seen that the outermost oxide is mainly composed of Fe and O, that is, it is mainly iron.
The middle layer oxide is mainly composed of Cr, Fe, Ti, and O, mainly Cr rich (Fe, Cr)₂O₃ as well as some Ti oxides; The internal oxides are mainly Al and Ti oxides.

From the cross-sectional morphology of the oxide film, although the effect of temperature on the oxidation kinetics of 18Cr alloy is not obvious (slightly increasing the weight gain), the effect on the oxide film microstructure is still significant. The oxide scale formed at 650 °C exhibits the nodule-crater morphology, while that formed at 700 °C displays a single-layer scale with serious internal oxidation.

For the internal oxidation at 700 °C, a large number of cavities extending into the matrix are formed at the grain boundary of the alloy under the oxide film, which is obviously caused by the diffusion of cations in the alloy. It can be seen from the EDS mapping results (figure 6(c)) that Cr in the matrix under the oxide film is obviously depleted, Fe is also consumed at the grain boundary, and Ti and Al are obviously enriched at the grain boundary. Generally, the diffusion of ions in the grain boundary is faster, because the diffusion activation energy of ions in the grain boundary is much less than that in the lattice, and the grain boundary diffusion can be regarded as a short-distance diffusion channel of ions [20]. At the initial stage of oxidation, Cr with high activity is preferentially oxidized to form Cr₂O₃ film, but the Cr content of the alloy is not high enough to form a complete Cr₂O₃ film immediately. A certain amount of Fe is oxidized and the two oxides grow together. Therefore, there are flake Fe and Cr oxide inlays on the Cr₂O₃ film. At the same time, Ti with high chemical activity is also oxidized, nucleated and grown, but the content of Ti in the alloy is very small, so the Ti oxide is only scattered in the oxide film. During the formation of oxide film, Cr³⁺, Fe²⁺, Fe³⁺ and Ti⁴⁺ rapidly diffuse

**Figure 6.** Cross-section morphology of 18Cr alloy after 500 h steam exposure at 700 °C (a) at low magnification, (b) at higher magnification, and (c) EDS mapping.
outward along the grain boundary, and the relative cation vacancy flow diffuses in the opposite direction, so as to form a cavity at the oxide film/metal interface and extend into the matrix. The oxygen partial pressure at the cavity is very low, resulting in the decomposition of oxides at the cavity. The decomposed oxygen continues to react with highly active Al at the grain boundary to form Al2O3, so Al enrichment can be seen in the matrix cavity. Therefore, in the oxidation process, TiO2 and Al2O3 basically exist in the form of oxides.

In comparison, no cavity was formed at the interface of 18Cr alloy at 650 °C, but there were different degrees of internal oxidation at the whole scale/metal interface. This situation shows that the diffusion of oxygen to the alloy is dominant in the early stage of oxidation, and oxygen rapidly penetrates along the metal grain boundary at the scale/metal interface, and then forms oxide. With the increase of oxidation time, the formed Cr2O3 film is gradually complete, the outward diffusion of metal ions begins to dominate, and the internal oxidation is inhibited. According to the classical oxidation theory, the diffusion coefficient of metal ions in grain boundary and lattice increases with the increase of temperature, so the change of temperature has a great influence on the morphology of oxide film. When the temperature rises to 700 °C, the cation diffusion is dominant in the initial stage of oxidation, so there is no serious internal oxidation at the scale/metal interface.

