

Effects of composite scale on high temperature oxidation resistance of Fe-Cr-Ni heat resistant alloy

*Wang Haitao¹, Wang Yuqing², Yu Huashun¹, Min Guanghui¹ and Wang Zhifu¹

(1. Key Laboratory for Liquid Structure and Heredity of Education Ministry, School of Materials Science and Engineering, Shandong University, Jinan 250061, China; 2. Jinan Railway Institute of Technology, Jinan 250013, China)

Abstract: Fe-Cr-Ni heat resistant alloys with aluminum and silicon addition, alone and in combination, were melted using an intermediate frequency induction furnace with a non-oxidation method. By the oxidation weight gain method, the oxidation resistances of the test alloys were determined at 1,200 °C for 500 hours. According to the oxidation weight gains, the oxidation kinetic curves were plotted and the functions were regressed by the least squares method. The results show that the oxidation kinetic curves follow the power function of $y = ax^b$ ($a > 0$, $0 < b < 1$). The effects of scale compositions on oxidation resistance were studied further by analyses using X-ray diffraction (XRD) and scanning electron microscope (SEM). It is found that the composite scale compounds of Cr_2O_3 , $\alpha\text{-Al}_2\text{O}_3$, SiO_2 and FeCr_2O_4 , with compact structure and tiny grains, shows complete oxidation resistance at 1,200 °C. When the composite scale lacks $\alpha\text{-Al}_2\text{O}_3$ or SiO_2 , it becomes weak in oxidation resistance with a loose structure. By the criterion of standard Gibbs formation free energy, the model of the nucleation and growth of the composite scale is established. The forming of the composite scale is the result of the competition of being oxidized and reduced between aluminum, silicon and the matrix metal elements of iron, chromium and nickel. The protection of the composite scale is analyzed essentially by electrical conductivity and strength properties.

Key words: Fe-based alloy; heat resistant alloy; oxide scale; oxidation resistance

CLC number: TG142.73

Document code: A

Article ID: 1672-6421(2009)02-109-06

Heat resistant alloys not only can bear specific stress, but also have oxidation and corrosion resistance at high temperature. With more abundant resource, lower price, and an easier manufacturing process than nickel and cobalt super-alloys, now Fe-Cr-Ni heat resistant alloys are employed popularly in national defense, energy resources, aviation, and nuclear reaction fields as high temperature structure materials. The main alloying element for oxidation and corrosion resistance in heat resistant alloys is chromium, which is solidified in ferrite and with a certain amount can form a layer of Cr_2O_3 outside to protect the matrix at high temperature. In order to improve its oxidation resistance, aluminum or silicon is added to the matrix. Silicon can be oxidized to be SiO_2 scale, which has high heat stability, so it is usually added to heat resistant alloys to improve the oxidation resistance. For example, in Fe-Cr-Si, Fe-Cr-Ni-Si and Fe-Cr-Mn-Si series heat resistant alloys, SiO_2 not only increases the compactness of Cr_2O_3 scale, but also enhances the adhesion strength of scales

with the matrix and reduces the tendency of scale exfoliating^[1-3]. With the presence of aluminum, the Fe-Cr-Al, Fe-Cr-Ni-Al series heat resistant alloys are famous for high temperature oxidation resistance though their mechanical properties are not ideal. Al_2O_3 scale, forming at high temperature, hard and compact, without volatility, is combined tightly with Cr_2O_3 scale, enhancing the oxidation resistance for heat resistant alloys greatly^[4-7]. However, little research has been done on Fe-Cr-Ni heat resistant alloys containing aluminum and silicon at the same time to form composite scales to raise high temperature oxidation resistance. So this paper will inquire further into the influence of composite scale derived from chromium, aluminum and silicon on high temperature oxidation resistance by experiments with the aim to provide necessary experimental basis for developing new kinds of heat resistant alloys with higher qualities.

