Effects of Long-Term Aging at 760 °C on the Microstructure and Mechanical Properties of a Ni-Cr-W-Fe Alloy Postprint

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Abstract

The microstructural evolution of a Ni-Cr-W-Fe alloy during long-term aging at 760 ℃ was investigated using OM, SEM, and TEM. The mechanical properties of the alloy at room and elevated temperatures were tested, and the tensile fracture surfaces were analyzed. The results indicate that after solution treatment at 1100 ℃, the average grain size of the alloy is approximately 80 mm, with annealing twins present within the grains. Following aging at 760 ℃, M23C6 and g' phases precipitate in the alloy. The g' phase exhibits a size of approximately 29 nm and a volume fraction of approximately 19%. After long-term aging at 760 ℃, the average size of g' particles satisfies the Ostwald equation with respect to time t. The solution-treated alloy demonstrates excellent room temperature ductility, and the tensile fracture surface exhibits a ductile fracture morphology. The aged alloy exhibits a significant increase in room temperature yield strength, accompanied by a decrease in ductility. With increasing holding time at 760 ℃, the yield strength of the alloy at both room and elevated temperatures gradually decreases. Compared with the aged alloy, the room temperature ductility of the alloy aged for 1000-3000 h decreases, while the elevated temperature ductility remains at approximately 15%, which is essentially comparable to that of the aged state.

Full Text

Effect of Long-Term Aging at 760 ℃ on Microstructure and Mechanical Properties of a Ni-Cr-W-Fe Alloy

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Abstract: Significant efforts have been made in recent years to develop advanced ultra-supercritical (A-USC) fossil-fired power plants with steam conditions of 700 ℃ and 30 MPa or higher. The most critical consideration is the development of materials for superheater and reheater tubes capable of operating at temperatures up to 760 ℃. During the design and application of these materials, phase stability, creep rupture strength, and corrosion performance at 700–760 ℃ must be evaluated. A new Ni-Cr-W-Fe alloy has been designed for A-USC power plants, and this work investigates its microstructure and mechanical properties after long-term aging at 760 ℃ using optical microscopy (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and tensile testing, with fractographic analysis of tested specimens. The results show that after solution-annealing at 1100 ℃, the alloy exhibits an equiaxed austenitic structure with an average grain size of approximately 80 m and annealing twins present within the grains. After aging at 760 ℃, $M_{23}C_6$ carbides and γ' phase precipitate in the alloy. The γ' phase has an average particle size of about 29 nm and a volume fraction of approximately 19%. During long-term aging at 760 ℃, the average γ' particle size follows Ostwald ripening kinetics with respect to time t. The solution-annealed alloy demonstrates excellent room-temperature ductility with a ductile fracture morphology. Aging treatment significantly increases room-temperature yield strength but reduces ductility. With extended holding time at 760 ℃, both room- and elevated-temperature yield strengths decrease gradually. Compared to the aged condition, alloys aged for 1000–3000 h exhibit reduced room-temperature ductility, while elevated-temperature ductility remains at approximately 15%, essentially equivalent to the initial aged condition.

Keywords: Ni-Cr-W-Fe alloy, long-term aging, γ' phase, tensile property

1. Introduction

Coal-fired power generation dominates China' s energy structure, accounting for 70–80% of annual electricity production [1]. However, coal combustion generates substantial greenhouse gases and pollutants, including CO_2, SO , and NO [2,3], creating significant environmental burdens. To reduce resource consumption and emissions, numerous clean coal technologies have been developed, with ultra-supercritical (USC) technology gaining widespread attention due to its feasibility and becoming the primary development direction for thermal power plants both domestically and internationally.

Following the establishment of 600 ℃ USC technology, European, American, and Japanese countries are now developing 700 ℃ class advanced ultra-supercritical (A-USC) coal-fired power technology [4,5], aiming to increase steam temperature to 700 ℃ and pressure above 30 MPa, thereby raising coal thermal efficiency to over 50% and substantially reducing coal consumption and greenhouse gas emissions.

These elevated steam temperature and pressure parameters impose more stringent requirements on materials for high-temperature structural components, including superheaters and steam piping, which must possess high-temperature strength, corrosion and oxidation resistance, and good workability. When steam temperature increases to 700 ℃, the operating temperature of high-temperature components such as superheaters and steam pipelines reaches 700–760 ℃. The heat-resistant steels currently used in 600 ℃ USC units, such as T91 and Super304H, cannot meet the high-temperature strength and corrosion resistance requirements for 700 ℃ power plants, necessitating the use of nickel-based or Fe-Ni based superalloys [6].