3.3. Anomalous temperature dependent oxidation of 12–16 Cr alloys

The oxidation rate of 12Cr, 14Cr and 16Cr alloys is negatively correlated with temperature, that is, the oxidation rate decreases with the increase of experimental temperature. Figures 7–9 show the cross-sectional morphology and EDS mappings of 12Cr, 14Cr, and 16Cr alloys after 500 h steam oxidation. It can be seen that the surface oxide film cracks, bulges and falls off in varying degrees at 650 °C, while the surface oxide film is relatively complete at 700 °C, which is consistent with the oxidation kinetics; At 650 °C, the oxide film has the characteristics of nodule-crater structure (figures 7(a)–9(a)). There are a large number of holes in the surface oxide film, and some oxide film interfaces form obvious gaps. At 700 °C, only 12Cr alloy has the characteristics of nodule-crater structure (figure 7(b)), and the thickness of oxide film on the surface of other alloys is relatively uniform (figures 8(b) and 9(b)). No obvious holes or gaps are found; From the element composition of oxide film, in the tumor crater oxide film structure formed at 650 °C, the outer tumor is iron oxide, and the inner crater oxide area contains iron chromium spinel and locally continuous Cr-rich oxide, while the tumor crater oxide film structure formed at 700 °C is different, mainly because the continuous Cr-rich oxide at the edge of the crater is more obvious. In addition, Ti and Al oxides are formed; The thickness of oxide film formed by 14Cr and 16Cr alloys at 700 °C is uniform, the oxide film is rich in Cr, Ti, and Al. The oxide phases were mainly (Fe,Cr)2O3, Fe(Al,Cr)2O4 identified from XRD patterns as shown in figure 10.
3.3.1. Exfoliation of oxide scales
The peeling of oxide film is usually caused by a large amount of stress in the oxide film, which cannot be released by other ways. For thin oxide films, the elastic energy stored per unit area at the oxide film/alloy interface can be expressed by the equation (2) [21].

\[
W^* = (1 - V_p) E_{\text{ox}} (\Delta T \Delta \alpha)^2
\]

where \(V_p\) and \(E_{\text{ox}}\) are Poisson’s ratio and elastic modulus of oxide film; \(\Delta T\) and \(\Delta \alpha\) are the change of temperature and the change of thermal expansion coefficient of alloy and film. In this study, the oxide film is relatively thick. When the temperature and thermal expansion coefficient change greatly, the strain energy stored in the film is greater than the strain energy required for fracture, and the oxide film at the film/alloy interface will crack or peel off. A large number of almost connected cavities are generated between the outer Fe containing oxide films, and a large amount of strain energy is easier to release at the cavities.

In addition, it can also be seen from the cross-sectional morphology that many cavities appear near the scale/metal interface in 12Cr alloy, while a large number of gaps appear at the same position of 14Cr and 16Cr alloys (figures 7(a)–9(a)) and gradually extend to the matrix. Obviously, this is similar to 18Cr alloy. The formation of voids is due to the rapid outward diffusion of cations from the grain boundary and the opposite diffusion of cation vacancy flow, so as to form voids at the scale/metal interface. The increasing voids are connected together to form gaps and extend to the substrate. The formation of these holes or pores also causes the outer iron rich oxide layer to fall off easily.

3.3.2. Critical Cr content
In the theory of high temperature oxidation, the critical chromium content is the key to maintain sufficient Cr flux from the alloy matrix to the oxide film/metal interface to form Cr₂O₃ film. Some studies believe that the insufficient diffusion rate of Cr at low temperature is the reason for the separation and falling off of oxide film [22, 23]. According to Wagner’s analysis, the critical Cr content is related to \(K_p\) and \(D_{\text{int}}\) of the alloy [8]. These two parameters are not only related to the experimental temperature and atmosphere environment, but also related to the activation energy \(E_A\) and the diffusion activation energy \(Q\) of Cr in the alloy. The critical
The selective oxidation of Cr is the key to determine the oxidation resistance of stainless steels and corrosion resistant alloys. It is generally considered that the ratio of Cr content to critical Cr content in the alloy directly reflects whether the alloy can form protective chromium oxide film. As mentioned above, the critical Cr content required for the alloy to form and maintain a protective Cr rich oxide film can be described according to equation (3), which is inversely proportional to the oxidation temperature, that is, when the temperature increases, the critical Cr content of the alloy will decrease [18]. Othman et al [27] predicted that the critical Cr content of Fe-Cr alloy was 12% in water vapor containing environment at 700 °C and 17% at 600 °C. It can be seen that the increase of temperature reduces the critical Cr content to a great extent. According to the results of the present work, it can be inferred that the critical Cr content of Ni-Fe-Cr alloy in this study is higher than 18% in steam environment at 650 °C, while the critical Cr content is about 12~14% at 700 °C. Therefore, the results of this study are consistent with the literature reports.