1 Experimental procedure

1.1 Manufacture of test alloys

This experiment was to study the effects of jointly adding aluminum and silicon on high temperature oxidation resistance of Fe-Cr-Ni heat resistant alloys. Though aluminum and silicon are elements that resist oxidation, they both easily form brittle phases, adding too much of them lead to great

*Wang Haitao

Male, born in 1972, Ph. D candidate, senior engineer. Research areas: special Fe-based alloys

E-mail: htwangsd@126.com

Correspondence to Professor Yu Huashun

E-mail: yuhuashun2002@yahoo.com.cn

Received: 2008-11-29; Accepted: 2009-03-01

loss of strength and toughness at high temperature. According to the results of reference [8], the content of aluminum and silicon were designed to be 3 wt% and 2 wt% respectively, taking account of excellent oxidation resistance and not much reduction in high temperature strength. The other elements of the test alloys were fixed. In comprehensive consideration of high temperature oxidation resistance and strength, 0.06 wt% C, 23 wt% Cr and 12 wt% Ni were determined. To ensure a certain high temperature strength, 1 wt.% Mo and 0.5 wt.% Ti were added to solid solution strengthen the matrix. Being harmful to matrix structure, P and S were both to be controlled lower than 0.01 wt.% in test alloys.

The experimental materials involved industry-pure iron, tinny carbon-chrome iron, pure nickel plate, industry-pure silicon, aluminum wire and ferrotitanium. By a non-oxidation

method, these materials were smelted in an intermediate frequency induction furnace with lime and fluorite to remove dregs. Because aluminum is not only the alloying element, but also the de-oxidation element, its content and metallurgical state should be controlled strictly. Aluminum should be added after the ultimate de-oxidation by the yielding rate of 94 wt% considering oxidation burning loss.

The smelting temperature was controlled at 1,580 to 1,620°C and the pouring temperature was at about 1,520 to 1,550°C. The roughcasts were made in graphite moulds, which were pre-heated to prevent blow holes. In order to analyze the influence of jointly adding aluminum and silicon on high temperature oxidation resistance and compared with that of single addition Al or Si and without Al and Si, four groups of test alloys were cast. The chemical compositions are listed in Table 1.

Table 1 Chemical compositions of test alloys (wt%)

Alloy No.	C	Cr	Ni	Al	Si	Mo	Ti	P, S	Fe
1	0.061	23.14	11.97	2.96	1.94	1.11	0.53	<0.01	Bal.
2	0.058	22.97	12.06	3.04	0	0.98	0.52	<0.01	Bal.
3	0.059	23.11	11.96	0	2.01	1.09	0.52	<0.01	Bal.
4	0.062	22.92	12.03	0	0	0.96	0.49	<0.01	Bal.

1.2 Oxidation testing

The oxidation resistance experiment was carried out by oxidation weight gain method according to the China National Standard GB/T13303-1991. The roughcasts were machined to be $\Phi 15$ mm \times 30 mm specimens with surface roughness Ra 0.8 μ m. Three specimens of each group were held in different corundum crucibles and heated to 1,200 °C for 500 hours oxidation in SX2-8-13 silicon controlled heating furnace. Every 100 hours the oxidation weight gains were measured using a TG3288 10-4g photoelectric analysis balance. Then the oxidation weight gain rates of each group were calculated as the mean value of three for the last 100 hours.

The composition and morphology of scales were analyzed using a D/MAX-RB type X-ray diffraction (XRD) and a JXA-840 type scanning electron microscope (SEM).

2 Results and discussion

2.1 Oxidation kinetics of test alloys

The oxidation weight gains of four groups of alloys and the calculated gain rates are listed in Table 2. From the data, the oxidation kinetic curves are plotted in Fig. 1.

Figure 1 shows that the oxidation weight gain curve of test alloy No. 1 lies in the lowest position among the four. With the least weight gain in equal oxidation time, the oxidation resistance of alloy No. 1 is obviously better than that of other three alloys. Its oxidation weight gain rate is only 0.084 g/(m²·h), reaching the complete oxidation resistance according to the Standard. The oxidation weight gain curves of alloys No. 2 and No. 3 are both higher than that of alloy No. 1. Their oxidation resistances are worse, and the oxidation weight gain rates are 0.89 g/(m²·h) and 0.94 g/(m²·h), respectively, at 1,200 °C. When aluminum and silicon are both absent in alloy No. 4, its oxidation weight gain was much higher than the others at the beginning, and scales shelled off layer by layer with time. Being oxidized in 200 hours at 1,200 °C, the matrix cracked deeply, and the experiment was stopped. With few oxidation weight gain data and simple composition, the oxidation kinetics and scale composition effects on oxidation resistance of alloy No. 4 were omitted in later discussion.

