Vol. 1, No. 1 Materials Research and Development October, 2022
第 1 卷第 1 期 材料研究与发展 2022 年 10 月

Analysis on Oxidation Behavior of HR3C Steel at 700 ℃ in Water Vapor

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Abstract: HR3C is an advanced heat-resistant alloy, and its high-temperature oxidation resistance directly determines the service performance of the material. Therefore, exploring the high-temperature oxidation behavior of HR3C is of great significance for the theoretical research and practical application of the material. The oxidation kinetic curve, oxide film morphology, oxide film composition, and oxide film phase composition of HR3C samples in the supply state after being oxidized in water vapor at 700 ℃ for 50h, 150h, 250h, 350h, 450h, 550h and 600h were analyzed by SEM (Scanning Electron Microscopy), EDS (Energy Dispersive Spectroscopy) and XRD (X-ray diffraction). The results show that the oxidation kinetic curve of the material conforms to the parabolic law, the oxide film first forms a lamellar oxide, and the lamellar oxide film grows alternately to form a loose and porous oxide film surface, the oxide is composed of three oxides: Fe_3O_4, $FeCr_2O_4$ and Fe_2O_3. The $FeCr_2O_4$ is a spinel compound, which can form a dense oxide film, and the diffusion coefficient of metal ions in it is small, which hinders the diffusion and mass transfer of ions, thereby improving the high temperature oxidation resistance of stainless steel. The element Cr is mainly enriched in the inner oxide layer, and the element Fe is relatively high in the outer oxide layer.

Keywords: HR3C Steel; High Temperature Oxidation; Water Vapor; Oxide Film

DOI: 10.57237/j.mater.2022.01.005

1 Introduction

HR3C heat-resistant steel (25Cr-20Ni-Nb-N steel) is a new type of austenitic heat-resistant steel improved by adding Nb and N in the basis of TP310 heat-resistant steel [1-4]. HR3C steel is widely used in supercritical and ultra-supercritical units due to its excellent properties, and HR3C steel has high oxidation resistance and high temperature corrosion resistance, which is more suitable than 18-8 type heat-resistant steel in ultra-supercritical unit boiler environment [5-8]. Lyta et al. [9] studied the microstructure evolution of the new austenitic stainless-steel Fe-20Cr-30Ni-2Nb (at%) during the oxidation process under the condition of water vapor at 800 ℃. Compared with traditional austenitic stainless steel such as 316, Fe-20Cr-30Ni-2Nb material has stronger oxidation resistance and high temperature corrosion resistance. Jeremy Cockrem et al. [10] conducted oxidation comparison tests on reheater and superheater steel TP347HFG steel, Super304H steel and HR3C steel in a closed-loop system with three different steam flow rates at 650 ℃ and 700 ℃, and concluded that the increase in temperature can accelerate oxidation of 18Cr series heat-resistant steel. Water vapor can also accelerate the oxidation of steel and promote the formation of surface junction oxides. For HR3C heat-resistant steel, water vapor has a greater effect on its oxidation than temperature, and

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Funding: National Natural Science Foundation of China (51071113);
Scientific Research Project of Hubei Provincial Department of Education (B2021409)

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Received: October 8, 2022; Accepted: November 7, 2022; Published Online: November 23, 2022

with Cr the increase of the content can form more protective Cr-rich oxide layers. The three steels have good oxidation resistance, among which HR3C steel has the strongest oxidation resistance, Super304H steel is the second, and TP347HFG steel is the weakest. At present, there are few reports on the high temperature oxidation performance analysis of HR3C steel, and such research is of great significance for ensuring the safe use of materials [11-14], improving the performance of materials and exploring the development of new materials [15-18]. In this paper, the specimens of HR3C steel after being oxidized in water vapor at 700 ℃ are analyzed to explore the oxidation law of HR3C steel at high temperature in water vapor, and provide reference for engineering practice and material modification.

2 Materials and Methods

The material used in the experiment is untreated as receive HR3C steel, and its chemical composition is shown in Table 1. The specimen is cut into 10 × 10 × 5 (mm) small specimens by wire cutting, and the surface of the specimen is polished with 400#, 800#, 1000# and 1500# metallographic sandpaper.

Table 1 Chemical component of HR3C steel (wt%)

Element	**C**	**Cr**	**Ni**	**Nb**	**Mn**	**N**	**Si**	**Fe**
HR3C	0.070	24.57	20.80	0.40	0.85	0.22	0.47	Bal

The treated HR3C specimens were oxidized for 50h, 150h, 250h, 350h, 450h, 550h and 600h in a self-made high-temperature water vapor oxidation furnace in a water vapor environment of 700 ℃. Weigh with an analytical balance to determine the oxidation kinetics curve, use Quanta 400 to observe the morphology of the oxide film on the surface and cross-section of the specimen, use the attached EDS to determine the element change of the cross-section of the oxide film, use XRD to analyze the composition characteristics of the oxide film.