When the Cr content in the alloy is lower than the critical Cr content, the protective Cr rich oxide film cannot be formed and maintained on the alloy surface, resulting in the rapid oxidation of Fe and the formation of outward growing iron rich oxide film. Because the iron rich oxide film is usually loose and porous, and it is easy to form voids and even gaps at the interface with the inner oxide layer, it is easy to peel off and cannot effectively prevent the diffusion of water vapor to the matrix, so the oxidation rate of the alloy is at a relatively high level. When the Cr content in the alloy is higher than the critical Cr content, the Cr element in the alloy is selectively oxidized at the initial stage of oxidation, and a continuous protective Cr-rich oxide film is preferentially formed on the alloy surface, so as to effectively block the contact between the corrosive medium and the alloy matrix and greatly reduce the oxidation rate of the alloy. In addition, Al and Ti in Ni-Fe-Cr alloy has higher oxygen affinity and will also form oxides such as Al2O3 and TiO2. However, due to the low content of these alloy elements in the alloy, it is not enough to form a continuous oxide film, so the film structure of the alloy will not be changed. For example, at 700 °C, the corrosion product films on the surfaces of 14Cr and 16Cr are basically the same.

\[
\ln N_{Cr, crit} = C + \frac{Q - E_A}{2RT}
\]  

(3)

Where \( N_{Cr, crit} \) is the critical chromium content, \( R \) is the gas constant, \( t \) is the experimental temperature, \( C \) is a constant, \( Q \) is the diffusion activation energy, and \( E_A \) is the activation energy.

It can be seen from equation (3) that when \( Q - E_A > 0 \) and the experimental temperature decreases, the critical Cr content required by the alloy will increase. Young et al [22] obtained \( Q (179 \text{ KJ mol}^{-1}) > E_A (110 \text{ KJ mol}^{-1}) \) in the experimental environment of Ar-4% H2-20% H2O, which explained that the critical Cr content required by the alloy decreased at high temperature (800 °C), resulting in the formation of protective \( \text{Cr}_2\text{O}_3 \) film, but \( \text{Cr}_2\text{O}_3 \) was not formed at low temperature (<800 °C). This shows that with the increase of temperature, the protective property of the oxide film increases gradually until a complete protective oxide film is formed. This is consistent with this result, that is, 12Cr-16Cr alloy does not reach the critical Cr content for forming and maintaining protective Cr-rich oxide film at 650 °C, showing iron rich nodular oxide crater structure (as indicated in figures 7(a)–9(a)), but the Cr content in 14Cr and 16Cr reaches the critical Cr content for forming and maintaining protective Cr-rich oxide film at 700 °C, showing a thin single-layer Cr rich oxide film structure (as indicated in figures 8(b), 9(b)).
3.4.2. Evolution of oxide films

From the oxide film morphology, it can be seen that the effect of temperature on the oxidation behavior of Ni-Fe-Cr alloy is essentially a significant effect on the oxide film structure and its evolution with time. At 650 °C, the oxide film shows a tumor crater structure, the tumor is an outward growing iron rich oxide, the crater area is an inward growing Cr-rich oxide, and the outer iron rich oxide layer is prone to fall off; At 700 °C, the tumor crater structure gradually disappears, especially with the gradual increase of Cr content in the alloy, the oxide film presents the characteristics of a single layer with network internal oxidation zone, and there are obvious oxides such as Al₂O₃ and TiO₂ in the internal oxidation zone.