The oxidation kinetic curves of heat resistant alloys follow the parabolic law shown by many studies^[9-12]. The common characteristic of oxidation kinetic curves of the heat resistant alloys is that the oxidation weight gain in equal time decreases

Table 2 Oxidation weight gains and rates of test alloys in 500 hours oxidation at 1,200 °C

Alloy No.	Oxidation weight gain (g/m ²)					Weight gain rate g/(m ² ·h)
	100 h	200 h	300 h	400 h	500 h	
1	146.4	198.5	237.9	268.7	277.1	0.084
2	152.2	280.1	394.7	491.1	580.5	0.89
3	169.2	308.4	423.1	511.7	605.9	0.94
4	198.4	379.2				

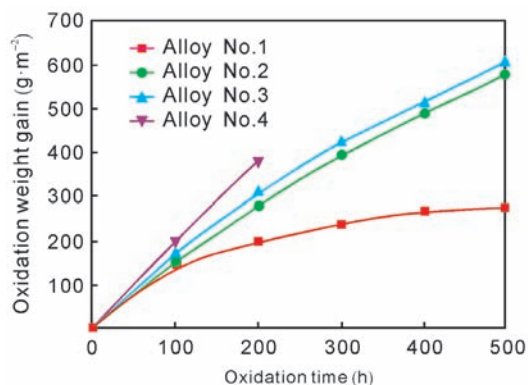


Fig. 1 Oxidation kinetic curves of test alloys at 1,200 °C

gradually, or the curve slope diminishes continuously. In the writer’s opinion, such curves could not always be regressed to be parabolic functions, but merely look like parabolic curves. The oxidation behavior of heat resistant alloys is affected by many factors, such as chemical composition and experimental

conditions and so on. So the oxidation kinetic curves from zero origin will display variously, not only following the parabolic function of $y^2 = 2px$, in which the oxidation time x goes by simple equation, the oxidation weight gain y goes by quadratic equation, and the unique variable is the focus p . Thus, only depending on the gap size of parabola to explain the varieties of oxidation weight gain curves is obviously oversimplified.

In this experiment, by the least square method regression of data from Table 2 and non-linear curve fitting, the oxidation weight gain curves of test alloys are found to follow the power function $y = ax^b$ ($a>0, 0<b<1$). The regression equations and parameters of the three oxidation weight gain curves are shown in Table 3. In the equations the parameters a and b together influence the shape and height of the curves, so fixing the oxidation resistance of alloys. Here it is not difficult to notice that the curve power function becomes parabolic if parameter b is 0.5. That is to say the parabola is only a special case of the power function law. Only when every condition is prepared well, will the oxidation weight gain curve follow the parabolic law.

Table 3 Regression equations of kinetic curves of test alloys at 1,200 °C

Alloy No.	Regression equation y: oxidation weight gain (g/m ²), x: oxidation time (h)	Regression time zone (h)	Correlation coefficient, R
1	$y = 10.0465 x^{0.5433}$	0 – 500	0.9318
2	$y = 3.1982 x^{0.8347}$	0 – 500	0.9958
3	$y = 4.2138 x^{0.7974}$	0 – 500	0.9946

The significance of the regression equations and parameters of these oxidation weight gain curves are evaluated by t test and F test; giving the significance level α : 0.01.

The t test for regression coefficients of alloy No. 1 can be calculated from the formula:

$$T = \frac{R\sqrt{n-2}}{\sqrt{1-R^2}} = \frac{0.9318\sqrt{6-2}}{\sqrt{1-0.9318^2}} = 5.134$$

While $t_{0.5\alpha}(n-2) = 4.604$ taken from the Mathematical Statistics t Distribution Critical Value Table. Because $T > t_{0.5\alpha}(n-2)$, the statistical assumption H_0 (known as the original assumptions or null hypothesis) is refused, and another statistical hypothesis H_1 (known as the alternative assumption) is accepted. So the regression coefficients: $a = 10.0465$ and $b = 0.5433$ are both significant and the confidence level is 99 %.