3 Results and Analysis

3.1 Oxidative Weight Gain Kinetic Analysis

Figure 1 shows the data (kinetic curve) of the oxidation weight gain per unit area of HR3C steel oxidized in water vapor at 700 ℃ for different times and its fitting curve.

The kinetic curve of HR3C oxidized in high temperature water vapor at 700 ℃ is analyzed and studied, and the following rules can be obtained.

(1) The oxidation kinetic curve of the material conforms to the parabolic law, and the fitting equation is a type of $y = ax^b$, and the parameters of the fitting curve is show in Table 2.

(2) Before the oxidation for 20h, the slope of the curve is large, indicating that the oxidation rate is fast in the initial stage. At this time, a complete oxide film is not formed on the surface of the substrate, most of which are exposed to water vapor, and the thickness of the oxide film is very thin. The oxidation rate is determined by adsorption and decomposition rates of H_2O, and after 50h, the oxidation rate has slowed down compared with the previous period. At this time, the oxide film has a certain thickness, and the oxidation rate is determined by the diffusion and mass transfer rate of ions in the film. After 80h of oxidation, the oxidation rate became slower and smoother, indicating that a dense protective oxide film was formed in the film, which hindered the diffusion of ions and hindered the oxidation of metals.

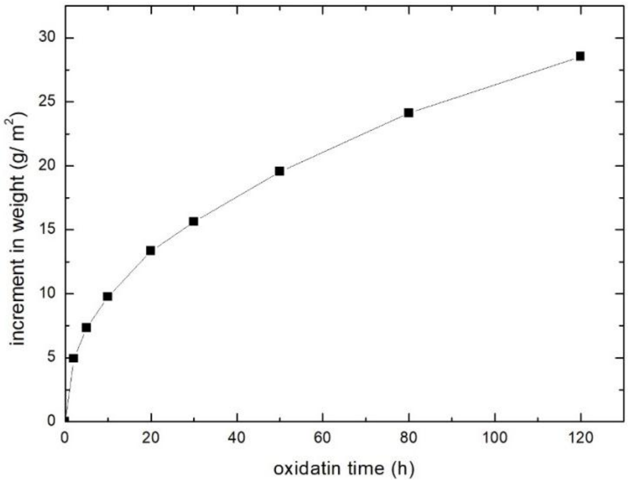


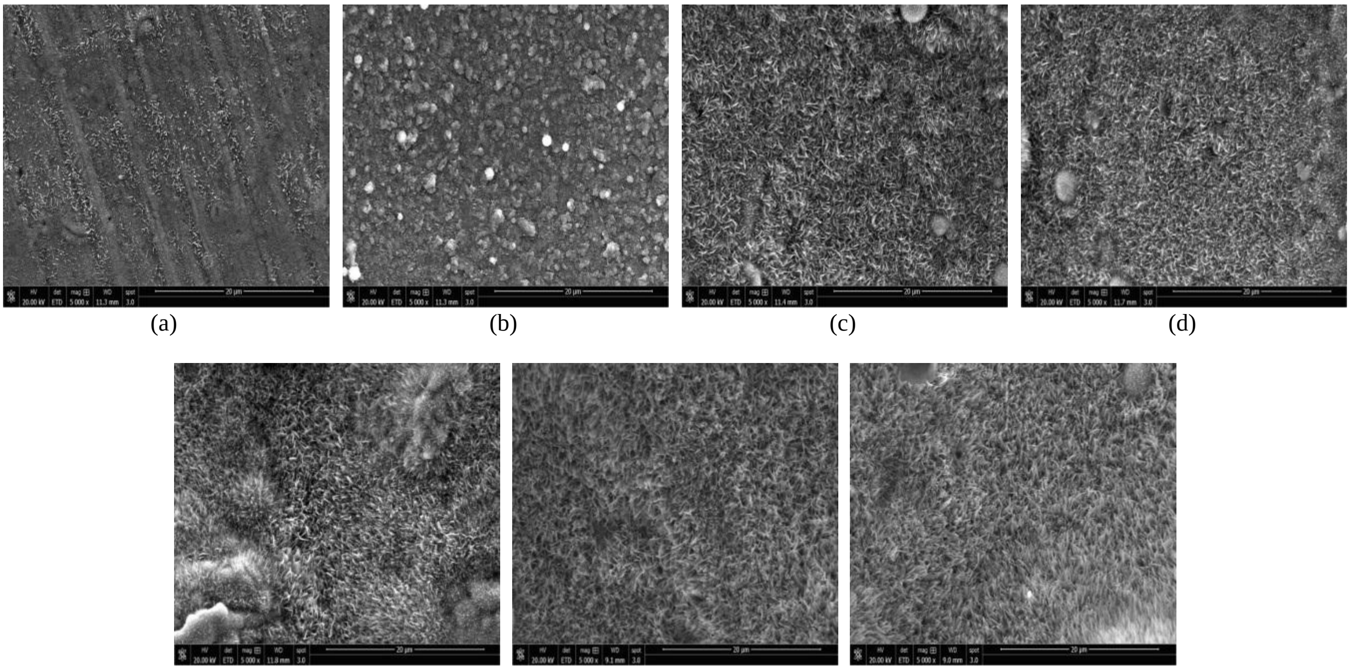
Figure 1 Oxidation kinetics curve of HR3C steel at 700 ℃

