Early Precipitation Behavior of Cu-rich Phase in 18Cr9Ni3CuNbN Austenitic Heat-Resistant Steel (Postprint)

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Abstract

Three-dimensional atom probe microscopy was employed to investigate the early precipitation behavior of the strengthening phase, namely the Cu-rich phase, in 18Cr9Ni3CuNbN austenitic heat-resistant steel for superheaters/reheaters of 600°C ultra-supercritical power plant boilers, and the C-curve for the Cu-rich phase in 18Cr-9Ni type austenitic heat-resistant steel was established. The results demonstrate that during high-temperature aging, the Cu-rich phase can precipitate rapidly at both 650°C and 700°C. The formation process entails the initial formation of Cu-rich clusters within a short period; with increasing aging time, Cu atoms continue to diffuse into these Cu-rich clusters, while other atoms such as Fe, Cr, Ni, etc., are expelled from the Cu-rich clusters and diffuse into the austenite matrix, eventually forming the Cu-rich phase.

Full Text

Precipitation Behavior of Cu-rich Phase in 18Cr9Ni3CuNbN Austenitic Heat-Resistant Steel at Early Aging Stage

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ABSTRACT

The precipitation behavior of the strengthening Cu-rich phase at the early aging stage in 18Cr9Ni3CuNbN austenitic heat-resistant steel—commonly used for superheater and reheater tubes in 600°C ultra-supercritical (USC) power plants—

has been investigated using three-dimensional atom probe (3DAP) microscopy. The C-curve for Cu-rich phase precipitation in 18Cr-9Ni type austenitic heat-resistant steel has been established. Experimental results demonstrate that Cu-rich phase precipitates rapidly during long-term aging at both 650°C and 700°C. The formation process involves rapid formation of Cu-rich segregation clusters, followed by continued diffusion of Cu atoms from the austenite matrix into these clusters while Fe, Cr, and Ni atoms are expelled outward into the matrix, ultimately forming the Cu-rich phase.

KEY WORDS
metallic materials, austenitic heat-resistant steel, 18Cr9Ni3CuNbN, 3DAP, Cu-rich phase, C-curve

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Introduction

With rapid economic development, electricity demand continues to increase. Simultaneously, growing environmental awareness requires coal-fired power plants to further improve thermal efficiency and reduce emissions. Developing ultra-supercritical (USC) power plants represents one of the most effective current measures to address these challenges. To meet material requirements for USC boiler applications, various modified ferritic and novel austenitic heat-resistant steels have been successively developed. Super304H (18Cr9Ni3CuNbN) is now widely used for high-temperature, high-pressure components such as superheater and reheater tubes in 600°C USC power plants.

18Cr9Ni3CuNbN steel is a typical 18Cr-9Ni type austenitic heat-resistant steel developed from ASME SA-213 TP304H by reducing the upper Mn content limit and adding approximately 3 wt% Cu. During long-term service, nano-sized Cu-rich phases gradually precipitate. Additionally, 0.45 wt% Nb and controlled N additions promote precipitation of complex carbonitrides, which together with M23C6 carbides at grain boundaries produce excellent strengthening effects. The high-temperature creep rupture strength of 18Cr9Ni3CuNbN steel exceeds 100 MPa at 650°C and 10^5 hours, enabling its widespread application in superheaters and reheaters.

Previous studies have investigated the hot working processes and microstructural evolution of 18Cr9Ni3CuNbN steel during long-term high-temperature aging, confirming that Cu-rich phases, MX phases, and M23C6 carbides provide effective strengthening. However, detailed reports on the early precipitation behavior of the strengthening Cu-rich phase remain limited. Sumitomo has published temperature-time curves for precipitates in 18Cr9Ni3CuNbN steel, suggesting that Cu-rich phases, M23C6 carbides, and MX phases precipitate sequentially during long-term aging, with MX phases potentially transforming to NbCrN at longer times. Nevertheless, the Cu-rich phase precipitation curve remains dashed (unconfirmed), and early precipitation behavior has not been explicitly reported. Since early precipitation behavior significantly influences subsequent precipitation, growth, and coarsening, in-depth investigation is necessary. This study employs three-dimensional atom probe microscopy to investigate the early precipitation behavior of Cu-rich phases in 18Cr9Ni3CuNbN steel during high-temperature aging.

Experimental Methods

The experimental material was 18Cr9Ni3CuNbN austenitic heat-resistant steel with the chemical composition listed in . To isolate the precipitation behavior of Cu-rich phases in 18Cr-9Ni type steel, a simplified alloy (designated S steel) was designed containing only Cu additions—i.e., 3 wt% Cu without Nb or N. The composition of S steel is also listed in . This design ensures that only Cu-rich phases precipitate within grains during short-term high-temperature aging, facilitating investigation of early precipitation characteristics.

Considering that 18Cr9Ni3CuNbN steel serves in superheater/reheater components at approximately 650°C, C-curve determination temperatures were designed from 550°C to 700°C at 50°C intervals, with aging times ranging from 0.5 to 5 hours. Since Cu-rich phases are nanoscale during early precipitation stages and difficult to capture with other techniques, 3DAP microscopy was employed to observe fine Cu-rich particles and obtain their chemical composition evolution. Based on 3DAP results, the C-curve for the nano-strengthening Cu-rich phase was constructed and the early precipitation behavior was analyzed.