Likewise the F test for the regression equation of alloy No. 1 can also be calculated from the formula:

$$F = (n-2) \frac{R^2}{1-R^2} = (6-2) \frac{0.9318^2}{1-0.9318^2} = 26.36$$

While $F_{\alpha}(1, n-2) = 21.2$ taken from the Mathematical Statistics F Distribution Critical Value Table. For $F > F_{\alpha}(1, n-2)$, H_0 is refused and H_1 is accepted. So the regression equation: $y = 10.0465x^{0.5433}$ is significant and the confidence level is also 99 %.

So the oxidation weight gain curve of alloy No. 1 strictly follows the power function law: $y = ax^b$ ($a>0, 0<b<1$). In the

same way, curves of alloys No. 2 and No. 3 are also found to follow the power function law.

2.2 Effects of scale composition on oxidation resistance of test alloys

With enough chromium, aluminum and silicon, the scale of alloy No. 1 involves all of the composition Cr_2O_3 , $\alpha-Al_2O_3$ and SiO_2 after 500 hours oxidation at 1,200 °C. By X-ray diffraction analysis (see Fig. 2(a)), it is a multi-oxide structure with the main composition of Cr_2O_3 and the complements of $\alpha-Al_2O_3$ and SiO_2 to protect the alloy matrix. Cr_2O_3 , $\alpha-Al_2O_3$ and SiO_2 all have the properties of high melting point, high heat stability and high formation enthalpy. They are not easy to decompose at high temperature, so each of them has the excellent oxidation resistance. As studied in some references [13-16], $\alpha-Al_2O_3$ or SiO_2 not only are supplies for Cr_2O_3 scale to elevate the compactness, but also greatly enhance the adhesive force of Cr_2O_3 scale with the matrix by penetrating, compounding and pinning. So the anti-exfoliating ability of scale is improved and the oxidation resistance of alloy is strengthened. The scale morphology of alloy No. 1 is shown in Fig. 2(b). The scale structure is flat and compact, without bulge, pit or crimple. The multi-oxide grains connect tightly and penetrate each other without holes. During oxidation at high temperature, the growth of Cr_2O_3 grain is hindered by the forming of aluminum and silicon oxides. So the multi-oxide grains are all fine and even in size, without abnormal growth.

Such scale of the compounded multi-oxide of Cr_2O_3 , $\alpha\text{-Al}_2\text{O}_3$, SiO_2 and spinel $\text{Fe}(\text{Ni})\text{Cr}_2\text{O}_4$ is the strongest resistant scale in this experiment. It has the complete oxidation resistance and the lowest oxidation weight gain curve in Fig. 1.

When there is no silicon or aluminum in the test alloys, the composition SiO_2 or $\alpha\text{-Al}_2\text{O}_3$ would be absent in scales accordingly (see Figs. 3(a) and 4(a)). For alloy No. 2 and alloy No. 3, the oxidation resistance dropped obviously without the complementing and compounding of SiO_2 or $\alpha\text{-Al}_2\text{O}_3$, Figure 3(b) and Fig. 4(b) show that these scales are both loose in structure and have many holes and crimples. The oxides grains are coarse and uneven.

Because the adhesive force decreased without the pinning and strengthening of the absent oxides, a bit of scale exfoliated during oxidation. $\alpha\text{-Al}_2\text{O}_3$ is more stable than SiO_2 , so the oxidation resistance of alloy No. 2 is a bit better than that of alloy No. 3. It also can be seen from Fig. 1 that the oxidation weight gain curve of alloy No. 3 goes a little higher than that of alloy No. 2.

According to the characterization and analyses above, a theoretical model was constructed by the writers to explain the formation process of the composite scale. Besides iron, the test alloys contain high contents of chromium (23 wt%) and nickel (12 wt%), so iron, chromium and nickel can all be regarded as matrix metal elements. At the beginning of oxidation, as