Table 2 Parameters of oxidation kinetics fitting curve

Temperature (℃)	**a**	**b**	**Adj. R-Square**	**Fitting equation**
700	3.6578	0.4672	0.9459	$y = 3.65x^{0.43}$

3.2 Analysis of the Oxide Film Morphologies on the Surface of the Specimen

The surface morphologies of HR3C steel after 700 ℃ high temperature water vapor oxidation for different time are shown in Figure 2.



(a) (b) (c) (d)

(e) (f) (g)

Figure 2 Surface morphology of oxide film results of HR3C steel after oxidized at 700 ℃ in water vapor (a) 50h, (b) 150h, (c) 250h, (d) 350h, (e) 450h, (f) 550h, (g) 600h

When HR3C steel is oxidized at 700 ℃ for 50h, a small amount of lamellar oxides can be observed on the surface. The distribution is relatively dispersed and the size is small, which is nano-scale or nearly nano-scale, indicating that the oxidation has begun to nucleate and grow. As the oxidation time extend, the oxides continue to increase. At 150h, the surface is mainly granular oxides, and the formation of fine lamellar oxides can be observed on the oxides. From the thermodynamic point of view, the granular oxides are impossible to convert to flaky oxide, so new oxide nuclei are generated in the process. The oxides of 350h and 450h are lamellar and unevenly distributed. The number and size of oxides in 550h are obviously larger than that in 450h, and the oxides grow up. The shape of this lamellar structure is strip or needle shape, because it grows perpendicular to the surface of the oxide film during the oxidation process, so when observing, only one of the lamellar structures can be seen from the direction perpendicular to the basal plane side. It can be observed that the oxide distribution is not uniform during the oxidation process. This may be due to the uneven distribution of water vapor in the self-made water vapor oxidation furnace, or because there may be impurities or defects on the surface, which lead to preferential nucleation of these positions during oxidation, and the oxidation rate of this region will be higher than that of other regions.

After 550h and 600h of oxidation, the oxides continued to increase, and the surface was loose and porous, which was basically completely covered by lamellar oxides, and clustered oxides appeared in some areas. When certain conditions are met during oxidation, some areas of the oxide film first grow lamellar oxides and grow convexly. As the oxidation continues, the lamellar oxides nucleate more and grow faster. When they are in contact with each other, due to the limited growth space, they cannot grow freely, and they will cross each other and grow together.

Therefore, in the end, the flaky oxides in the same direction will gradually fuse and grow close to each other, forming lamellar clusters, and flaky oxides in different directions or the clusters of lamellae will interleave each other and grow together to form a loose and porous oxide film surface.

To sum up, the oxidation process of HR3C steel is as follows: in the early stage of oxidation, lamellar oxides are first formed, and then the lamellar oxides continue to grow and thicken, intertwined and fused with each other to form lamellar clusters, and then grow up to a granular oxide, and then the formed granular oxide re-nucleates, grows a new lamellar oxide film, and repeats the above process.

3.3 Analysis of the Energy Spectrum Results of Oxide Film on the Surface of the Specimen

The oxidation film of the specimen after oxidation was scanned, and the composition comparison of different elements in the oxide film of HR3C steel oxidized in water vapor at 700 ℃ for different times is shown in Table 3.

