

Postprint: Study on σ Phase Precipitation Behavior in HR3C Steel for Ultra-supercritical Boilers

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Abstract

The precipitation behavior of sigma phase in an ultra-supercritical HR3C steel during long-term aging at 700 and 750 °C up to 2000 h was investigated using OM, SEM, and TEM, and the factors influencing sigma phase precipitation were explored through phase calculation methods. The results show that irregular blocky second phases precipitated at grain boundaries after aging for 1000 h at 700 and 750 °C, and these increased and coarsened with increasing aging time; EDS analysis indicated that this phase mainly contained Fe and Cr, and combined with SAED analysis results, it was ultimately identified as a sigma-Fe-Cr intermetallic compound; through phase calculation analysis of the as-received HR3C steel, it was concluded that differences in microstructure or phase structure may be responsible for affecting subsequent sigma phase precipitation behavior.

Full Text

Study on σ Phase Precipitation Behavior in HR3C Steel for Ultra-Supercritical Boilers

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Abstract

HR3C steel is a new type of austenitic heat-resistant steel widely used for superheater and reheater tubes in ultra-supercritical (USC) boilers. The mechanical properties of HR3C steel depend on microstructural stability, particularly the numerous precipitates formed during service. This study investigated σ phase precipitation in HR3C steel during long-term aging up to 2000 h at 700 and 750 °C using optical microscopy (OM), scanning electron microscopy (SEM),

and transmission electron microscopy (TEM), and applied phase calculation methods to understand the influencing factors. The results show that irregular blocky second phases precipitated at grain boundaries after 1000 h of aging, increasing in number and coarsening with extended aging time. Energy-dispersive spectroscopy (EDS) analysis revealed these phases were rich in Fe and Cr, and selected-area electron diffraction (SAED) analysis confirmed them as σ -FeCr intermetallic compounds. Phase calculations on the initial-state HR3C steel suggest that differences in microstructure or phase structure may affect subsequent σ phase precipitation behavior.

Keywords: HR3C steel, aging, σ phase, phase computation, microstructure

Introduction

Improving power generation efficiency in thermal power plants by increasing steam parameters of supercritical (SC) and ultra-supercritical (USC) units represents a primary development direction for future thermal power construction, offering benefits in coal resource conservation and environmental protection. HR3C steel was developed by adding N and Nb to TP310H austenitic stainless steel. Due to its excellent high-temperature mechanical properties, corrosion resistance, and superior process performance, HR3C has become the preferred material for superheater and reheater tubes in USC power plant boilers [1–6].

The precipitation behavior of second phases in HR3C steel during long-term service under USC conditions has attracted widespread attention. Bai et al. [6] reported that during aging at 650 °C for 300 h, M23C6 phases rapidly precipitated at grain boundaries and twin boundaries, with further precipitation and growth of MX particles occurring as aging time increased. Wang et al. [7] noted that M23C6 phase size was more susceptible to aging time and temperature than Z phase (CrNbN), suggesting that M23C6 coarsening was the main reason for the decrease in high-temperature yield strength of HR3C steel during long-term aging. Sandström et al. [8] analyzed the precipitation strengthening effect of Nb(C,N) in HR3C steel. However, research on σ phase precipitation in HR3C steel remains limited. References [9,10] indicated that σ phase precipitation was suppressed during long-term creep stages of HR3C steel. Yin et al. [11] observed significant embrittlement in HR3C steel after 25,000 h of service during flattening tests, attributing this to the transformation of grain boundary M23C6 to M6C-type carbides. Our previous work [12] identified NbCrN and M23C6 phases in Sumitomo HR3C steel aged at 750 °C for 500 h, and detected σ -FeCr phase through X-ray diffraction (XRD) of extracted powders. TEM-EDS analysis suggested that a new phase appearing within grain boundary M23C6 might be a Cr-rich σ phase, though more accurate structural analysis was not provided.

This work focuses on σ phase precipitation in HR3C steel, analyzing the precipitate composition during aging at 750 °C, predicting σ phase precipitation

tendency using a new phase calculation method based on d-electron alloy theory, and investigating factors influencing σ phase precipitation behavior to provide insights for evaluating the long-term service condition of HR3C steel in USC units.