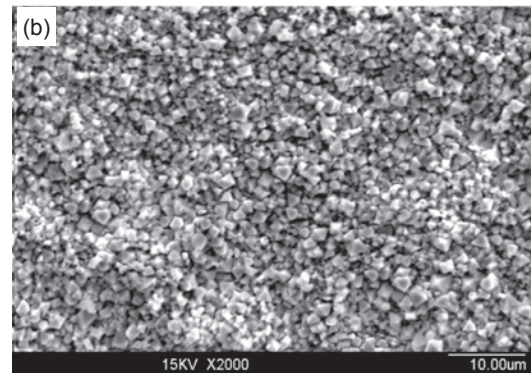
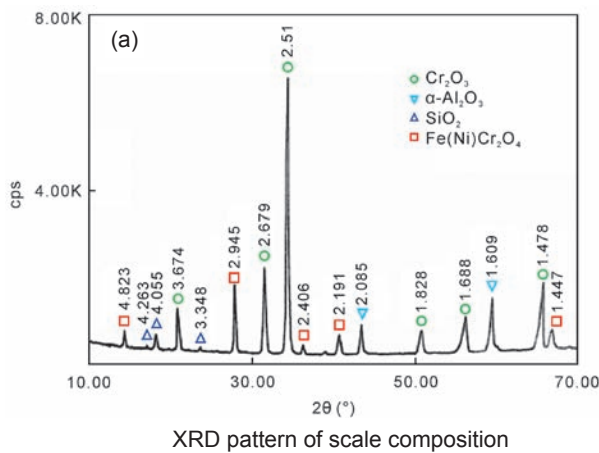


Fig. 2 Scale composition and morphology of test alloy No. 1, 1,200 °C, 500 h

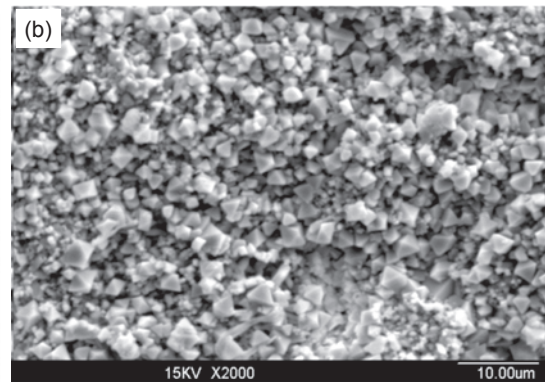
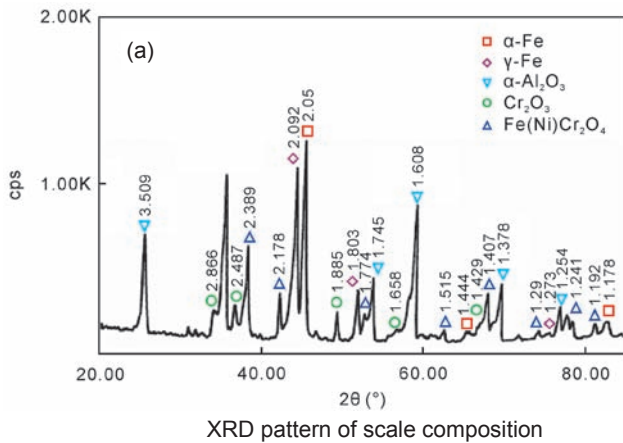


Fig. 3 Scale composition and morphology of test alloy No. 2, 1,200 °C, 500 h

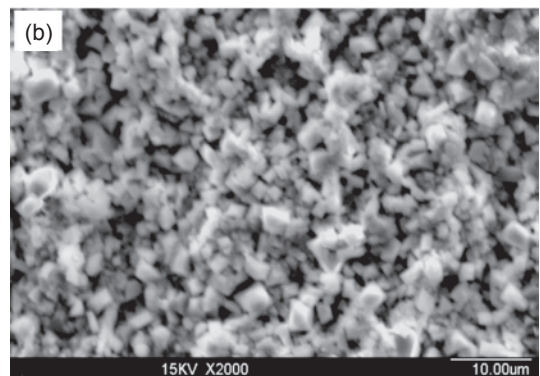
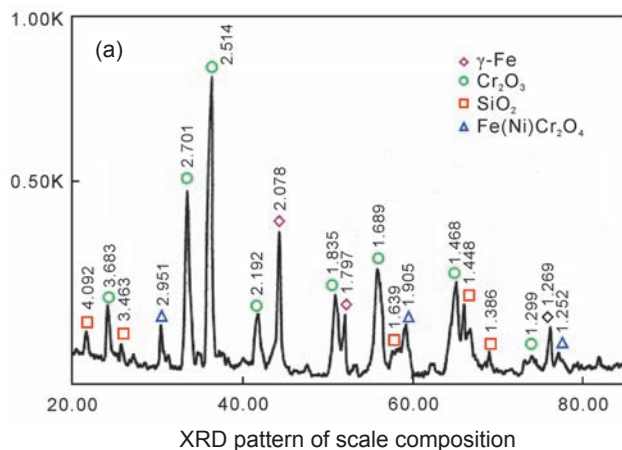


