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**PAPER**

**Effect of minor Zr on oxidation resistance and mechanical property of nickel-saving austenitic heat-resistant cast steel**

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**Abstract**

In order to study the effect of minor Zr on the oxidation resistance and the mechanical properties of nickel-saving austenitic heat-resistant cast steel, the oxidation resistance at 900 °C and the tensile properties at room temperature and at 900 °C of Zr-containing and Zr-free steels were carried out. The results showed that the addition of 0.011% Zr could slightly reduce the oxidation rate and improve the oxidation resistance of Zr-containing steel. In addition, the tensile properties of Zr-containing steel at room temperature and at 900 °C were significantly improved. Brittle fractures occurred in two experimental steels at both temperatures, and brittle characteristics appeared in the fractures.

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### 1. Introduction

Zirconium, characterized as a strong carbide/nitride- and oxide-forming element, has the similar properties to those of titanium. Initially, Zr was used to suppress austenite grain growth and control sulfide formation[1]. With the upgrading of the casting process, this role of Zr has gradually faded. Researchers began to pay attention to the influence of Zr alloying on the microstructure and properties of steel [2–5]. It was found that the addition of trace amounts of Zr can change the morphology of MnS inclusions in HSLA steel and precipitate Zr-containing nitrides to fine grains to improve the low temperature and the room temperature impact toughness of HSLA steel. In terms of high-temperature strength, moon et al [6] found that Zr deteriorated the high-temperature strength of Nb-bearing alumina-forming austenitic heat-resistant steel for the large-sized (Nb, Zr) (C, N) phase weakened the effect of precipitation strength. Wen et al [7] studied the effect of Mo/Zr ratio on the high-temperature performance of 310 S austenitic stainless steel. It was found that 310 S stainless steel has the best high-temperature strength when Zr/C ratio was 1. For the high-temperature oxidation aspect, in the 1970s, Japanese researchers Moroishi et al [8] studied the effect of Zr content on the oxidation resistance of 17 wt.% Cr ferritic stainless steel and pointed out that when the concentration of Zr exceeded the total amount of C and N in steel where the Zr/(C + N) ratio was higher than 8.1, the Zr-containing steel has the best oxidation resistance.

Due to the shortage of Ni resources and the fluctuation of Ni price, the cost of traditional Cr-Ni austenitic heat-resistant steel is increasing, and the austenitic heat-resistant steel with Mn and N instead of Ni is excellent in the high-temperature performance. It is an alternative material for Cr-Ni austenitic heat-resistant steel. As the high-temperature structural materials, the high-temperature oxidation resistance and high-temperature strength of austenitic heat-resistant steel are the key to determining the long-term service. Alloying is the main measures to improve its heat resistance. Therefore, in this study, nickel-saving austenitic heat-resistant cast steel was chosen as the research object to investigate the effect of minor Zr on the high-temperature oxidation resistance and mechanical properties at room temperature and high temperature, and provides data accumulation for the application of Zr-microalloyed austenitic heat-resistant cast steel.
2. Methods

Y-block-shaped cast steel ingots of two experimental steels were fabricated by using medium frequency induction furnace. The chemical composition of main elements of two experimental steels are confirmed by ICP-OES and listed in table 1. The Zr-free and Zr-containing steels are labelled as Z0 and Z1, respectively. The as-cast microstructures of two experimental steels were observed and analyzed using optical microscopy, scanning electron microscopy (SEM, Hitachi SU8220) equipped with an energy dispersive spectrometer (EDS, Oxford X-MaxN) and x-ray diffraction (XRD, Rigaku SmartLab). The specimens for microstructure analysis were mechanically polished and chemically etched using 5 g FeCl₃ + 15 mL HCl + 100 mL ethanol. The samples for high-temperature oxidation and mechanical property testing were respectively processed by wire cutting, wherein the high-temperature oxidation samples were the steel blocks of 10 mm × 10 mm × 5 mm, and the geometrical dimensions of the tensile samples were shown in figure 1 (according to the standards of GB/T 2282–2015 and ASTM E8/E8M-16a).

The isothermal oxidation experiments were carried out in a high-temperature muffle furnace at 900 °C. The experimental environment was laboratory air atmosphere. The oxidation time interval was 5 h, 10 h, 25 h, 50 h, 100 h, 150 h and 200 h. When the temperature reached 900 °C, the samples were put into the muffle furnace. Then the oxidation test started. After the set oxidation time was reached, the sample was taken out and cooled to room temperature in air. Before and after the oxidation experiment, the samples were weighed using an electronic analytical balance (accuracy of 0.001 g), and the oxidation behavior of two experimental steels was investigate by weight gain per unit area. XRD (Rigaku SmartLab) and SEM (FEI Quanta200) were used to identify the oxidation products and observe the oxidation surface and the morphology of cross-section of the oxide scale.

