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Postprint: Relationship Between Embrittlement of In-Service HR3C Steel Superheater Tubes and Evolution of Grain Boundary M23C6 Phase Parameters

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Abstract

The relationship between variations in grain boundary carbide M23C6 phase parameters (area fraction M23C6 and equivalent width W) and embrittlement was investigated in HR3C steel superheater tube samples under different service conditions. Using the ASTM E112 standard austenitic steel grain size rating chart, the total grain boundary perimeter (Lgb) in 2D images corresponding to each grain size level (GL) was calculated, and the relationship Lgb(GL) was fitted. From scanning electron microscope secondary electron (SEM-SE) images of each tube sample, the corresponding M23C6 and W were obtained, thereby establishing the relationship W(GL, M23C6). Combined with Charpy impact tests, the relationship between impact value (aKV) and W, aKV (W), was obtained. Additionally, the elastic modulus (Er) of the grain boundaries was measured using a nanoindenter. The results show that all tube samples exhibited intergranular fracture morphology in their impact fractures. When M23C6 is constant, a smaller GL corresponds to larger W and Er, and a smaller aKV, indicating a greater tendency for grain boundary embrittlement. This reveals the essence of embrittlement caused by the increase (coarsening) in the equivalent width of grain boundary M23C6 plates.

Full Text

Preamble

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Relationship Between the Evolution of Phase Parameters of Grain Boundary M23C6 and Embrittlement of HR3C Superheater Tubes in Service

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Abstract

This study investigates the relationship between embrittlement and the evolution of grain boundary carbide M23C6 phase parameters (area fraction M and equivalent width W) in HR3C superheater tube samples exposed to different service conditions. Using ASTM E112 standard charts for austenitic grain size rating, we calculated the total perimeter of grain boundaries (Lgb) corresponding to each grain size level (GL) and derived their relationship as Lgb(GL). From scanning electron microscopy secondary electron (SEM-SE) images of each tube sample, we obtained the corresponding M and W values, thereby establishing the relationship between W, GL, and M as W(GL, M). Combined with Charpy impact testing, we obtained the relationship between impact value (aKV) and W as aKV(W). Additionally, the elastic modulus (Er) of grain boundaries was measured using a nanoindenter. The results demonstrate that all impact fracture surfaces exhibited intergranular fracture morphology. At a constant M, smaller GL values corresponded to larger W and higher Er, resulting in lower aKV values and thus greater embrittlement tendency. This reveals that embrittlement is fundamentally caused by the increase (coarsening) of the equivalent width of grain boundary M23C6 plates.

Keywords: HR3C steel, embrittlement, M23C6, equivalent width, Charpy impact value

Introduction

The increasing parameters of ultra-supercritical power units demand that boiler high-temperature heating surfaces possess enhanced resistance to steam oxidation and high-temperature strength. HR3C steel is a new heat-resistant steel developed by Sumitomo based on TP310 through the combined addition of Nb and N alloying elements. The steel matrix is strengthened by fine, dispersed Z-phase and MX-phase precipitates along with M23C6, endowing it with superior high-temperature strength and comprehensive properties. Iseda et al. studied the creep rupture strength and microstructural changes of HR3C steel, while Fang et al. investigated the types, structures, and distribution characteristics of precipitates during aging at 750°C. Komai et al. reported on the microstructure and properties of HR3C steel superheater tubes from Eddystone Power Station Unit 1 after 75,075 hours of operation. In China, HR3C steel has only a few years of service history, and research on its microstructure and properties remains limited.