Experimental Materials and Methods

The experimental material was unused HR3C steel pipe with an outer diameter of 45 mm and wall thickness of 7 mm, which had undergone solution treatment at approximately 1093 °C. X-ray fluorescence spectroscopy (XRF) determined its chemical composition (mass fraction, %) as: Fe 53.26, Cr 24.91, Ni 19.78, Mn 1.30, Nb 0.39, Si 0.32, S 0.006, P 0.029. Samples were cut from the HR3C steel pipe by wire electrical discharge machining. Aging treatments were conducted in an SX-5-12 high-temperature box furnace at 700 and 750 °C for durations of 500, 1000, and 2000 h, followed by air cooling.

Samples in different heat treatment states (including solution state) were mechanically ground and polished, then etched. For etching: solution-state and 2000 h-aged HR3C steel samples were etched with 40% aqua regia (HCl:HNO₃ = 3:1) for 4 and 20 min, respectively; 500 and 1000 h-aged samples were electrolytically etched with 10% oxalic acid (C₂H₂O₄ · 2H₂O) at approximately 5 V for 3 s.

Microstructures of initial-state and aged HR3C steel samples at 700 and 750 °C were observed using a MEF4 optical microscope (OM). A JSM-5600LV scanning electron microscope (SEM) equipped with EDS analyzed phase composition and distribution in initial-state and 750 °C/2000 h-aged samples. A Tecnai G2 20S transmission electron microscope (TEM) performed selected-area electron diffraction (SAED) analysis on large precipitates at grain boundaries in the latter sample. The second phase types in initial-state HR3C steel were identified using an EPMA-1600 electron probe microanalyzer.

Finally, the new phase calculation method (New PHACOMP) based on d-electron alloy theory was employed to calculate the average electron orbital parameter value and predict σ phase precipitation tendency in HR3C steel.

2.1 Precipitate Phase Analysis in HR3C Steel

Figure 1 [Figure 1: see original paper] shows the microstructures of HR3C steel in different heat treatment states. Comparing initial-state and aged samples reveals granular particles distributed in the HR3C matrix, which increased in size and number after aging, with grain boundaries becoming more distinct. Comparison of samples aged at 700 and 750 °C shows that after 1000 h aging, obvious blocky second phases precipitated at grain boundaries with relatively large sizes. As aging time increased, these blocky precipitates showed significant growth and coarsening.

Figure 2 [Figure 2: see original paper] presents SEM images and EDS analysis

results of large precipitates at grain boundaries in HR3C steel aged at 750 °C for 2000 h. As shown in Figure 2a, these phases are located at grain boundaries as irregular blocky shapes 5–10 nm in size, corresponding to the black blocky precipitates observed at grain boundaries in Figure 1. EDS analysis (Figure 2b) indicates the main constituents are Fe and Cr, with small amounts of Ni and Si, where the sum of atomic fractions of Fe and Ni is nearly equal to the Cr content.

Hu et al. [13] reported that in Fe-based alloys, σ phase typically has a tetragonal structure and can be expressed as FeCr or $(\text{Fe,Ni})_x(\text{Cr,Mo})_y$, with composition varying within a certain range. It tends to nucleate at grain boundaries, particularly at triple junctions, distributing as particles or continuous films, and its extensive precipitation causes grain boundary weakening and embrittlement [14,15]. Based on composition and morphology, this phase can be preliminarily identified as tetragonal σ phase.

Figure 3 [Figure 3: see original paper] shows TEM images, SAED patterns, and EDS analysis results of large grain boundary precipitates in HR3C steel aged at 750 °C for 2000 h. The phase is approximately 10 nm in size with irregular shape, similar to the grain boundary precipitates shown in Figures 1 and 2. EDS analysis (Figure 3b) shows the phase contains mainly Cr and Fe with minor Ni, with composition very similar to Figure 2b, confirming it is the same precipitate type. Combined analysis of precipitation location, morphology, SAED pattern, and EDS results definitively identifies this precipitate as tetragonal σ -FeCr phase. The experimental material is domestic HR3C steel, and our previous work on Sumitomo HR3C steel [12] preliminarily identified σ phase precipitation. The present work provides more accurate structural analysis, demonstrating that σ phase precipitation during long-term aging at 700 and 750 °C in HR3C steel is not an accidental phenomenon. In Fe-Cr-Ni systems, when σ phase content reaches or exceeds 5%, alloy impact toughness decreases significantly [16], making σ phase precipitation in HR3C steel during service a concern requiring attention.