The tensile tests were conducted on an electronic universal testing machine equipped with a high-temperature resistance furnace in laboratory air at a tensile rate of 2 mm min⁻¹. The experimental temperature was room temperature and 900 °C. For high-temperature tensile test, the sample was heated in the furnace at a heating rate of 10 °C min⁻¹. After the end of the test, the sample was cooled to room temperature in the furnace and then was taken out. The tensile fractures and the microstructure beneath the fracture surface were observed and analyzed by SEM (FEI Quanta200).

3. Results and discussion

3.1. Microstructure

Figure 2 exhibits the OM images and XRD patterns of as-cast microstructures for two experimental steels. According to the results of XRD analysis, the as-cast microstructure of two experimental steels are both austenite. In figures 2(a) and (b), it can be observed that the microstructures of two experimental steels are austenite dendrites and precipitates preferentially formed along grain boundaries. The magnification images and the EDS point results of the cellular precipitates are exhibited in figure 3. As can be seen in figure 3, the cellular microstructures are consisted of alternating lamellar precipitates. And the EDS results reveal that the lamellar precipitates are Cr-rich M₂₃C₆ precipitates.

| Steel | Cr  | Mn  | Ni  | Si  | C   | N   | Zr  | Fe  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|
| Z0    | 17.7| 10.4| 4.0 | 0.8 | 0.32| 0.24| —   | Bal.|
| Z1    | 0.011 |     |     |     |     |     |     |     |

Figure 1. Geometrical dimensions of the tensile sample (unit: mm): (a) high-temperature tensile sample; (b) room temperature tensile sample.
Figure 2. OM images and XRD patterns of as-cast microstructures for two experimental steels: (a) and (b) OM image for Z0 and Z1 steel, respectively, (c) and (d) XRD pattern for Z0 and Z1 steel, respectively.

Figure 3. Magnification view and EDS analysis result of cellar precipitates in two experimental steels: (a) and (b) morphologies of precipitates of Z0 and Z1 steel, respectively, (c) and (d) EDS point analysis results of precipitates in Z0 and Z1 steel, respectively.
3.2. Oxidation behavior

Figure 4(a) shows the relationship between weight gain per unit area and oxidation time of two experimental steels at 900 °C. The oxidation behavior of two experimental steels is divided into two stages. In the initial stage of the oxidation (before ∼15 h), the weight gain per unit area are both increased in a rapid oxidation rate for two experimental steels. At the second stage, the weight gain per unit area are still increased in a gradually reduced oxidation rate for two experimental steels. Before about 50 h, the weight gain per unit area of two experimental steels are basically the same, and after 50 h, the weight gain per unit area of Z1 steel is lower than that of Z0 steel. In general, the oxidation behaviors of two experimental steels oxidized in air at 900 °C are consistent with the parabolic law. Usually, the oxidation behavior that conforms to the parabolic law will satisfy the following formula [9]:

\[ \Delta W^2 = k_p t + C \]  

where \( \Delta W \) is weight gain per unit area, mg/cm², \( k_p \) is oxidation rate constant, g²cm⁴s⁻¹, \( t \) is oxidation time (h), \( C \) is a constant. Figure 4(b) presents the relationship between the square of weight gain per unit area and oxidation time of two experimental steels at 900 °C. The square of weight gain per unit area is linear with oxidation time, and the oxidation rate constant can be obtained by linear fitting. It is found that the oxidation rate constant of Z1 steel is lower than that of Z0 steel after adding minor content of zirconium element, indicating that Zr can improve the oxidation resistance of the nickel-saving austenitic heat-resistant cast steel, however the effect of the improvement is limited.