Nickel-based or Fe-Ni based alloys exhibit excellent high-temperature strength, readily satisfying the strength requirements for 700 ℃ power plant components. However, their weldability, formability, and corrosion resistance may not meet the demands of long-term high-temperature service. Consequently, research programs have been established worldwide to develop superalloys for 700 ℃ A-USC power plants, leading to alloys such as HR6W [6], GH984 [7], CCA617 [8], and Inconel 740 [9,10]. HR6W alloy demonstrates relatively high creep rupture strength at 650–700 ℃ [11] but still falls short of requirements for 700–760 ℃ operation. China has developed the Fe-Ni based superalloy GH984, with related research currently underway [12].

Existing data show that CCA617 and Inconel 740 alloys possess high creep rupture strength [13], but their weldability and welding processes remain under development. Furthermore, both alloys contain 12–20 wt% Co, significantly increasing material and power plant construction costs. China is actively developing 700 ℃ A-USC technology [10]. To reduce alloy and construction costs and develop power plant materials suited to China’ s raw material resources, this study designed a Ni-Cr-W-Fe alloy. This alloy contains no Co, uses W for solid solution strengthening, Al for precipitation strengthening, and trace elements C and B for grain boundary strengthening, with 5–10 wt% Fe added to reduce costs, targeting application as superheater tubing in 700 ℃ A-USC units. To evaluate the alloy’ s microstructural stability, this work investigates the evolution of microstructure during long-term aging at 760 ℃ and analyzes the effects of microstructural changes on tensile properties.

2. Experimental Methods

A Ni-Cr-W-Fe alloy ingot was melted in a vacuum induction furnace and cast, with a chemical composition (wt%) of: C 0.0071, Cr 20, Fe 5, W 6, Al 3.25, B 0.002, and Ni balance. The ingot was forged at 1150 ℃ into a 35 mm × 35 mm billet, then hot-rolled at 1100 ℃ into 14 mm diameter bar stock. The heat treatment consisted of solution treatment at 1100 ℃ for 30 minutes followed by water quenching, then aging at 760 ℃ for 16 hours with air cooling. After aging, specimens were held at 760 ℃ for 200–3000 h to evaluate microstructural stability and its influence on tensile properties.

Specimens were mechanically ground and polished, then chemically etched using a solution of 20 g $CuSO_4$ + 75 mL HCl + 100 mL H_2O. Grain structure was observed using an Axio Observer ZIm optical microscope (OM), with the average grain size of the solution-annealed alloy measured by the intercept method as an average of 10 OM images. A JEOL 6340 scanning electron microscope (SEM) was used to observe carbide and γ' morphologies, with carbide volume fraction and γ' particle size determined as averages from 5 SEM images. Transmission electron microscopy (TEM) observations were conducted on a JEOL 2100 TEM equipped with energy-dispersive spectroscopy (EDS). Bright-field imaging was used to analyze carbide and γ' morphologies, selected-area electron diffraction (SAED) was employed to analyze carbide structure, and EDS was used to determine carbide composition. TEM specimens were prepared by twin-jet electropolishing using a solution of 10% $HClO_4$ + 90% C_2H_5OH (by volume) at -18 ℃ and 10 V.

Tensile testing at room temperature and elevated temperature was performed according to GB/T 228.1-2010 and GB/T 4338-2006 standards on a SANS-CMT5205 universal testing machine. Cylindrical standard tensile specimens with a gauge length of 25 mm and diameter of 5 mm were machined from bars after solution treatment at 1100 ℃ and aging at 760 ℃ (for 16, 1000, 2000, and 3000 h). The room-temperature tensile rate was 0.45 mm/min before yielding and 3 mm/min after yielding. Elevated-temperature tensile tests were conducted at 704 and 750 ℃ with rates of 0.2 mm/min before yielding and 2 mm/min after yielding.

2.1 Microstructure of Alloys After Long-Term Aging

The microstructure of the Ni-Cr-W-Fe alloy after solution-annealing at 1100 ℃ and aging at 760 ℃ is shown in Figure 1 [Figure 1: see original paper]. As seen in Figure 1a, the solution-annealed alloy exhibits an equiaxed austenitic structure with uniform grain distribution, an average grain size of 80 m, and annealing twins within the grains. Figures 1b and c reveal that after aging at 760 ℃, carbides precipitate in the alloy, appearing as elongated and short rod-like morphologies primarily distributed along grain boundaries with a volume fraction of approximately 0.1%. The SAED pattern in Figure 1d identifies the grain boundary carbides as $M_{23}C_6$ with an fcc structure, maintaining good coherency with the matrix, expressed as: $\{001\}\gamma$ // $\{001\}M_{23}C_6$ and $<001>\gamma$ // $<001>M_{23}C_6$. EDS analysis shows that the metallic element M in $M_{23}C_6$ consists of 44.9% Cr, 25.1% Fe, 19.3% Ni, and 10.7% W (by mass). Figure 1e demonstrates that after aging at 760 ℃, the γ' phase precipitates in the matrix with a spherical morphology. Statistical analysis indicates γ' particle size of 29 nm and volume fraction of approximately 19%.

