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Effect of Aluminum on Microstructure and High-Temperature Oxidation Resistance of Austenitic Heat-Resistant Steel

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Abstract: The ZG40Cr20Ni20Alx (x = 0, 1.76, 3.45, and 5.34) heat-resistant steel has been newly developed on the basis of HK40 steel for aggressive oxidizing environments. The results reveal that the Al greatly enhances the oxidation resistance of ZG40Cr20Ni20 steel at high temperatures. The mass gain of ZG40Cr20Ni20 upon oxidation at 1100 °C for 480 h is up to 103.6 mg/cm², while the values for the steels containing 1.76 and 3.45 wt% Al are sharply decreased to 6.1 and 5.4 mg/cm², respectively. Both of their matrix phases are still austenite, which is the same as that of ZG40Cr20Ni20. Their FeCr₂O₄ spinel oxide scales appear to be more stable under high oxygen partial pressure than that of ZG40Cr20Ni20, and the continuous Cr₂O₃ film appears between their matrix and spinel oxide. As for the steel with 5.34 wt% Al, the mass gain is only 1.1 mg/cm². Its matrix is compared to those of austenite and ferrite, and the oxide scale is continuous Al₂O₃.

Keywords: heat-resistant steels; aluminum; oxidation resistance; microstructure

1. Introduction

Many high-temperature components of the petrochemical industry, such as thermal power plants and industrial furnaces, are usually made of austenitic heat-resistant steels with high Cr and high Ni, for example, HK40 (25% Cr-20% Ni) [1–5]. However, these materials are not quite satisfactory in terms of their high-temperature oxidation resistance, particularly in atmosphere containing water vapor. The oxidation resistance of austenitic heat-resistant steel is related to the oxide film formed on its surface [6–8]. The protective oxide film of high-Cr steels is mainly composed of Cr_2O_3 . At temperatures higher than 900 °C, the Cr_2O_3 is easy to oxidize into volatile CrO_3 , which makes the protective scale thin and is detrimental to oxidation resistance. In a vapor environment, the Cr_2O_3 becomes unstable even at temperatures higher than 650 °C with a higher steam pressure and flow rate [8–10].

In 2007, Brady and Lu et al. have reported a new type of alumina-forming austenitic (AFA) stainless steel with Al_2O_3 as an antioxidant layer, which has better oxidation and corrosion resistance without reducing creep resistance [11–13]. The main protective coating of the newly developed steel is Cr_2O_3 and Al_2O_3 . Al_2O_3 has better thermodynamic stability and compactness in high-temperature and corrosive environments, and thus greatly improves the oxidation resistance of AFA stainless steel [14–16]. However, the creep resistance of AFA stainless steel is lower than that of austenitic heat-resistant steel at high temperatures, because the carbon content of the former is usually less than 0.1 wt%. Recently, the alumina has been used as the main protective oxide scale of heat-resistant steels [17–19]. The carbon content of these alumina-forming heat-resistant steels is usually more than 0.3 wt%, and thus their high-temperature mechanical properties have been improved, which is favorable for application at higher temperatures.

We have added the aluminum to HK40 austenitic heat-resistant steel and found that the oxidation resistance of HK40 steel is greatly improved by 4.72 wt% Al, while its oxidation resistance shows no significant improvement when 1.68 wt% Al is added [18,19]. Unfortunately, the matrix of the sample containing 4.72 wt% Al transforms to ferrite, which is unfavorable for high-temperature applications. The high Ni content can avoid the formation of ferrite but increases the cost. In this work, the Cr content of HK40 steel was reduced to 20.0 wt%, and then a moderate quantity of aluminum was added. Thus, a new type of alumina-forming austenitic heat-resistant steel (ZG40Cr20Ni20Al*x*) was obtained. The 0.7 wt% Nb was also added in order to further improve the creep resistance. Here, the effect of aluminum content on the microstructure and 1100 °C oxidation resistance of newly developed, austenitic, heat-resistant steel was studied. The oxidation kinetics, composition, and formation mechanism of the oxide films were analyzed.