From the experimental data in Table 3, it can be seen that when HR3C steel is oxidized in high temperature water vapor, the relative content of element O first decreases during 50h-250h oxidation, and increases continuously from 250h to 600h in the later period. The reason is that in the early stage of oxidation, the reaction at the oxidation interface generates the rate of oxides is greater than the diffusion and migration rate of O atoms. Due to insufficient supply of O atoms, the consumption of O atoms in oxidation cannot be offset, so the content of O has been decreasing in the early stage of oxidation. As the oxidation progresses, the oxidation rate decreases due to the thickening of the oxide film in the later stage, and the diffusion rate of O atoms is greater than the interface reaction rate, so the content of element O increases. The content of element Fe decreases continuously, and the content of element Cr increases first and it decreases later, but it is basically the same as the content of the matrix. It may be due to the certain volatility of oxides formed by element Cr in the later stage of oxidation, resulting in a decrease in the content. As the oxidation progresses, the thickness of the oxide film increases, and the value of M:O also decreases accordingly, the M stands for alloying elements. When HR3C steel is oxidized in water vapor at 750 ℃, the value of M:O at 600h is 0.77, which is close to 0.75. It is speculated that the oxide film may be composed of M_3O_4 type of oxide composition. It can be seen from the comparison that the M:O of 750 ℃ water vapor oxidation is smaller than that of 700 ℃ water vapor oxidations, indicating that with the increase of temperature, the oxidation of HR3C steel is more sufficient.

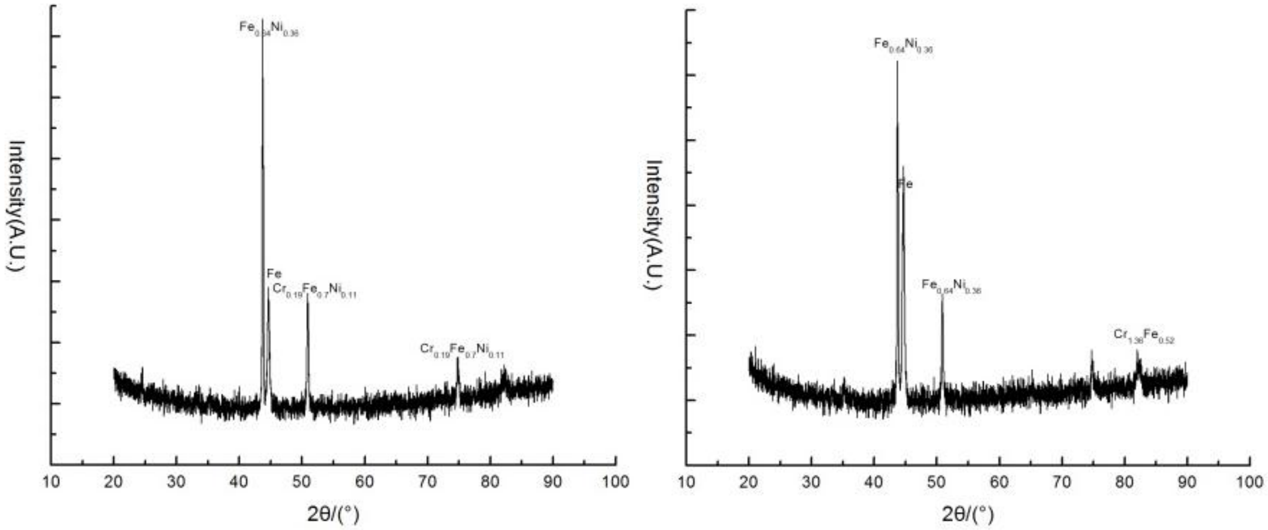
Table 3 Elements in oxidation film of HR3C steel after heated at 700 ℃ in water vapor

Time	**O**		**Cr**		**Fe**		**Ni**		**M:O**
	Wt%	**At%**	**Wt%**	**At%**	**Wt%**	**At%**	**Wt%**	**At%**	
50h	13.56	35.32	18.63	21.31	68.12	56.13	8.12	6.45	4.03
150h	6.23	21.43	17.82	21.67	66.84	55.23	8.01	6.32	3.60
250h	5.34	20.11	18.21	22.89	62.50	48.02	7.61	—	2.20
350h	16.98	39.54	19.11	26.98	62.79	48.73	7.30	—	2.41
450h	23.54	51.65	19.31	27.52	61.19	45.98	6.79	—	1.95
550h	23.98	52.32	21.98	24.77	53.94	37.52	6.71	—	1.35
600h	26.21	55.76	21.31	24.12	55.68	38.66	5.98	—	1.20