Fig. 4 Scale composition and morphology of test alloy No. 3, 1,200 °C, 500 h

shown in Fig. 5(a), the matrix metal elements are oxidized to be FeO, Cr₂O₃ and NiO, covering the surface of the test alloys. If there is Al or Si, the minimum Al or Si around the surface will be oxidized at the same time to be tiny particles of Al₂O₃ or SiO₂ dispersing in the matrix metal oxides. This is the first stage of oxidation. With nucleation and growth, the same kinds of oxides are prone to aggregate and polymerize to bigger ones. So the oxides grains are coarse and uneven in this

stage. The scales are not compact in structure, and have many holes, resulting in rapid oxidation and high oxidation weight gain rate. With the process of oxidation, in order to decrease the free energy, the reactions of forming spinels take place automatically around grain boundaries:

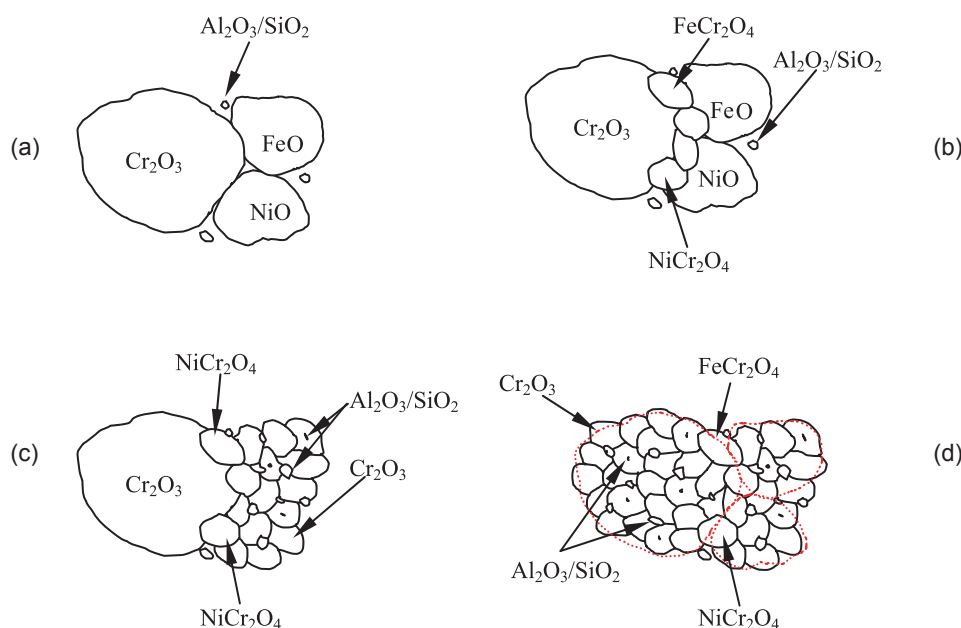
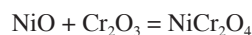
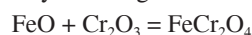
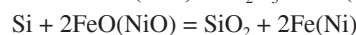
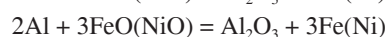
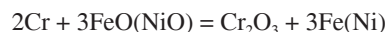


Fig. 5 The model of the nucleation and growth of the compounded scale

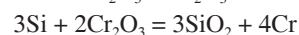
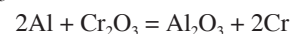
Figure 5(b) shows that the spinels FeCr₂O₄ and NiCr₂O₄ come into being around the grain boundaries of FeO and NiO.

As is well known, lower standard formation Gibbs free energy means higher stability. Alloying elements at high temperature compete to be oxidized with each other. The element with lower oxide formation energy can be oxidized prior to that with higher oxide formation energy, and the former can reduce the latter. As listed in Table 4, the calculated standard formation Gibbs free energies of Cr₂O₃, Al₂O₃ and SiO₂ at 1,200 °C are all lower than those of FeO and NiO, so FeO and NiO can both be reduced by Cr, Al or Si diffusing out from the matrix:



As shown in Fig. 5(c), the outer FeO and NiO decompose and are replaced by new Cr₂O₃, Al₂O₃, and SiO₂ gradually.