Results and Discussion

2.1 C-Curve of Cu-Rich Phase

[Figure 1: see original paper] presents the C-curve for nano-sized Cu-rich phase precipitation in S steel, where black squares indicate Cu-rich phase precipitation and white squares indicate absence of precipitation. At 700°C, Cu-rich phases precipitated after only 0.5 hours, while at 650°C, precipitation required 1 hour. At lower temperatures (600°C), no precipitation occurred at 0.5 or 1 hour, appearing only after 3 hours. At 550°C, no precipitation was observed even after 3 hours. This indicates rapid precipitation at high temperature (700°C), while at lower temperatures, short-term aging yields no precipitation though it may occur at longer times, as thermodynamic equilibrium diagrams confirm Cu-rich phase existence below 600°C. Given the actual service temperature near 650°C, this study focuses on comparing early precipitation characteristics at 650°C and 700°C.

2.2 Early Precipitation Behavior at 650°C

[Figure 2: see original paper] shows 3DAP results of Cu-rich phases in S steel after aging at 650°C, where each point represents a Cu atom and interfaces denote boundaries at 8% Cu concentration. After 1 hour at 650°C, extremely fine Cu-rich particles formed. When aging time increased to 5 hours, particle size and density increased significantly.

[Figure 3: see original paper] presents detailed 3DAP results of individual Cu-rich particles after aging at 650°C for 1 hour and 5 hours. After 1 hour, Cu atoms showed segregation but formed only small Cu-rich clusters. After 5 hours, the particles contained substantially more Cu atoms, grew to approximately 5 nm, and clearly formed Cu-rich phases.

[Figure 4: see original paper] shows concentration profiles of Cu, Fe, Cr, and Ni in the matrix and Cu-rich particles after aging at 650°C. After 1 hour, Cu concentration in the particles was approximately 40%, indicating only Cu-rich segregation zones. After 5 hours, Cu concentration exceeded 60% while Fe concentration was significantly lower than in the matrix, confirming formation of Cu-rich phases. The average radius was approximately 3 nm after 1 hour and increased with longer aging time.

2.3 Early Precipitation Behavior at 700°C

[Figure 5: see original paper] shows 3DAP results of Cu-rich phases after aging at 700°C for 1 hour and 5 hours. After just 1 hour, Cu-rich particles formed, and after 5 hours, they grew substantially with markedly increased density.

[Figure 6: see original paper] presents detailed 3DAP results of a Cu-rich particle after 700°C/1 hour aging. Cu atoms showed clear segregation, forming distinct Cu-rich phases approximately 5-6 nm in size. Compared with 650°C/1 hour results, the 700°C/1 hour particles contained significantly more Cu atoms and formed well-defined Cu-rich phases rather than mere segregation zones.

[Figure 7: see original paper] shows concentration profiles after 700°C/1 hour aging. Cu concentration exceeded 90% while Fe concentration dropped below 10%, substantially lower than matrix Fe content. This Cu concentration is far higher than that at 650°C/1 hour, confirming Cu-rich phase formation.

[Figure 8: see original paper] illustrates the average radius evolution of Cu-rich particles during short-term aging. At 650°C, the average radius was approximately 1 nm after 1 hour and grew to about 2 nm after 5 hours. At 700°C, the radius was larger at equivalent times, indicating accelerated precipitation kinetics.

The formation process of Cu-rich phases involves both crystal structure and chemical composition changes. For 18Cr9Ni3CuNbN steel, the austenite matrix has an FCC structure with lattice parameter 0.35698 nm, while pure Cu also has an FCC structure with lattice parameter 0.36153 nm. The precipitated Cu-rich phase, containing high Cu concentrations and remaining coherent with the austenite matrix, exhibits no crystal structure transformation during formation. Initially, Cu-rich clusters form; subsequently, Fe, Ni, and Cr atoms are expelled while Cu atoms continue enriching the clusters, ultimately forming Cu-rich phases. Based on composition fluctuations, this study defines Cu-rich phase formation when Cu concentration exceeds 50%; below this threshold, only Cu-rich segregation zones exist. At 650°C, only segregation zones formed after 1 hour, while Cu-rich phases appeared after 5 hours. At 700°C, Cu-rich phases formed within just 1 hour.

In summary, Cu-rich phases precipitate rapidly in 18Cr-9Ni type austenitic heat-resistant steel at both 650°C and 700°C, with slow subsequent growth. Even after 10,000 hours at 650°C, particle sizes remain in the tens of nanometers, maintaining coherency with the matrix and demonstrating excellent thermal stability and strengthening effectiveness. This suggests potential for application in other heat-resistant steels to improve high-temperature strength.

Conclusions

1. In 18Cr-9Ni type austenitic heat-resistant steel, the strengthening Cu-rich phase precipitates rapidly within extremely short aging times at both 650°C and 700°C.
2. The formation process during high-temperature aging involves: initial Cu atom enrichment creating Cu-rich segregation zones; with extended aging, continued Cu diffusion into these zones while Fe, Cr, and Ni atoms are expelled into the austenite matrix, ultimately forming Cu-rich phases.
3. The Cu-rich phases precipitated during short-term aging at 650°C and 700°C are extremely fine, with sizes of only a few nanometers. Particles formed at 700°C are slightly larger than those at 650°C under equivalent aging times.

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