Oxidation products have a significant influence on the oxidation resistance of steel. The composition of the oxide scales, including the residual scale and the spalled scale, formed on the surface of two experimental steels were identified by XRD. Figure 5 shows the XRD patterns of the oxide scales for two experimental steels after oxidizing for 100 h and 200 h. According to the analysis results, the oxide scales formed on two experimental steels are mainly consisted of Mn₂O₃-type and Mn₃O₄-type oxides, which may include (Fe₀.₆Cr₀.₄)₂O₃ (ICDD-PDF No. 34-0412), (Mn₀.₉₈Fe₀.₀₁₇)₂O₃ (ICDD-PDF No. 24-0507), MnCr₂O₄ (ICDD-PDF No. 54-0876), FeCr₂O₄ (ICDD-PDF No. 34-0140). It indicates that the oxide scales formed on two experimental steels are of a stratified structure, which is consistent with many researchers’ literatures on Mn-containing austenitic steels [10–13]. As shown in figure 6, after oxidation for 100 h, the oxide scale of two experimental steels were severely spalled during the cooling process. However, it is still observed on the surface of Z1 steel that the residual outermost oxide layer is spinel oxides. It infers that the oxide scale of two experimental steels are composed of an outer layer of (Fe, Cr, Mn)₂O₄ spinel and an inner layer of (Fe, Cr, Mn)₃O₄ corundum oxide. Comparing the results of XRD analysis, it can be seen that the oxidation products of two experimental steels are the same, so it is difficult to summarize the reason for the improvement of the oxidation resistance of the Zr-containing steel by the oxidation products. Besides, the peaks of \( \alpha \)- and \( \gamma \)-iron were also detected, which means that the phase transition has occurred in the sublayer in the oxidation process. It can be speculated that the enhancement of the oxidation resistance of Zr-containing steel is attributed to the role of the microstructural evolution in the subsurface.

Figure 7 shows the cross-section morphology of two experimental steels after oxidation for 100 h. Internal oxidation has occurred during the process of oxidation for two experimental steels. The oxidation resistance of heat resistant steel depends on whether a protective chromia layer can be formed and maintained. In our present
study, the stratified oxide scale formed on the surface of two experimental steel show that there is not enough chromium content in the matrix to maintain the Cr₂O₃ layer, thereby forming a nonprotective oxide scale, causing the internal oxidation. As shown in figure 7, the morphology of the internal oxidation zone (IOZ) are basically the same for two experimental steels. The structure of the IOZ is composed of the compact oxide bands and the remaining alloys (in white) [14, 15] and the cavities (in black). According to the line scan results, the oxide band is enriched in chromium. Col et al [16] found that after breakaway oxidation, the process of the internal oxidation is controlled by the oxide band at the border of the IOZ. The oxidation front is stopped at the oxide band which is a Cr₂O₃ layer, whereas the oxidation front is propagated when the Cr₂O₃ is converted into the FeCr₂O₄ for the insufficient supplement of chromium. As indicated by the black arrows in figures 7(b) and (d), there is a Cr-depleted zone formed beneath the oxide band/matrix interface. And the thickness of the Cr-
depleted zone of Z0 and Z1 steel is 6.365 μm and 2.506 μm, respectively. It manifests that the replenishment of chromium from the matrix to the border of the IOZ in Z1 steel is relatively faster than that in Z0 steel.

As mentioned above, the peak of α-iron was identified by XRD analysis for two experimental steels. This is attributed to the outward diffusion of manganese which acts as an austenite-stabilizer [11, 17]. The α-iron content in the subsurface for two experimental steel after oxidation for 100 h and 200 h was measured and plotted in figure 8. As presented in figure 8, the α-iron content in the subsurface of Z1 steel for long-term oxidation is higher than that in Z0 steel. When the manganese in the subsurface is removed by the outward diffusion, part of γ-iron in the subsurface is transformed into α-iron as the manganese content is insufficient to stabilize γ-iron. In addition, as a strong carbide and nitride forming element, the addition of Zr consumes the austenite stabilizing element C and/or N in the matrix [8], thereby improving the transformation of γ- to α-iron in the subsurface of Z1 steel. It is known that the diffusion coefficient of Cr in α-iron is higher than that in γ-iron. The lattice diffusivity of Cr in α-iron and γ-iron at 900 °C is calculated to be ∼3.3 × 10⁻¹¹ cm² s⁻¹ and

Figure 7. Cross-section morphology of two experimental steels after oxidation for 100 h: (a) and (c) BSE images of cross-section morphology of Z0 and Z1 steel, respectively, (b) and (d) line scan results for Z0 and Z1 steel, respectively.

Figure 8. The α-iron content in the subsurface of two experimental steels after oxidation for 100 h and 200 h at 900 °C.
After adding Zr in Z1 steel, the increased α-iron in the subsurface provides a fast diffusion path for chromium during oxidation process. Therefore, the thickness of the Cr-depleted zone beneath the oxide band/matrix interface in Z1 steel is smaller than that of Z0 steel. This means that the propagation of the internal oxidation front in Z1 steel would be retarded for the delayed transition from Cr2O3 to nonprotective FeCr2O4, due to the relatively sufficient replenishment of chromium. However, the formation of α-iron also accelerates the inward diffusion of oxygen, thereby causing a limited enhancement in the oxidation resistance of Zr-containing Z1 steel.