Regarding embrittlement studies of HR3C steel, Yin et al. demonstrated that compared with the as-received condition, HR3C steel final-stage reheater tubes operating at 605°C outlet steam temperature and 5.04 MPa pressure for 25,000 hours exhibited significantly increased brittleness with agglomeration and coarsening of grain boundary carbides. Du et al. showed that continuous lamellar M23C6 formed at grain boundaries caused grain boundary embrittlement in HR3C reheater tubes after 42,000 hours of service at 605°C and 4.9 MPa. Okada et al. reported that the reduction in impact values of HR3C steel final-stage superheater tubes after 75,075 hours at 615°C and 35 MPa was closely related to grain boundary precipitation. Additionally, Li et al. found that HR3C steel exhibited significant aging embrittlement tendency at 650°C, with intergranular brittle fracture dominating after long-term aging. Bai et al. suggested that continuous precipitation of grain boundary carbides during aging at 650°C up to 3,000 hours caused the impact fracture mechanism to transition from transgranular to intergranular. Zheng noted that the significant decrease in impact energy after aging was caused by M23C6 precipitation at grain boundaries. Gao et al. demonstrated that after aging at 700°C, coarse precipitates formed a network at grain boundaries, leading to reduced impact values. Peng et al. attributed the decrease in impact values after aging at 700°C to reduced intergranular bonding strength caused by M23C6 precipitation along grain boundaries. However, to date, no quantitative studies have been reported on the relationship between impact toughness and grain boundary precipitates in these tubes after short-term and long-term service. Addressing the widespread embrittlement problem in such tubes, this work investigates the relationship between embrittlement tendency and the content and size of grain boundary precipitates, providing practical reference for life assessment and safe operation of in-service HR3C steel tubes.

Experimental Methods

The as-received and service-exposed HR3C steel superheater tube samples used in this study were obtained from different ultra-supercritical thermal power units. Their service conditions and chemical compositions are shown in Table 1 and Table 2 , respectively. The compositions were measured using a SpectroLab direct-reading spectrometer, with all major element contents within the ASTM-A 213/A 213M specification. Sample SH4.0 had the highest carbon content, while SH3.2 had the lowest.

Sample preparation proceeded as follows: Each service-exposed superheater tube was circumferentially divided into eight equal sections. Microhardness was measured on the radial cross-section using an HXS-1000A digital microhardness tester to identify the locations of highest and lowest hardness. Three impact specimens were then cut from each of these locations for Charpy impact testing at room temperature. Due to limited tube wall thickness, non-standard impact specimens measuring 55 mm × 10 mm × 2.5 mm with a V-notch depth of 2 mm were used.

Analysis using electron probe microanalysis (EPMA), energy-dispersive spectroscopy (EDS), and multiphase separation technology (MPST) revealed that the microstructure of all HR3C steel superheater tube samples consisted primarily of intragranular Z-phase (NbCrN), grain boundary M23C6 phase, and austenite matrix. Since Z-phase particles were fine and discretely distributed within grains, and all tube samples exhibited intergranular brittle fracture, this work focused on quantitative analysis of austenite grain size (G), M23C6 phase parameters, and grain boundary elastic modulus (Er) and their relationship to embrittlement tendency.

The procedure was as follows: Samples were ground with 01-010 grit sandpaper, mechanically polished with W0.5 diamond paste, and etched with a solution of 5 g $FeCl_3$ + 10 mL HCl + 30 mL alcohol. Optical microscopy (OM) images were obtained using a PMG3-U microscope. According to ASTM E112 standard methods (NAE = 2^(G-1), where NAE is the number of grains per square inch at 100× magnification and G is the grain size number), the mean austenite grain size (GM) was determined using the area and intercept methods. Based on ASTM E112 austenite grain size standard charts, the two-dimensional grain boundary perimeter (Lgb) corresponding to each grain size level (3-8; note that levels 1 and 2 were not included as they differ insignificantly from level 3 in the ASTM E112 charts) was measured using Image-Pro Plus software to derive the relationship between Lgb and austenite grain size (GL). Using SEM-SE images from a JSM-7100F microscope and Image-Pro Plus software, the area fraction of grain boundary carbides (M) was measured, and the equivalent width (W) was calculated using the proposed formula. This established the relationship between W, GL, and M, and subsequently between impact value (aKV) and W. Impact fracture morphologies were examined using a Quanta-400 SEM. To characterize the embrittlement tendency of grain boundary M23C6, the elastic modulus (Er) was measured using a HYSITRON TI950Ubi nanoindenter equipped with SEM. The nanoindenter parameters were: maximum load 1 mN, loading time 5 s, holding time 2 s, unloading time 5 s. All results represent averages of data from the highest and lowest hardness locations.