The microstructures of the Ni-Cr-W-Fe alloy after long-term aging at 760 ℃ for 200, 500, 1000, 2000, and 3000 h are presented in Figure 2 [Figure 2: see original paper]. The grain boundary $M_{23}C_6$ carbides appear as elongated strips distributed relatively uniformly, indicating continued carbide precipitation during long-term aging. Quantitative analysis reveals that after aging at 760 ℃ for 200-3000 h, the carbide volume fraction is approximately 0.15%, slightly increased compared to the initial aged condition. After aging for 200-500 h, the width of grain boundary $M_{23}C_6$ is about 0.16 m, showing slow growth (Figures 2a and b). After 1000, 2000, and 3000 h, the average width of grain boundary carbides increases to 0.20, 0.26, and 0.29 m, respectively (Figures 2c-e).

TEM analysis of grain boundary carbide morphology and structure after long-term aging is shown in Figure 3 [Figure 3: see original paper]. SAED analysis confirms that the grain boundary precipitates maintain the fcc structure identical to the $M_{23}C_6$ shown in Figure 1c, preserving good coherency with the austenitic matrix. The $M_{23}C_6$ carbides distribute as elongated strips, with size increasing with aging time. In nickel-based alloys for thermal power applications, besides $M_{23}C_6$, MC and M_6C type carbides can also form. GH984 alloy precipitates NbC and Ti(C,N) [7], while HR6W [11], CCA617 [14], and Inconel 740 [15] alloys contain M_6C and MC carbides. Carbide precipitation type is closely related to alloy composition; alloys with higher Nb or Ti contents tend to precipitate MC carbides, such as GH984 and Inconel 740. The Ni-Cr-W-Fe alloy primarily employs Al for precipitation strengthening and contains no Ti or Nb, making MC carbide formation difficult. M_6C carbides typically precipitate in superalloys when W and Mo contents exceed 6-8 at% [16], whereas the Ni-Cr-W-Fe alloy contains only about 2 at% W, making M_6C formation unlikely.

The effect of long-term aging at 760 ℃ on γ' morphology is illustrated in Figure 4 [Figure 4: see original paper]. The γ' particles remain essentially spherical at all holding times without obvious shape changes. The relationship between particle size and aging time is shown in Figure 5 [Figure 5: see original paper]. Figure 5a indicates that γ' size increases noticeably after aging for 200 and 500 h, with the coarsening rate gradually decreasing as holding time extends to 1000-3000 h. As shown in Figure 5b, the particle size (d) and time (t) follow the Ostwald ripening equation [17,18]:

$$d_t^3 = kt$$

where d represents the γ' particle diameter after long-term aging for time t (in nm), and k is the coarsening coefficient. Analysis of Figure 5b yields a k value of 1061 for the γ' phase in the Ni-Cr-W-Fe alloy at 760 ℃, indicating a greater coarsening tendency than in CCA617 (k = 442) [14], GH984 (k = 187) [12], and Inconel 740 (k = 145) [15].

The coarsening coefficient k is related to factors including γ' phase volume fraction, elemental diffusivity, and Al concentration in the matrix [19-21]. According to Lifshitz and Slyozov [20] and Wagner [22], k can be expressed as:

$$k = \frac{8\gamma D\Omega^2 C_0}{9RT}$$

where D is the diffusion coefficient, γ is the interfacial energy between precipitate and matrix, C_0 is the solute concentration in the matrix, Ω is the atomic volume, R is the gas constant, and T is the thermodynamic temperature. For a given alloy system and temperature, C_0 and Ω remain essentially constant. The interfacial energy γ in multicomponent nickel-based alloys ranges from 60-90 mJ/m^2, having minimal influence on k [23]. γ' coarsening during thermal aging is primarily controlled by diffusion of constituent elements such as Al, Ti, or Nb. Al diffuses more rapidly [24,25], and compared to Ti-rich alloys like GH984 and Inconel 740, the high Al content in the Ni-Cr-W-Fe alloy results in significantly greater γ' coarsening. Additionally, the γ' phase volume fraction in the Ni-Cr-W-Fe alloy (~19%) is higher than in CCA617, GH984, and Inconel 740, indicating smaller γ '-γ' particle spacing that facilitates atomic diffusion and γ' phase coarsening.