The structure of nodular crater oxide film is the characteristic of breakdown oxidation of Fe-Cr alloy in water vapor containing environment. Jonsson et al. [28] deemed that the oxidation behavior of Fe-Cr-Ni alloy is similar to that of Fe-Cr alloy. Before breakdown oxidation, the alloy mainly forms a protective (Cr₆Fe₁₋ₓ)₂O₃ oxide film with Cr-rich corundum structure, and after breakdown oxidation, a similar nodule-crater like oxide scale is formed. It is generally believed that Cr-rich oxide film with certain protection can be formed at the initial stage of the alloy, but due to the insufficient Cr content in the alloy to maintain the protection and integrity of Cr-rich oxide film, when the oxide film formed at the initial stage is locally damaged, iron ions and oxidants will rapidly diffuse outward and inward respectively, therefore iron rich oxide nodules and Cr-rich crater oxides below them are formed [17]. The composition of crater oxide is complex, mainly composed of Cr, Fe, Ni, and O, and the morphology presents a black-and-white grid shape. The dark contrast is oxide, and the bright contrast is unoxidized metal [29]. Jooshyar et al. [19] designated this crater zone as the reaction zone, which is composed of ‘oxygen-poor’ nanosized spinel oxide particles and nanosized FeNi metal. Its formation depends on the diffusion of cations (e.g., Cr⁺³ and Fe⁺²) in the spinel phase, the immiscible gap of Fe-Cr spinel oxide and the equilibrium composition of spinel.

The single-layer with internal oxidation includes two parts: one is the external Cr and Ti rich oxide film, and the other is the internal oxidation zone below it. The formation mechanism of the outer film may be as follows: at the initial stage of oxidation, thermodynamically stable oxides such as Al₂O₃, Cr₂O₃ and TiO₂ are rapidly formed on the alloy surface; Then, depending on the concentration of alloying elements and their oxidation activity, a specific oxide film will be preferentially formed. According to calculation of Dudziak et al. [30], Ti has the highest oxidation activity and Cr has the lowest oxidation activity. However, because the Cr content in the alloy is much higher than that of Ti and Al, Cr-rich oxide film will be preferentially formed on the alloy surface. Nevertheless, the formation of protective Cr-rich oxide film will change the oxidation activity of Ti and Cr. With the growth of Cr-rich oxide film, Ti oxide preferentially forms due to the slightly higher oxidation activity of Ti than that of Al, so as to form the external oxide film as shown in figures 8(b) and 9(b). The formation mechanism of the internal oxidation zone below the external oxide film may be as follows: due to the high oxygen affinity of Ti and Al, their oxides can be formed under very low oxygen partial pressure. Therefore, when the external oxide film is formed, the oxygen partial pressure at the scale/metal interface is sufficient to maintain the oxidation of Ti and Al. As part of Ti is consumed during the formation of outer oxide, Ti on the interface is depleted and the concentration of Al element is relatively dominant. Therefore, an internal oxidation zone dominated by Al₂O₃ and supplemented by TiO₂ is formed as shown in figures 8(b) and 9(b).

4. Conclusions

Steam oxidation of Ni-Fe-Cr alloys at 650 °C–700 °C was investigated through long-term oxidation kinetics, surface and cross-sectional morphology, oxide phase identification, and elemental mapping of oxide scales. Based on the results, the following conclusions can be made.

1. Abnormal oxidation of 12Cr-16Cr occurs, that is, the oxide film formed at lower temperature is seriously peeled off, and the increase of temperature is conducive to the formation of stable and complete oxide film.

2. Temperature and Cr content have an obvious coupling effect on Ni-Fe-Cr oxidation, that is, the temperature increases from 650 °C to 700 °C, which greatly reduces the critical Cr content required for the formation of protective Cr-rich oxide film, resulting in obvious changes in the microstructure of oxide film on the alloy surface. The breakdown oxide film presents the structure of outer Fe-rich nodule and inner crater like oxidation zone, while the protective oxide film is mainly a single-layer Cr and Ti rich oxide film with the internal oxidation of Al and Ti.

3. A small amount of Ti and Al in the alloy can affect the oxidation behavior at higher temperature, mainly because Ti participates in the formation of external protective oxide film, while Al and Ti with high oxygen affinity at the oxide film/alloy interface can react with inward diffusion oxidant to form an obvious internal oxidation zone.
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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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