3.3. Mechanical property

Figure 9 shows the tensile curves of two experimental steels at room temperature and at 900 °C. As shown in figure 9, the addition of minor amount of Zr both improves the yield strength and the tensile strength of Z1 steel at room temperature and at 900 °C. At room temperature, the elongation of Z1 steel is higher than that of Z0 steel, however, at 900 °C, the elongation of Z1 steel is lower than that of Z0 steel. The mechanical property data of two experimental steels at both temperatures are listed in table 2. At room temperature and at 900 °C, compared with Z0 steel, the yield strength and the tensile strength of Z1 steel increase by 1.7%, 10.7% (at room temperature) and 4.5%, 9.1% (at 900 °C), respectively.

Figure 10 is the morphologies of the tensile fracture of two experimental steels at various temperatures. It can be seen from the macro fracture (figures 10(a), (c), (e) and (g)) that two experimental steels have no obvious necking at room temperature and at 900 °C, and brittle fracture occurred. Meanwhile, both the intergranular facets and transgranular facets existed on the fracture surface. At room temperature, the cleavage facets can be observed in Z0 steel, and the cleavage facets and a small number of dimples can also be seen in Z1 steel. The localized plastic deformation in Z1 steel is contributed to the improvement of elongation. At 900 °C, cleavage facets and shallower dimples can be observed locally in Z0 steel. The local plastic deformation makes the elongation of Z0 steel at 900 °C not significantly lower than that at room temperature. However, cleavage facets and few dimples can be observed in the fracture of Z1 steel. From room temperature to 900 °C, the disappearance of ductile fracture characteristics causes the elongation of Z1 steel at 900 °C to decrease by nearly 50% compared with the elongation at room temperature.

Figure 11 shows the cross-sectional morphologies beneath the fracture surface of two experimental steels at room temperature and at 900 °C. For two experimental steels at various temperatures, the cracks are found along the grain boundaries as indicated by arrows, along which they are connected to develop to the final fracture. It suggests that the main crack is easily propagated in an intergranular mode. Besides, some
Microcracks are also observed along the cellular precipitates/matrix interface in Figure 11. It has been reported that when the cracks initiated along the grain boundaries and propagated to the cellular carbides near grain boundaries, a shear zone caused by the cracking of cellular carbides developed in the adjacent matrix to induce the appearance of transgranular fracture [20, 21]. This could be the explanation for the appearance of intergranular and transgranular facets existed in the fracture surface of two experimental steels at room temperature and at 900 °C. And at both temperatures, the intergranular fracture manner is dominant for two experimental steels.

Figure 12 presents the SEM images and EDS analysis results of Zr-containing inclusions and precipitates in Z1 steel. As shown in figure 12, the inclusions are ZrO₂ + MnS (point A) and Zr(C, N) + ZrO₂ (point B) and
the precipitate is Zr(C, N) (point C). The complex inclusion of ZrO$_2$ + MnS is formed as follow. ZrO$_2$ is an anion vacancy oxide and is unstable at normal temperature, which can be stabilized by the addition of Mn, and thus, precipitation of MnS on ZrO$_2$ occurs [22, 23]. In addition, the formation of fine ZrO$_2$ inclusions could act as the nuclei for MnS to form the complex inclusions, and consequently, reduce the growth of MnS [24, 25]. It is considered that the formation of complex inclusion of ZrO$_2$ + MnS is beneficial to the enhancement in the impact toughness [26]. Since zirconium is strong carbide/nitride forming element, the addition of Zr can form Zr-containing carbides and/or nitrides as shown in figure 12(b). It indicates that the improvement of the yield strength and the tensile strength of Z1 steel at various temperatures is attributed to the formation of Zr-containing inclusions and precipitates, which act as the obstacles to impede the motion of the dislocation.

4. Conclusion

1. The addition of 0.011 wt% Zr improves the oxidation resistance at 900 °C in air for the enhancement in the formation of α-iron in the subsurface that accelerates the outward diffusion of Cr and retards the propagation of the internal oxidation zone.

2. The Zr-containing steel possesses the highest yield strength and tensile strength at room temperature and at 900 °C, and at both temperatures, the intergranular fracture manner is dominant for the Zr-containing steel and the Zr-free steel.

3. The complex inclusions of ZrO$_2$ + MnS and the Zr-containing precipitates exist in the Zr-containing steel, and is attributed to the improvement of the strength at various temperatures.

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