2.2 Mechanical Properties of the Alloy

Table 1 lists the room- and elevated-temperature tensile properties of the Ni-Cr-W-Fe alloy after solution-annealing at 1100 ℃ and aging at 760 ℃. Figure 6 [Figure 6: see original paper] shows the fracture morphologies after tensile testing at room and elevated temperatures. The solution-annealed specimen exhibits a ductile fracture morphology at room temperature, characterized by equiaxed dimples with relatively smooth edges, reflecting good plasticity (Figure 6a). Table 1 data show that compared to the solution-annealed condition, the aged alloy exhibits significantly increased room-temperature yield strength, but elongation and area reduction decrease to 36% and 48%, respectively. As test temperature increases from room temperature to 704 and 750 ℃, yield strength ($Rp_{0 \cdot 2}$) and ultimate tensile strength (Rm) gradually decrease, while ductility also drops significantly. Correspondingly, the fracture morphology transitions to intergranular brittle fracture with numerous grain boundary cracks (Figures 6b–d).

Carbides play an important role in superalloys, with their morphology significantly affecting mechanical properties [26]. As shown in Figures 1b and c, elongated grain boundary carbides precipitate in the Ni-Cr-W-Fe alloy after aging treatment. These carbides strengthen grain boundaries while the γ' phase strengthens the matrix, resulting in significantly increased room- and elevated-temperature strengths compared to the solution-annealed condition. During tensile deformation, the elongated grain boundary carbides become crack initiation sites [27], causing intergranular brittle cracking and fracture, leading to substantially reduced tensile ductility. The fracture mode changes from ductile (Figure 6a) to brittle (Figures 6b–d), with this detrimental effect being more pronounced on elevated-temperature ductility.

Figure 7 [Figure 7: see original paper] illustrates the variation of room- and elevated-temperature tensile properties during long-term aging at 760 ℃. Figure 7a shows that both room- and elevated-temperature yield strengths decrease slowly with extended aging time. Comparative analysis of Figure 7 and Table

1 reveals that after 3000 h aging, the yield strengths at room temperature, 704 ℃, and 750 ℃ decrease by 5%, 7%, and 8%, respectively, compared to the initial aged condition, indicating a relatively slow changing trend. The strength variation correlates closely with microstructural evolution. As shown in Figures 4 and 5, the primary strengthening phase γ' gradually coarsens during long-term aging, progressively reducing the dispersion strengthening effect and resulting in gradually decreasing room- and elevated-temperature strengths.

Figure 7b indicates that after aging at 760 ℃ for 1000–3000 h, room-temperature elongation and area reduction remain essentially stable but are lower than in the initial aged condition (16 h). This reduction in room-temperature ductility results from increased grain boundary carbide content and carbide film formation (Figure 2), which makes the alloy more brittle. However, gradual γ' coarsening during long-term aging reduces its strengthening effect and improves ductility. The combined effects of carbide and γ' evolution result in relatively stable room-temperature ductility during long-term aging. After 1000–3000 h aging, elevated-temperature area reduction and elongation remain at approximately 15%.

Fracture morphologies after long-term aging are shown in Figure 8 [Figure 8: see original paper]. The fractures exhibit brittle fracture characteristics dominated by intergranular fracture. However, high-temperature tensile fracture surfaces show numerous fine, dense dimples distributed in grain boundary regions, with dimple distribution becoming more pronounced with longer aging times. This microscale ductile fracture behavior in grain boundary regions contributes to improved elevated-temperature tensile ductility in the Ni-Cr-W-Fe alloy.

Conclusions

1. After solution-annealing at 1100 ℃, the Ni-Cr-W-Fe alloy exhibits an equiaxed austenitic structure with ductile fracture morphology at room temperature. After aging at 760 ℃, $M_{23}C_6$ carbides and γ' phase precipitate in the alloy. The γ' particles are approximately 29 nm in size with a volume fraction of about 19%. The aged alloy shows intergranular fracture characteristics.
2. After long-term aging at 760 ℃, the primary precipitates in the Ni-Cr-W-Fe alloy are $M_{23}C_6$ carbides and γ' phase. The $M_{23}C_6$ carbides distribute as elongated strips along grain boundaries. The γ' phase remains essentially spherical, with average particle size following the Ostwald ripening equation with respect to aging time.
3. With increasing holding time at 760 ℃, both room- and elevated-temperature yield strengths decrease gradually. Compared to the initial aged condition, alloys aged for 1000–3000 h show reduced room-temperature elongation and area reduction, primarily associated with brittleness caused by elongated grain boundary $M_{23}C_6$ precipitation. Holding time at 760 ℃ has minimal effect on ductility at both tempera-

tures; room-temperature ductility remains essentially stable from 1000-3000 h, while elevated-temperature area reduction and elongation remain at approximately 15%.

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