2.2 Phase Calculation Analysis of Factors Influencing σ Phase Precipitation in HR3C Steel

Phase calculation is an important method for predicting the tendency of topological close-packed (TCP) phase precipitation in alloys, based on the theory that TCP phases are electron compounds where electronic factors dominate their formation. Through calculations and verification of hundreds of Fe-, Co-, and Ni-based superalloys, the new phase calculation method (New PHACOMP) based on d-electron alloy theory has proven more realistic in prediction than the electron vacancy theory-based PHACOMP method [17]. Therefore, this work adopted the New PHACOMP method based on d-electron alloy theory, which is an alloy design method developed from DV- $X\alpha$ Cluster molecular orbital calculations [18]. A single electron orbital parameter M_d (d-orbital energy of alloy elements) characterizes the combined effects of atomic size, electronegativity,

and alloying factors. The average Md for an alloy (or a phase) is calculated as:

$$\overline{Md} = \sum_i X_i \cdot Md_i$$

where X_i and Md_i are the mole fraction and Md value of element i , respectively. According to d-electron alloy theory, lower Md values of alloy elements favor phase stability. Md values for each element are [19]: Fe 0.858, Ni 0.717, Cr 1.142, Mn 0.957, Si 1.900, Nb 2.117.

The critical Md value (Md_c) for σ phase formation in Fe-based superalloys is 0.900 [18]; exceeding this value indicates a tendency for σ phase formation, with precipitation tendency increasing as Md increases. Based on the HR3C steel composition measured by XRF, the calculated Md is 0.910, indicating that from an overall compositional design perspective, the Md value is near the critical value and σ phase precipitation tendency is not particularly strong. However, this work shows significant σ phase precipitation at grain boundaries in HR3C steel after 1000 h aging at 700 and 750 °C. Previous work on Sumitomo HR3C steel also observed such large grain boundary precipitates (now confirmed as σ phase) after 2500 h at 700 °C and 2000 h at 750 °C [20]. This demonstrates that σ phase precipitation in HR3C steel at 700 and 750 °C is not accidental, yet two HR3C steels with identical composition show significant differences in σ phase precipitation time under the same aging conditions. The experimental temperatures in this work exceed the actual service temperature of HR3C steel (620–680 °C) [1,21] to accelerate aging, but the fundamental nature of σ phase precipitation is equivalent to actual precipitation during service, making σ phase precipitation during long-term service a significant concern.

Figure 4 [Figure 4: see original paper] shows SEM analysis results of the initial-state HR3C steel microstructure and phase structure. Numerous white second-phase particles of varying sizes are dispersed in the initial-state HR3C steel, with larger particles approaching 3 μ m (Figure 4a). EDS analysis shows these contain mainly Nb, Cr, and N (Figure 4c), and EPMA micro-area composition analysis reveals an atomic mole fraction ratio of Nb:Cr:N = 33.045:31.143:35.879 1:1:1, identifying them as incompletely dissolved CrNbN phase in austenite after solution treatment [6,7]. Literature [11,15] indicates that σ phase only precipitates when C and N contents in the matrix are sufficiently low. Precipitation of CrNbN phase in initial-state HR3C steel reduces N content in the matrix, creating favorable conditions for σ phase precipitation. Using the phase calculation method for different regions in Figure 4a, EDS results (Figures 4b and c) yield: the austenitic matrix region (region 1) has an Md of 0.910, similar to the critical value; region 2 (CrNbN phase) has an Md of 1.599, significantly higher than region 1. This shows that different regions in initial-state HR3C steel have varying Md values. Combined with phase calculation results, we speculate that if compositional design effects are excluded, differences in microstructure or phase structure between the domestic HR3C steel used in this work and Sumitomo HR3C steel may influence subsequent σ phase precipitation

behavior during aging. However, further research is needed to determine the specific reasons affecting σ phase precipitation.

Conclusions

1. Through EDS and SAED analysis, σ phase with tetragonal structure was definitively identified as precipitating at grain boundaries in HR3C steel during long-term aging at 700 and 750 °C.
2. Combined with New PHACOMP analysis of initial-state HR3C steel, differences in microstructure or phase structure are suggested to be factors influencing subsequent σ phase precipitation behavior.

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

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