2. Experiment

The steel was melted in a medium-frequency (500–1500 Hz) induction furnace. The raw materials were scrap steel, ferrochrome, pure nickel, ferromanganese, ferrosilicon, and pure aluminum. The alloy melt was poured into a Y-block mold, the tapping temperature of which was controlled at 1630–1670 °C. The chemical compositions of steels were analyzed by an inductively coupled plasma (ICP) spectrometer and shown in Table 1. The oxidation test was performed at 1100 °C in a muffle furnace under atmospheric pressure. An analytical balance with an accuracy of 0.01 mg was used for weighing. Taking the oxide delamination and caving during cooling into account, the total mass of the specimen and alumina crucible was taken as a whole, where the crucible was preheated at 1150 °C for 6 h prior to carrying out the oxidation test.

 Table 1. Chemical composition of ZG40Cr20Ni20Alx steel (wt%).

Sample	С	Si	Mn	Р	S	Cr	Ni	Nb	Al
1#	0.42	0.80	0.96	0.026	0.011	18.69	20.72	0.77	0
2#	0.39	1.04	1.00	0.024	0.008	18.33	20.23	0.76	1.76
3#	0.37	1.22	1.01	0.023	0.010	18.26	20.42	0.74	3.45
4#	0.37	1.41	1.05	0.021	0.007	18.18	20.46	0.76	5.34

The microstructure and surface morphology of alloy were observed by FEI-QUANTA-200 scanning electron microscopy (SEM, FEI, Hillsboro, America). The composition of the oxide film was investigated by energy-dispersive X-ray spectrometry (EDS, FEI, Hillsboro, America). The specimens were mounted with resin, followed by grinding on SiC sandpaper up to 1000# and polishing for cross-sectional observation. The phases of alloys and oxides were analyzed by X-ray diffraction (XRD, SHIMADZU, Kyoto, Japan) using the Cu (K α) target.

3. Results and Discussion

3.1. Microstructures of Steels

The microstructures of steels are shown in Figure 1. They can be divided into two categories according to the alloy microstructure: ZG40Cr20Ni20Al*x* alloy with 0, 1.76, and 3.45 wt% Al have the same structure of uniform γ -phase and carbide precipitates (dark) at grain boundaries (Figure 1a–c); the alloy with more Al (5.34 wt%) exhibits many extra dark-precipitates (Figure 1d). It is presumed that when aluminum is added to 5.34 wt%, the single austenite matrix becomes a dual-phase matrix because the Al element can promote ferrite formation. From the XRD patterns of alloys (Figure 2), we can see that the austenite is the primary phase for ZG40Cr20Ni20Al*x* (*x* = 0, 1.76, 3.45) alloys. When the Al content is increased to 5.34 wt%, in addition to the austenite peaks, new ferrite peaks appear.



Figure 1. Microstructures of the steels with (a) 0, (b) 1.76, (c) 3.45, and (d) 5.34 wt% Al.



Figure 2. X-ray diffraction (XRD) patterns of cast alloys.

3.2. Oxidation Kinetic Analysis

The oxidation kinetics curves of ZG40Cr20Ni20Al*x* steels at 1100 °C are presented in Figure 3. Clearly, the oxidation mass gain of ZG40Cr20Ni20Al*x* steel is sharply decreased with the increase in aluminum content. For example, the mass gain of ZG40Cr20Ni20 upon oxidation for 480 h is 103.6 mg/cm² (Figure 3a), while the corresponding values for the steels containing 1.76 and 5.34 wt% Al are only 6.1 and 1.1 mg/cm² (Figure 3b), respectively. In particular, the mass gain of the steel containing 3.45 wt% Al is 5.4 mg/m² (480 h), which is only 0.7 mg/cm² lower than that of the steel containing 1.76 wt% Al. Further, the oxidation mass gain curves of ZG40Cr20Ni20 steel exhibits an approximately linear trend. However, the mass gain curves of ZG40Cr20Ni20Al*x* (*x* = 1.76, 3.45, and 5.34) alloys approximately follow a parabolic law (Figure 3b), where the mass gain of each sample is more rapid in the early stage than that in the late stage.



Figure 3. Isothermal oxidation kinetics of ZG40Cr20Ni20Al*x* steels (**a**) *x* = 0, 1.76, 3.45, and 5.34, (**b**) *x* = 1.76, 3.45, and 5.34.