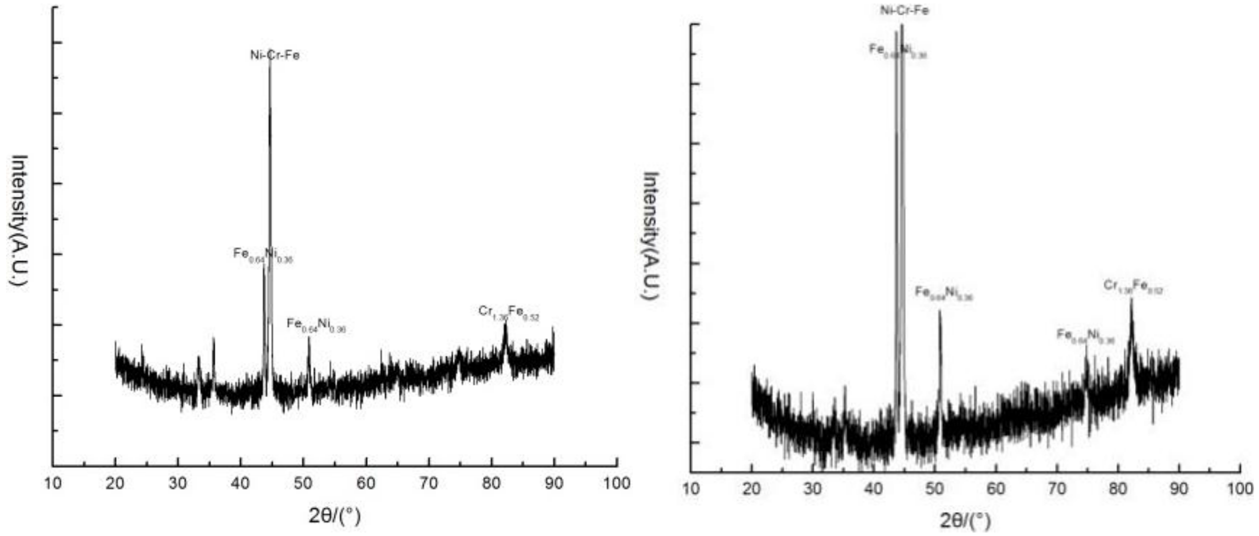
3.4 Analysis of XRD Results of the Oxide Film on the Surface of the Specimen

Figure 3 shows the XRD phase analysis results of the oxide film of HR3C steel oxidized for different times in high temperature water vapor.

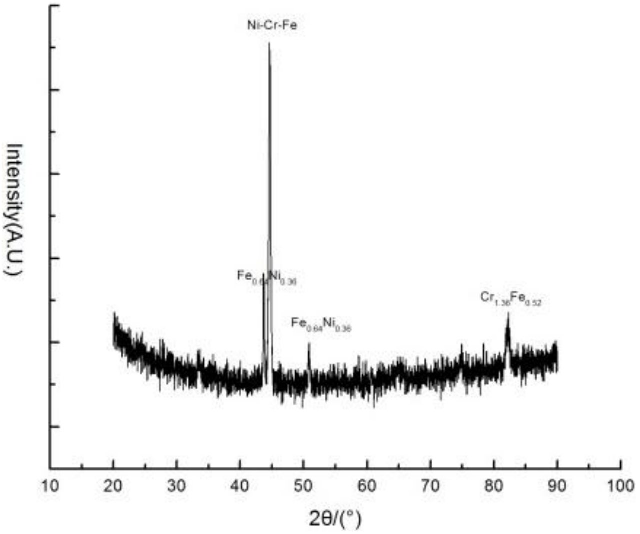
Figure 3 shows the results of XRD patterns of HR3C steel oxidized in water vapor at 700 ℃ for different times. It can be seen from Figure 3 that when oxidized at 700 ℃ for 50h, the oxidized surface material is measured as Fe-Cr. After 250h of oxidation, the oxide is composed of three oxides of Fe_3O_4, $FeCr_2O_4$ and Fe_2O_3. $FeCr_2O_4$ is a spinel compound, which can form dense oxide film, and the diffusion coefficient of metal ions in it is small, which hinders the diffusion and mass transfer of ions, thereby improving the high temperature oxidation resistance of stainless steel. After 600h oxidation, the oxidation products of water vapor oxidation at 700 ℃ are still Fe_3O_4, $FeCr_2O_4$ and Fe_2O_3.



