High-Temperature Oxidation Imprint of a Nickel-Saving Economical Duplex Heat-Resistant Cast Steel

Authors: Wu Lincai, An Licong, Yang Yitao

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Abstract

Isothermal oxidation experiments were conducted on ZG40Cr25Ni20 heat-resistant cast steel and nickel-saving economical duplex heat-resistant cast steel to obtain the oxidation kinetic behavior curves of both materials. The differences in high-temperature oxidation resistance were investigated using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD), and the microscopic mechanism of high-temperature oxidation was explored. The results show that although the nickel-saving economical heat-resistant cast steel reduces Ni content, increasing Cr and Mn can form a stable protective oxide film Cr2O3 on the outer layer of the oxide scale, which to some extent blocks the outward diffusion of metal cations and inward diffusion of oxygen ions, increasing its oxidation activation energy from 148.4 $\mathrm{kJ \cdot mol^{-1}}$ to 245.7 $\mathrm{kJ \cdot mol^{-1}}$, thereby reducing the oxidation rate and improving the high-temperature oxidation resistance of the material.

Full Text

High Temperature Oxidation of a Low-Nickel Economical Duplex Heat-Resistant Cast Steel

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Wu Lincai, An Licong, Yang Yitao* School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China

*Corresponding author: Tel: (021)56334465, E-mail: yyt@staff.shu.edu.cn

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Abstract

Isothermal oxidation experiments were conducted on ZG40Cr25Ni20 heat-resistant cast steel and a low-nickel economical duplex heat-resistant cast steel to obtain oxidation kinetic curves for both materials. The differences in high-temperature oxidation resistance were investigated using scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), and X-ray diffraction (XRD), and the underlying microscopic mechanisms were explored. The results demonstrate that although the nickel-saving heat-resistant cast steel contains reduced Ni content, the increased Cr and Mn concentrations facilitate the formation of a stable protective Cr_2O_3 oxide film at the outer layer of the oxide scale. This film effectively inhibits the outward diffusion of metal cations and inward diffusion of oxygen ions, increasing the oxidation activation energy from 148.4 $\mathrm{kJ \cdot mol^{-1}}$ to 245.7 $\mathrm{kJ \cdot mol^{-1}}$ and thereby reducing the oxidation rate and improving high-temperature oxidation resistance.

Keywords: materials failure and protection, high-temperature oxidation behavior, heat-resistant steel, microstructure, low nickel

Introduction

Austenitic heat-resistant steels are primarily used for manufacturing support plates in ammonia synthesis equipment, superheaters and reheaters in boiler tubes, and exhaust valves in high-power automotive engines. Austenitic heat-resistant steels operate at higher temperatures than ferritic steels, with Cr being the principal alloying element. The primary purpose of adding Cr to heat-resistant steels is to enhance corrosion resistance and high-temperature oxidation resistance. Ni serves to form and stabilize the austenite phase, ensuring a fully austenitic microstructure, while Mn is added to expand the austenite phase field and strengthen the alloy through solid solution strengthening, thereby improving thermal fatigue resistance.

ZG40Cr25Ni20 steel exhibits high creep and rupture strength along with excellent resistance to high-temperature gas corrosion, making it suitable for furnace rollers, radiant tubes, steel billet skids, heat treatment furnace rollers, tube supports, reformer tubes, and ethylene cracking tubes. Although ZG40Cr25Ni20 steel can withstand temperatures up to 1050°C, it contains high levels of the expensive element Ni. Therefore, reducing Ni content while maintaining high-temperature oxidation resistance and corrosion resistance in aggressive atmospheres offers significant cost advantages. This study conducts continuous high-temperature oxidation experiments on ZG40Cr25Ni20 and a low-nickel economical duplex heat-resistant cast steel (hereinafter referred to as the "experimental material"), comparing their properties and investigating their high-temperature oxidation mechanisms.

1 Experimental Methods

Both experimental materials were melted in a 50 kg vacuum induction furnace and cast into ingots. The ingots were heated to 1200°C in a resistance furnace, held for 2 hours, and then furnace-cooled. The chemical compositions of both samples were analyzed using a PMI-MASTER PRO mobile spectrometer, with results listed in Table 1 . Samples were cut into 10 mm × 10 mm × 5 mm plates using wire electrical discharge machining and ground with 200, 400, 600, 800, 1000, and 1200 grit sandpaper to a surface roughness below 0.8 m.

High-temperature oxidation resistance was evaluated using the weight gain method according to GB13303-1991-T. Oxidation tests were conducted in a box-type resistance furnace with vent holes to allow free air circulation at 900°C, 1000°C, and 1100°C for durations of 24, 48, 72, 96, 120, 144, and 168 hours. Samples were removed at regular intervals and air-cooled to room temperature in sealed crucibles. The weight gain per unit area was measured using an electronic analytical balance (precision 0.1 mg), and average values from three tests were used to plot oxidation kinetic curves for evaluating high-temperature oxidation behavior. The microstructure of oxidized samples was examined using a HITACHI SU-1500 tungsten filament scanning electron microscope (SEM), with EDS and XRD (18KW D/MAX2500V+/PC) analysis of surface oxides.