Because the standard formation Gibbs free energy of Al₂O₃ and SiO₂ is lower than that of Cr₂O₃, the competition of being oxidized and reduction between Al, Si and Cr go along with oxidation. The coming Al and Si, coming from inner matrix can reduce Cr₂O₃:



At the same time, the micro particles of the new Al₂O₃ and SiO₂ are both heterogeneous nucleus of Cr₂O₃. So re-crystallization of Cr₂O₃ takes place at high temperature in the last stage of oxidation. Figure 5(d) shows that the former coarse Cr₂O₃ is disassembled to be fine isometric grains by re-crystallization, and a small fraction of Cr₂O₃ is replaced by fine grains of Al₂O₃ and SiO₂. During oxidation at high temperature, the high stable scattering Al₂O₃ and SiO₂ not only are the heterogeneous nucleus of Cr₂O₃, FeCr₂O₄ and NiCr₂O₄, but also prevent oxides grains from growing. As shown in the composite scale of alloy No. 1 (Fig. 2(b)), the grains are very fine and even, the size is only about 1 to 2 μm, the structure is so compact without holes. It is the results of the competition of oxidation, reduction, heterogeneous nucleation and re-

Table 4 Standard Gibbs formation free energy, conductivity and semiconductor type of oxides

Oxide	Standard Gibbs free energy of formation at 1,200 °C (kJ·mol ⁻¹)	Conductivity at 1,000 °C (s·cm ⁻¹)	Type of semiconductor
FeO	-334.96	10 ²	P
Cr ₂ O ₃	-496.00	10 ⁻¹	P
NiO	-228.60	10 ⁻²	P
Al ₂ O ₃	-804.93	10 ⁻⁷	N
SiO ₂	-646.99	10 ⁻⁶	N
FeCr ₂ O ₄	-830.96	0	Insulator
NiCr ₂ O ₄	-724.60	0	Insulator

crystallization.

The protection of the composite scale can be analyzed by the electrical conductivity and strength properties. According to Wagner theory, the conductivity is of great importance to the oxidation resistance. High conductivity can promote the metal and oxygen ions to penetrate oxides scales, so oxidation speeds up. Protective scales always have lower conductivity. A majority of metal oxides are semiconductors. The type and conductivity are listed in Table 4. As said in reference [17], semiconductor P and semiconductor N contribute to insulation. That is to say: P type oxides + N type oxides = insulator. So the composite scale composed of different oxides of Cr_2O_3 , $\alpha\text{-Al}_2\text{O}_3$, SiO_2 , FeCr_2O_4 and NiCr_2O_4 has insulating status, forming a barrier to elements diffusion. As a result, the composite scale exhibits complete oxidation resistance. This explanation is consistent with the experimental results of alloy No. 1. When $\alpha\text{-Al}_2\text{O}_3$ or SiO_2 is absent, the insulation of scales becomes weaker to some extent; it can not completely prevent the ions from diffusing along scales completely. So the oxidation weight gain rate goes up, and the oxidation resistance goes down.

On the other hand, with much more area of grain boundaries, the fine grains of the composite scale can absorb the creeping deformation and release the stress resulting from the different heat expansion between the scale and matrix. So the bond strength and exfoliation resistance are reinforced greatly. What is more, fine grains can enormously reduce the volume of the hole in scale, and decrease the non-connecting area with matrix. So the adhesion of scale with matrix is strengthened remarkably. All these advantages endow the composite scale with higher oxidation resistance.

3 Conclusions

(1) The oxidation kinetic curves of test alloys follow the power function of $y = ax^b$ ($a > 0$, $0 < b < 1$). The parameters a and b , in the regression equations, together decide the shape and height of the oxidation kinetic curves and reflect the oxidation resistance property of scales.

(2) The composition of oxide scale is the decisive factor affecting the oxidation resistance of heat resistant alloys. The composite scale, compounded of Cr_2O_3 , $\alpha\text{-Al}_2\text{O}_3$, SiO_2 , FeCr_2O_4 and NiCr_2O_4 , with flat and compact structure, fine and even grains, exhibits complete oxidation resistance at 1,200 °C. Its oxidation weight gain rate is only 0.084 g/(m²·h). When either $\alpha\text{-Al}_2\text{O}_3$ or SiO_2 is absent the scale becomes poor with loose structure and coarse grains.