(a) 50h (b) 250h



(c) 350h (d) 450h

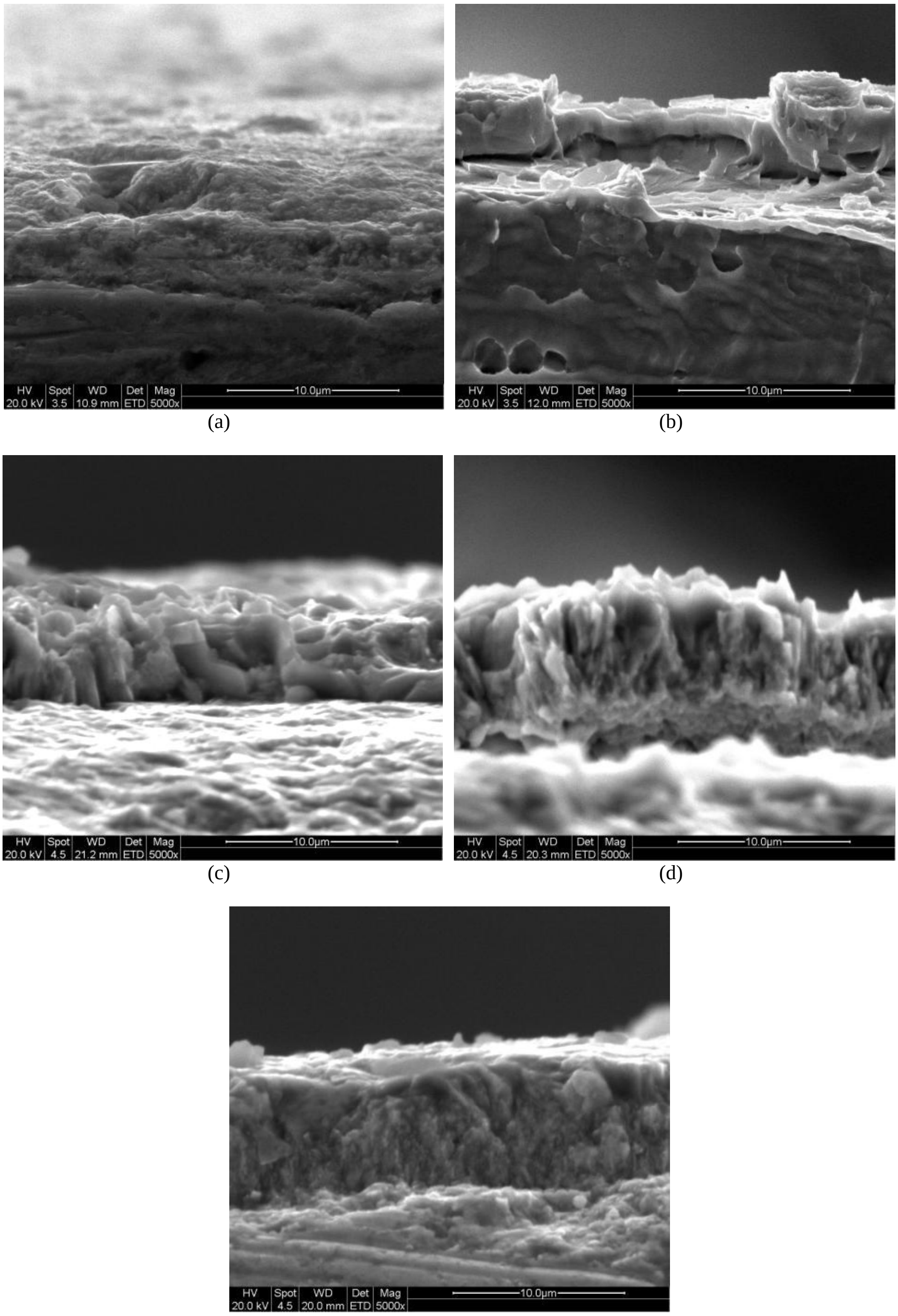


(e) 600h

Figure 3 XRD results of oxidation film of HR3C steel after oxidized at 700 ℃ in water vapor (a) 50h, (b) 250h, (c) 350h, (d) 450h, (e) 600h

3.5 The Cross-sectional Morphology of the Oxide Film of the Specimen

Figure 4 shows the scanning morphology of the cold brittle fracture obtained by HR3C steel after being oxidized in high temperature water vapor at 700 ℃ for different times.



(a) (b)

(c) (d)