2 Results and Discussion

Macroscopic observations of samples oxidized at 900°C, 1000°C, and 1100°C revealed that at 900°C, both materials developed a dense, adherent oxide film with good protective properties. After 5 days at 1000°C, ZG40Cr25Ni20 exhibited localized cracking and spallation of oxides, whereas the experimental material maintained a relatively flat surface oxide layer with good adhesion, showing no cracking or spallation. At 1100°C, oxide film formation consumed significant Cr. Once spallation occurred in ZG40Cr25Ni20, severe Cr depletion occurred at the surface, leading to progressive oxidation, multi-layer spallation, and internal oxidation, with substrate deformation and cracking. In contrast, the experimental material maintained its shape at 1100°C, with oxidation not penetrating into the substrate and no catastrophic oxidation such as cracking, deformation, or collapse.

Based on weight gain per unit area, oxidation kinetic curves were plotted as shown in Figure 1 [Figure 1: see original paper]. The weight gain per unit area for both materials increased with temperature and time. At 900°C, both materials exhibited simple parabolic oxidation kinetics. At 1000°C, ZG40Cr25Ni20 showed repeated parabolic behavior, indicating cyclic oxide formation and spallation according to Wagner theory. The experimental material displayed parabolic kinetics at all three temperatures, transitioning to steady-state oxidation after approximately 48 hours at 900°C and 1000°C, with reduced oxidation rates. Under identical conditions, the experimental material showed lower weight gain than ZG40Cr25Ni20.

2.1 Oxidation Kinetics Curves

According to Wagner oxidation theory, when high-temperature oxidation kinetics follow a parabolic law, the relationship can be expressed as:

$$\Delta m^n = K_P t$$

$$\ln K_P = \ln K_0 - \frac{Q}{RT}$$

where Δm is the weight gain per unit area (mg/cm^2), n is the exponent, t is oxidation time, K__P is the oxidation rate constant, K__0 is a constant, Q is the activation energy ($\mathrm{kJ \cdot mol^{-1}}$) representing the energy barrier for oxidation, T is the oxidation temperature, and R is the gas constant. Taking logarithms of both sides of the equation and performing linear fitting on the parabolic regions in Figure 1 [Figure 1: see original paper] yielded the oxidation rate exponent n and rate constant K__P for each temperature, summarized in Table 2 .

At 900°C, both materials exhibited similar and relatively low oxidation rate constants, indicating slow oxide scale growth and good substrate protection. Above 1000°C, the difference in oxidation rate constants became pronounced, with ZG40Cr25Ni20 showing a dramatic increase to 2.2 $\mathrm{mg \cdot cm^{-2} \cdot h^{-1}}$ at 1100°C, causing severe substrate degradation and loss of protection. The experimental material maintained low oxidation rates at 1000°C and 1100°C, with rate constants lower than ZG40Cr25Ni20 at all temperatures. Although Ni content was reduced, the increased Cr and Mn content raised the oxidation activation energy from 148.4 $\mathrm{kJ \cdot mol^{-1}}$ to 245.7 $\mathrm{kJ \cdot mol^{-1}}$ and the oxidation rate exponent from 1.9523 to 2.1354, explaining the improved oxidation resistance.

Oxide layer thicknesses after 168 hours at 900°C, 1000°C, and 1100°C were measured as shown in Figure 2 [Figure 2: see original paper]. The experimental material exhibited significantly thinner oxide layers than ZG40Cr25Ni20. Thickening of the oxide layer causes the adhesion energy between oxide and substrate to decrease exponentially, severely weakening their bonding strength.

2.2 Oxide Microstructure Analysis

SEM images of sample surfaces after 168 hours at 900°C, 1000°C, and 1100°C are shown in Figure 3 [Figure 3: see original paper]. At 900°C, both materials developed a fine, dense, and uniform oxide layer that blocked reaction between external O_2 and the metal substrate, providing excellent oxidation resistance. XRD analysis revealed that both materials formed Cr_2O_3 and $MnCr_2O_4$ oxides (Figures 4a and 4b [Figure 4: see original paper]). Due to the thin oxide film on the experimental material (only 0.71 m), X-rays penetrated through to detect the austenite substrate.