Results and Discussion

2.1 Impact Fracture Morphology Figure 1 [Figure 1: see original paper] shows the impact fracture morphologies of HR3C tube samples. All fracture surfaces exhibit typical rock-candy features, with cracks initiating at grain boundaries and propagating intergranularly, indicating that all samples failed by intergranular brittle fracture.

2.2 Austenite Grain Size Figure 2 [Figure 2: see original paper] presents OM images of HR3C tube samples. The prior austenite grains in samples SH3.2 and SH4.0 are significantly coarser than those in SH1.6 and SH5.6, indicating that the solution heat treatment temperature was too high or the holding time too long for the SH3.2 and SH4.0 tubes from different sources.

2.3.1 Area Fraction (M) and Equivalent Width (W) of Grain Boundary M23C6 Figure 3 [Figure 3: see original paper] shows SEM-SE images of HR3C superheater tube samples. The grain boundary carbides exhibit varied morphologies (granular and lamellar), thicknesses, and distributions (discontinuous and continuous). EPMA+EDS+MPST analysis confirmed these carbides as M23C6.

Since the morphology and dimensions of grain boundary M23C6 vary among different tube samples and even within different fields of view of the same sample, a unified measurement approach was established through the concept of equivalent width (W) of grain boundary M23C6 plates. The product of W and the total grain boundary length in the observed field (Lgb), expressed as WLgb = AM (where AM is the area of grain boundary M23C6 plates), divided by the observed field area (Ameas), gives the area fraction of grain boundary M23C6 plates:

M = AM/Ameas = LgbW/Ameas

where both AM and Ameas can be directly measured. Furthermore, based on ASTM E112 standard grain size charts, the total grain boundary perimeter (Lgb) corresponding to each austenite grain size level (GL) within a 5000 mm^2 area at 100× magnification was measured (Figure 4 [Figure 4: see original paper]), yielding the fitted relationship:

Lgb = -0.27 + 0.35 × GL

with a goodness-of-fit $R^2 = 0.99$. This allows determination of the austenite grain size level from grain boundary perimeter measurements, showing excellent agreement with GM values obtained from ASTM E112 grain size rating methods (Figure 5 [Figure 5: see original paper]).

Thus, W can be expressed as a function of GL and M, i.e., W(GL, M), and Equation (1) can be rewritten as:

$$W = \ M \times \mathrm{Ameas}/\mathrm{Lgb}$$

It should be noted that GL in Equation (2) is determined by solution heat treatment temperature and time (all tubes were in solution-treated condition), while M depends on service conditions (which can be considered as temperature T, stress σ, and time t acting on the tubes).

Figure 6 [Figure 6: see original paper] illustrates the relationship between W, GL, and M. At constant M, smaller GL (coarser grains) yields larger W; at constant GL, larger M also yields larger W. Compared with samples SH1.6 and SH5.6, samples SH3.2 and SH4.0 have smaller GL values corresponding to larger W.

In the context of this study, sample SH4.0 has the highest grain boundary M (directly related to service conditions), while SH3.2 has the lowest. This is because M is a function of T, σ, and t (SH4.0 and SH3.2 tubes have identical service conditions and dimensions, but SH4.0 has higher carbon content and longer service time, resulting in larger M at grain boundaries). However, the W of grain boundary M23C6 plates in SH4.0 is slightly smaller than in SH3.2 because W also relates to Lgb (GL) (Equation (3)). Clearly, both the original solution treatment parameters (determining austenite grain size) and service conditions (T, σ, t) collectively determine these differences among tube samples.

Although SH1.6 experienced the highest service temperature and pressure, it had fine austenite grains (large Lgb), thicker wall, and shortest service time. Sample SH5.6, despite long service time, had fine austenite grains (large Lgb) and the lowest service temperature. Consequently, both tubes exhibited small W values. In contrast, SH3.2 and SH4.0 had coarse austenite grains (small Lgb) and relatively high service temperatures, resulting in large W values, with SH3.2 showing even larger W than SH4.0 due to its smaller grain size (coarser grains, smaller Lgb).