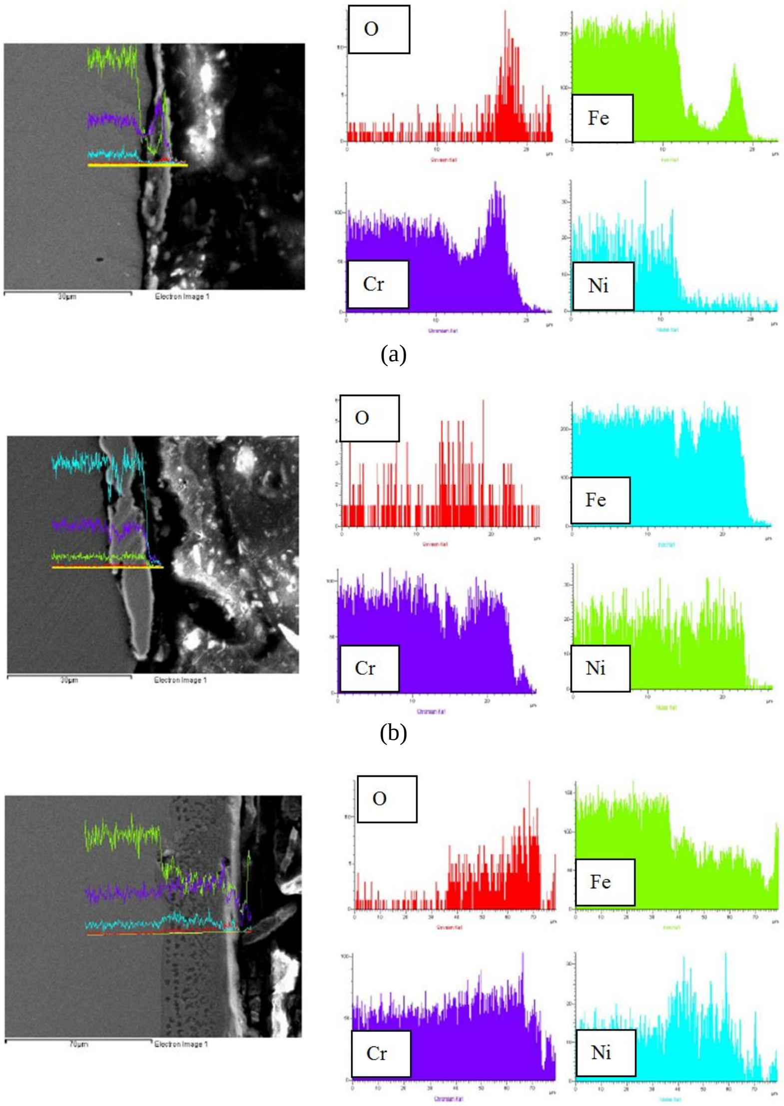
(e)

Figure 4 Section morphology of oxide film of HR3C steel after oxidized at 700 ℃ in water vapor (a) 50h, (b) 250h, (c) 350h, (d) 450h, (e) 600h

It can be seen from Figure 4 that the fracture section at 700 ℃ is uneven when oxidized for 50h, and the oxide particles are scattered in it, and a complete oxide film is not formed. The protrusions on the surface should be preferentially nucleated and grown by oxides area. After 250h of oxidation, the oxides increased and grew up, and two shapes of oxides, granular structure and lamellar structure, could be observed from the side. And a relatively complete oxide film is formed. The oxide film has a double-layer structure, and there is a wide gap between the inner and outer oxide layers, which may develop into cracks in the subsequent oxidation process, resulting in the peeling of the oxide scale. After 350h and 450h of oxidation, the thickness of the oxide film increased with the prolongation of the oxidation time. And the phenomenon of delamination appears obviously, and the oxide film is composed of two layers of grains. The outer layer of the oxide film has relatively coarse grains, which are micron-level equiaxed crystals, while the inner layer is relatively dense, with smaller grain sizes, which are nano-scale equiaxed crystals. After 600h of oxidation, the thickness of the oxide film continued to increase, and the equiaxed crystals in the outer layer gradually grew into columnar crystals with larger size.

3.6 Line Scan Results of the Oxide Film Cross Section of the Specimen

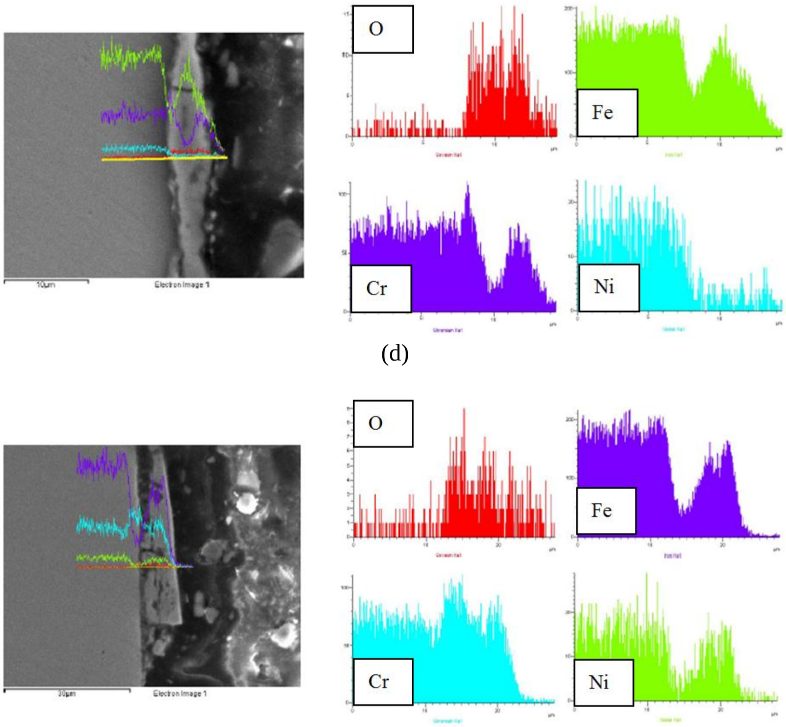
Figure 5 shows the element line scan results of the oxide film on the cross-section of HR3C steel with high temperature water vapor at 700 ℃.