(3) The formation of the composite scale is the results of the competition of oxidation and reduction between aluminium, silicon and the matrix metal elements iron, chromium, and nickel, according to the standard Gibbs free energy of formation.

(4) The excellent oxidation resistance of the composite scale mainly exists because different semiconductor scales compounded with each other promote the insulation status, preventing metal elements from being oxidized.

References

- [1] Hsu H W and Tsai W T. High temperature corrosion behavior of siliconized 310 stainless steel. *Mater Chem. Phys.*, 2000, 64: 147–155.
- [2] Huntz A M, Bague V, Beaulé G, et al. Effect of silicon on the oxidation resistance of 9 % Cr steels. *App. Surf. Sci.*, 2003, 207: 255–275.
- [3] Bamba G, Wouters Y, Galerie A, et al. Thermal oxidation kinetics and oxide scale adhesion of Fe-15Cr alloys as a function of their silicon content. *Acta Materialia*, 2006, 54(15): 3917–3922.
- [4] Wolff I M, Iorio L E, Rumpf T, et al. Oxidation and corrosion behaviour of Fe-Cr and Fe-Cr-Al alloys with minor alloying additions. *Materials Science and Engineering A*, 1998, 241: 264–276.
- [5] Gan L, Gomez R D, Castillo A, et al. Ultra-thin aluminum oxide as a thermal oxidation barrier on metal films. *Thin Solid Films*. 2002. 415: 219–223.
- [6] Adams T M, Korinko P, Duncan A. Evaluation of oxidation and hydrogen permeation in Al-containing stainless steel alloys. *Materials Science and Engineering A*, 2006, 424(1–2): 33–39.
- [7] Sharafi S and Farhang M R. Effect of aluminizing on surface microstructure of an HH309 stainless steel. *Surface and Coatings Technology*, 2006, 200: 5048–5051.
- [8] Wang Haitao. The study of cast dual-phase ferro superalloy [Dissertation]. Jinan: Shandong University, 1998.
- [9] Li Wenchao, Lin Qin, Ye Wen, et al. The kinetics effect of different rare-earth additives on the oxidation resistance of Fe-Cr-Al alloys. *Iron and Steel*, 1982, 17(1): 10–18. (in Chinese)
- [10] Ben Abderrazik G, Moulin G and Huntz A M. Relation between impurities and oxide-scale growth mechanisms on Ni-34Cr and Ni-20Cr alloys. *Oxidation of Metals*, 1990, 33 (3/4): 191–235.
- [11] Li Yun, Yuan Chao, Guo Jianting, et al. The oxidation kinetics of cast Ni-base superalloy K35. *Journal of Northeast University (Natural Science)*, 2003, 24(1): 75–78. (in Chinese)
- [12] Huntz A M, Reckmann A, Haut C, et al. Oxidation of AISI 304 and AISI 439 stainless steels. *Materials Science and Engineering A*, 2007, 447(1/2): 266–276.
- [13] Prescott R. The formation of aluminium oxide scales on high-temperature alloys. *Oxidation Metallurgy*, 1992, 38: 233–254.
- [14] Pérez F J, Cristóbal M J, Hierro M P, et al. The influence of implanted silicon on the cyclic oxidation behaviour of two different stainless steels. *Surface and Coatings Technology*, 1999, 120: 442–447.
- [15] Thobor-Keck A, Lapostolle F, Dehlinger A S. Influence of silicon addition on the oxidation resistance of CrN coatings. *Surface and Coatings Technology*, 2005, 200(1–4): 264–268.
- [16] Chang Y Y, Tsaur C C, and Rock J C. Microstructure studies of an aluminide coating on 9Cr-1Mo steel during high temperature oxidation. *Surface and Coatings Technology*, 2006, 200(22–23): 6588–6593.
- [17] Zhai Jinkun. *High Temperature Corrosion of Metals*. Beijing: Beihang University Press, 1994. (in Chinese)

This work is supported financially by Komatsu of Japan, grant number 31370011370804, in Shandong University, China.