After 168 hours at 1000°C, ZG40Cr25Ni20 showed non-uniform oxide particles and exposed substrate with evidence of oxide spallation, while the experimental material exhibited tetrahedral oxide particles with uniform size and dense packing without voids. XRD analysis indicated that ZG40Cr25Ni20 contained Cr_2O_3, Fe(Ni,Mn)Cr_2O_4, Fe_3O_4, and austenite substrate, whereas the experimental material consisted of Cr_2O_3, $MnCr_2O_4$, and Fe_3O_4. At 1000°C in Fe-based superalloys, Cr_2O_3 forms preferentially due to its lower Gibbs free energy, creating a concentration gradient. Prolonged oxidation consumes Cr, reducing its average content below the critical concentration for forming a continuous Cr_2O_3 film, allowing substrate elements to oxidize. Since Fe and Ni oxides grow rapidly, they destabilize the Cr_2O_3 film by diffusing outward along grain boundaries, accelerating oxidation. In ZG40Cr25Ni20, lower Cr and higher Fe/Ni contents, combined with oxide spallation, caused severe surface Cr depletion and increased participation of metallic elements in oxidation. In the experimental material, sufficient Cr diffused to the surface to sustain Cr_2O_3 grain growth, while displacement reactions reduced initially formed MO oxides (MnO, NiO, FeO) back to metallic elements, minimizing Fe, Mn, and Ni oxidation. Spinel phases $MnCr_2O_4$ and Fe(Ni,Mn)Cr_2O_4 formed later at oxide interfaces through polymerization reactions to lower free energy. These spinels have very low Gibbs free energy changes, are thermodynamically stable, and block outward diffusion of metal ions, providing additional oxidation resistance. Due to high Fe content in both alloys, not all FeO could be reduced by Cr, and residual FeO further oxidized to the more stable Fe_3O_4.

At 1100°C, ZG40Cr25Ni20 surface oxides became powdery with severe spallation, while the experimental material showed some spallation but retained dense granular oxides with continued oxidation resistance. XRD analysis revealed ZG40Cr25Ni20 surface consisted of Fe_3O_4, Fe(Ni,Mn)Cr_2O_4, and austenite substrate, whereas the experimental material contained Cr_2O_3, Fe_3O_4, and Fe(Ni,Mn)Cr_2O_4. In ZG40Cr25Ni20, once the initial Cr_2O_3 film ruptured, the protective oxide could not regenerate, leading to rapid outward metal diffusion and internal Cr oxidation. The experimental material, with higher Cr content, exhibited self-healing capability where Cr_2O_3 immediately reformed on exposed surfaces after local damage or spallation, resulting in lower oxidation rates.

SEM morphology and EDS analysis of surface oxides after 168 hours at 1100°C (Figure 5 [Figure 5: see original paper]) showed that the experimental material oxide contained higher Cr and Mn concentrations than ZG40Cr25Ni20, with Fe and Ni mass fractions of 6.96% and 2.01% respectively, compared to 20.43% and 6.48% in ZG40Cr25Ni20. These results indicate that under identical conditions, the experimental material oxide film contained more Cr_2O_3, providing greater resistance to Fe and Ni outward diffusion and O inward diffusion, thus exhibiting superior oxidation resistance.

Cross-sectional SEM and EDS analysis after 168 hours at 1100°C (Figures 6

[Figure 6: see original paper] and 7 [Figure 7: see original paper]) revealed a thin film adjacent to the substrate in the experimental material. Line scans showed Cr and O enrichment in the outer oxide layer, indicating primarily Cr_2O_3, which isolated the substrate from external oxygen. The inner oxide layer contained Cr, Mn, O, and minor Fe, corresponding to Cr_2O_3, $MnCr_2O_4$, and minor Fe_3O_4. In contrast, ZG40Cr25Ni20 lacked a substrate-adherent film and showed severe spallation. Line scans revealed Fe, Cr, Mn, Ni, and O enrichment throughout the oxide layer, indicating $Fe(Ni,Mn)Cr_2O_4$ and Fe_3O_4. High O content near the substrate in ZG40Cr25Ni20 demonstrated that the surface oxide could not prevent O diffusion into the metal, with oxidation penetrating into the substrate via O^{2-} inward diffusion.

The high-temperature oxidation behavior of the low-nickel economical duplex heat-resistant cast steel can be summarized as follows: During initial oxidation, the oxidation rate is rapid and controlled by surface reactions. After formation of a complete oxide film, the rate decreases and becomes controlled by diffusion of alloy elements from substrate to surface and oxygen through the oxide layer to the substrate. Below 1100°C, the main oxidation products are Cr_2O_3 and $MnCr_2O_4$. At 1100°C, the products are Cr_2O_3, Fe_3O_4, and $Fe(Ni,Mn)Cr_2O_4$. The protective Cr_2O_3 film distributes at the outer oxide layer, blocking outward metal ion diffusion and inward O ion diffusion, thereby reducing oxidation rate and improving high-temperature oxidation resistance.

Conclusions

1. Compared with ZG40Cr25Ni20, the experimental material exhibited reduced weight gain per unit area under identical conditions, with oxidation activation energy increased from $148.4\ kJ \cdot mol^{-1}$ to $245.7\ kJ \cdot mol^{-1}$, demonstrating improved high-temperature oxidation resistance.
2. Although Ni content was reduced relative to ZG40Cr25Ni20, increased Cr and Mn concentrations formed sufficient protective Cr_2O_3 film near the substrate, which blocked outward metal ion diffusion and inward O diffusion, reducing oxidation rate and improving high-temperature oxidation resistance.
3. The experimental material exhibited superior high-temperature oxidation resistance compared to ZG40Cr25Ni20 while significantly reducing Ni content, making it a promising alternative to conventional ZG40Cr25Ni20 heat-resistant cast steel.

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Note: Figure translations are in progress. See original paper for figures.