2.3.2 Relationship Between Equivalent Width (W) of Grain Boundary M23C6 Plates and Impact Value (aKV) The embrittlement of service-exposed tubes (i.e., significant reduction in impact properties) should relate to both original and service-exposed microstructures, meaning the heat treatment condition of as-received tubes and actual operating conditions (the original and current conditions causing impact value changes). Therefore, the impact value (aKV) can be characterized as a function of GL, T, σ, and t (aKV(GL, T, σ, t)), where GL is determined by solution heat treatment temperature and time, while T, σ, and t depend on operating conditions. Since operating conditions determine M (a function of T, σ, and t), aKV can be expressed as aKV(GL, M). This approach simplifies the complex operating conditions (T, σ, t) into a single variable contribution.

Thus, based on Equations (2) and (3), aKV can be expressed as aKV(W). The histogram in Figure 7a [Figure 7: see original paper] shows that larger W corresponds to smaller aKV. Samples SH3.2 and SH4.0, with larger W values, exhibit significantly lower aKV than SH1.6 and SH5.6. Using the average impact value of as-received HR3C tubes reported in literature (with no M23C6 at grain boundaries, i.e., W = 0) combined with the aKV (J/cm^2) and W (mm) data from the actual service-exposed tubes in this work, the fitted relationship shown in Figure 7b [Figure 7: see original paper] was obtained:

$$\text{aKV} = 1/(0.004 + 0.042\text{W} + 0.612\text{W}^2)$$

with a goodness-of-fit $R^2 = 0.99$. This result is physically reasonable and can be used to quantitatively assess the reduction in impact values of service-exposed HR3C steel tubes.

2.3.3 Elastic Modulus of Grain Boundary M23C6 Figures 8a and 8b [Figure 8: see original paper] show the Er distribution and average values of grain boundary M23C6 in HR3C superheater tube samples (SH3.2 and SH4.0 are from the same boiler with several thousand hours difference in service time; SH3.2 was selected for Er measurement due to its lowest impact value). In Figure 8a, fs represents the normalized counting frequency of measurement points, i.e., the proportion of measurement points below a certain Er value. The Er distribution with respect to fs decreases in the order SH3.2 → SH5.6 → SH1.6, indicating that SH3.2 has the highest grain boundary Er, followed by SH5.6, with SH1.6 having the lowest. The average Er values in Figure 8b follow the same trend. Since higher Er values reflect greater brittleness/lower ductility (brittle materials have high Er while ductile materials have low Er), this further confirms that SH3.2 exhibits the greatest brittleness and SH1.6 the least, consistent with impact test results.

Conclusions

1. A method for determining austenite grain size (GL) from two-dimensional grain boundary perimeter (Lgb) was proposed: Lgb = -0.27 + 0.35GL ($R^2 = 0.99$, applicable within a 5000 mm^2 observation area at 100× magnification, with Lgb in 10^4 mm and grain size levels 3-8). This method shows excellent agreement with the mean grain size numbers (GM) obtained from various ASTM E112 rating methods. The concept of equivalent width (W) of grain boundary M23C6 plates was introduced, expressed as W = M × Ameas/Lgb, where M = LgbW/Ameas is the area fraction of grain boundary M23C6 plates and Ameas is the field area.
2. At constant M, smaller GL (coarser austenite grains) yields larger W; at constant GL, larger M also yields larger W. GL is determined by solution heat treatment parameters, while M depends on service conditions.

3. All service-exposed HR3C superheater tube samples in this study failed by intergranular fracture. The relationship between impact value aKV and W follows: $aKV = 1/(0.004 + 0.042W + 0.612W^2)$ with $R^2 = 0.99$. Compared with SH1.6 and SH5.6, samples SH3.2 and SH4.0 with smaller GL values exhibited larger W and lower aKV, with SH3.2 showing the lowest impact value directly related to its smallest GL and larger W. Additionally, the high elastic modulus (Er) of grain boundary M23C6 in SH3.2 indicates greater embrittlement. Therefore, coarse austenite grains and thick grain boundary M23C6 plates are the fundamental causes of embrittlement in service-exposed HR3C steel superheater tubes.

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