3.3. Surface Morphology and Phase Composition of Oxide

The surface morphology of the oxide scale on the ZG40Cr20Ni20Alx steels is shown in Figure 4. Clearly, the oxide grains of the ZG40Cr20Ni20 steel surface is very coarse after being oxidized at 1100 °C for 480 h, being more than 30 μ m (Figure 4a). More importantly, some interstices appear between the oxide grains, which may act as a transport pathway of oxygen and alloy elements, leading to a high rate. According to the EDS analysis, the surface oxides are rich in Fe elements. As for the steel with 1.76 wt% Al, the grains of surface oxides are obviously refined to only several micrometers (Figure 4b). The surface oxides are mainly composed of Cr, Fe, and O elements in the EDS results. Some small holes appear between the oxide grains. In the process of oxidation, the produced FeO and Cr_2O_3 react spontaneously to form $FeCr_2O_4$ for decreasing free energy [20]: FeO + $Cr_2O_3 = FeCr_2O_4$. The cause of small holes could be that some spaces left by the disappearing reactants are not fully occupied by the newly formed oxides during the solid reaction. As the Al content is increased to 3.45 wt%, the grains of surface oxides are further refined to less than three microns (Figure 4c). The EDS analysis shows that the oxides are mainly composed of Cr, Fe, and O. Furthermore, the chromium oxides are also observed. When the Al content is approximately 5.34 wt%, the oxides on the steel surface are mainly composed of Al_2O_3 and almost no holes appear on the oxide surface (Figure 4d). The alumina scale could play a good protective role in a high-temperature environment.



Figure 4. Surface morphology of the oxide scale on the steels with (**a**) 0, (**b**) 1.76, (**c**) 3.45, and (**d**) 5.34 wt% Al. The steels were oxidized at 1100 °C for 480 h.

The corresponding XRD diffraction patterns of the oxides formed on the alloy surfaces are shown in Figure 5. From Figure 5a, it can be seen that the diffraction peak intensity of surface oxides mainly comes from γ -Fe₂O₃ for ZG40Cr20Ni20 steel. A trace amount of Fe_{0.98}O phase is also found, which could result in a sharp decrease in the oxidation resistance of oxide films. The oxide films are composed of FeCr₂O₄ with a typical spinel oxide structure for the steel with the addition of 1.76 wt% Al (Figure 5b), while the outer oxide films of ZG40Cr20Ni20 transform into iron oxides under the same conditions (Figure 5a, Figure 6a). This means the Al could prevent the Cr of FeCr₂O₄ oxide from turning into volatile CrO₃ under high oxygen partial pressure. As the aluminum content is increased to 3.45 wt%, the oxide films are still composed of the FeCr₂O₄ spinel phase and some diffraction peaks corresponding to Cr oxide (Cr₂O₃ and CrO) and Al₂O₃ appear (Figure 5c). As for the steel containing 5.34 wt% Al, the diffraction peaks of the oxide films primarily come from Al₂O₃ (Figure 5d). In addition, some Cr₂O₃ and CrO are also detected.



Figure 5. XRD patterns of oxide scales on the steels with (**a**) 0, (**b**) 1.76, (**c**) 3.45, and (**d**) 5.34 wt% Al. The steels were oxidized at 1100 °C for 480 h.

3.4. Examination of Cross Sections

In order to further study the oxidation resistance of ZG40Cr20Ni20Alx at high temperatures, SEM-EDS analysis was carried out on the cross-section of samples. Figure 6 shows the cross-sectional morphologies and EDS scan analysis of the steels oxidized at 1100 °C for 480 h in the air. The cross-sectional schematic diagram of ZG40Cr20Ni20Alx steels is summarized in Figure 7. It can be easily seen that the thickness of the oxide layer significantly decreases with the increase in aluminum content. As shown in Figure 6a, the external oxide scale of ZG40Cr20Ni20 is composed of Fe oxide, the thickness of which is about several hundred microns. The internal oxide film mainly contains Cr, Fe, and O, which is assumed to be $FeCr_2O_4$ spinel oxide according to the atomic ratio from EDS (27 at% Cr, 13 at% Fe, 42 at% O) and porous morphology. Furthermore, there are some Ni-rich oxides and cracks

in the $FeCr_2O_4$ spinel oxide near the matrix. The cracks and voids offer a convenient opportunity for the O ions to invade and corrode the matrix.