(a)

(b)

(c)



(d)

(e)

Figure 5 Cross-sectional line scan results of oxide film of HR3C steel after oxidized at 700 ℃ in water vapor (a) 50h, (b) 250h, (c) 350h, (d) 450h, (e) 600h

From the analysis of Figure 5, the change rules of elements in the cross section of the oxide film can be obtained, and the delamination and composition of the oxide film can be obtained. The law is as follows: the main constituent elements of the oxide film are O, Fe, Cr, and Ni, and the content of Ni is very small, so it is speculated that a composite oxide containing Cr and Fe is formed in the oxide film. During high-temperature water vapor oxidation at 700 ℃, the content of Cr increases from small to large in the direction from the substrate to the oxide film, until the bonding surface between the substrate and the inner oxide film reaches the maximum, and then greatly decreases in the outer oxide layer. The content of Cr in the inner oxide layer is higher than that in the matrix, indicating that the content of Cr in the inner oxide layer is high and is enriched in the inner oxide layer. On the contrary, element Fe, from the substrate to the oxide film, first decreased and then increased, and suddenly decreased at the interface between the inner oxide layer and the substrate. The content of Fe in the inner oxide layer was low, and then in the outer oxide layer. The content began to increase again and was higher than that of the matrix, indicating that the outer layer was basically composed of Fe oxides. Among them, the content of Fe is the lowest in the area with the largest Cr. When the element Cr increases, the element Fe decreases, indicating that there is a certain complementarity between Fe and Cr. The distribution of element O in the whole oxidation process has been relatively uniform. Whether it is in the inner layer of the oxide film or in the outer layer of the oxide film, its content is higher than that of the matrix, and the change in the 600h oxidation is relatively slow. The element Ni suddenly dropped at the interface between the inner oxide layer and the substrate, and maintained a very low content in the inner and outer oxide layers, indicating that the content of Ni in the oxide film was very little or almost no. The change law of element content in the process of high temperature steam oxidation at 750 ℃ is similar to that of high temperature steam oxidation at 700 ℃. And from 50h to 600h, the longer the oxidation time, the more obvious the change rule.

To sum up, the elements contained in the oxide film formed by high-temperature steam oxidation at 700 ℃ have a certain change law and a certain concentration change gradient. The element Cr is basically enriched in the inner oxide layer, and the content in the outer oxide layer is very small. It is probably because the Cr participates in the formation of the inner oxide layer and does not participate in the formation of the outer oxide layer, or because Cr is in the process of oxidation. The volatile $CrO_2(OH)_2$ generated in the oxidation process causes Cr in the outer oxide layer to be almost volatilized, so the content is low. Unlike Cr, element Fe has a higher content in the outer oxide layer and basically participates in the formation of the outer oxide layer, while the content of Fe in the inner oxide layer is higher than that in the matrix.

4 Conclusion

(1) Under the condition of water vapor oxidation at 700℃, the oxidation kinetics curve follows a parabolic law. The parabolic pattern of the metal shows good oxidation resistance, which indicates that the material can be effectively served at 700℃. During the oxidation process, the formation process of oxide film lamella clusters is: firstly, lamellar oxides are generated on the surface. It will gradually fuse and grow close to form lamellar clusters. The flaky oxides or lamellar clusters in different directions will intersect with each other and grow together to form a loose and porous oxide film surface. And the oxide film may exhibit higher compactness under high pressure, which needs to be further studied.

(2) The oxide is composed of three oxides: Fe_3O_4, $FeCr_2O_4$ and Fe_2O_3. The $FeCr_2O_4$ is a spinel compound, which can form a dense oxide film, and the diffusion coefficient of metal ions in it is small, which hinders the diffusion and mass transfer of ions, thereby improving the stainless steel high temperature oxidation resistance.

(3) The oxide film is a two-layer structure, the inner oxide film is composed of $FeCr_2O_4$, and the outer oxide layer is composed of Fe_3O_4 and Fe_2O_3. The element Cr is basically enriched in the inner oxide layer, and the content in the outer oxide layer is very small, and it suddenly drops at the junction surface of the inner oxide layer and the substrate. The content of element Fe in the outer oxide layer is relatively high, and it participates in the formation of the outer oxide layer. The element Ni suddenly drops at the interface between the inner oxide layer and the substrate, and maintains a very low content in the inner and outer oxide layers. Moreover, the effect of Cr element on the binding force between oxide and matrix and the compactness of oxide film is an important research direction.

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