Figure 6. Cross-sectional SEM images of ZG40Cr20Ni20Al*x* oxidized for 480 h: (**a**) 0, (**b**) 1.76, (**c**) 3.45, and (**d**) 5.34 wt% Al.



Figure 7. Cross-sectional schematic diagram of ZG40Cr20Ni20Al*x* steels with (**a**) 0, (**b**) 1.76, (**c**) 3.45, and (**d**) 5.34 wt% Al.

For the steel containing 1.76 wt% Al (Figure 6b), the oxide scale consists of an external FeCr₂O₄ layer with a spinel structure and internal Cr_2O_3 layer next to the matrix. The porosity of the FeCr₂O₄ layer evidently decreases from the surface to the interior. The low-porosity FeCr₂O₄ adhered to Cr_2O_3 prevents the volatilization of internal chromium oxide [20]. The Cr_2O_3 layer is compact and could effectively prevent the intrusion of O ions. For the steel containing 3.45 wt% Al (Figure 6c), the oxide scale is still composed of an external FeCr₂O₄ layer with a spinel structure and an internal Cr_2O_3 layer next to the matrix, which is similar to that of the steel containing 1.76 wt% Al. In addition, the scattered Al_2O_3 particles are found in the FeCr₂O₄ layer, which prevents the diffusion of oxygen ions and improves oxidation resistance. As the Al content increased to 5.34 wt% (Figure 6d), the major component of oxide film becomes Al_2O_3 layer could act as the diffusion barrier and improve the adhesion strength between the substrate and oxide scale, leading to higher oxidation resistance.

For ZG40Cr20Ni20 (without Al), the FeCr₂O₄ with the spinel structure forms first, which is very unstable. The Cr in the early-formed FeCr₂O₄ layer gradually changes into volatile CrO₃ under high oxygen partial pressure and flows over the oxide surface. Meanwhile, some internal Fe ions diffuse outwards. Therefore, a lot of iron oxides form on the surface. The initially formed FeCr₂O₄ spinel would consume Fe and Cr ions and result in the enrichment of Ni near the matrix. Ni is subsequently oxidized and forms Ni-rich oxides in the spinel oxide layer. The Ni-rich oxides in the FeCr₂O₄ spinel oxide layer interlace with each other, which makes the inner oxide layer more unstable and accelerates the diffusion of metal ions and oxygen ions.

For the steel containing 1.76 wt% Al, the Al content is small and cannot form a complete alumina layer. However, the addition of Al promotes the formation of a continuous and dense Cr_2O_3 layer, which can hinder the outward diffusion of metal ions in the matrix and the diffusion of oxygen to the matrix. The Al could also prevent the Cr in FeCr₂O₄ from transforming into CrO₃. The iron oxides do not appear in the oxide surface. The oxides of alloy containing 3.45 wt% Al are similar to those of alloy containing 1.76 wt% Al. However, some Al atoms form Al₂O₃ in the spinel oxide layer and fill some pores. As a result, the oxidation resistance of the alloy is slightly improved. As the Al content increases to 5.34 wt%, the Al diffuses to the surface and forms continuous and dense Al₂O₃, which has a higher thermal stability and higher oxidation resistance.

4. Conclusions

The newly developed ZG40Cr20Ni20Alx (x = 1.76, 3.45, 5.34) heat-resistant steels have much better oxidation resistance than the ZG40Cr20Ni20 steel at high temperatures. The mass gain of ZG40Cr20Ni20 upon oxidation at 1100 °C for 480 h is 103.6 mg/cm², while the values for the steels containing 1.76 and 3.45 wt% Al are sharply decreased to 6.1 and 5.4 mg/cm², respectively. Both of their matrix phases are still austenite, which is the same as that of ZG40Cr20Ni20. Their FeCr₂O₄ spinel oxide scales appear to be more stable under high-oxygen partial pressure than that of ZG40Cr20Ni20, and the continuous Cr₂O₃ film appears between their matrix and spinel oxide. As for the steel with 5.34 wt% Al, the mass gain is only 1.1 mg/cm². Its matrix is compared to those of austenite and ferrite, and the oxide scale is continuous Al₂O₃. These results show that the new heat-resistant steels with the addition of Al have good prospects in the field of high-temperature applications.

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