Microstructural evolution of Super304H stainless steel during high-temperature creep rupture

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Abstract. This study is aimed to explore the microstructural evolution of Super304H stainless steel during long-term creep. Creep-rupture specimens of this steel are analyzed via microhardness measurement, metallographic structure observation, X-ray diffraction, transmission electron microscopy, scanning electron microscopy, and energy-dispersive spectroscopy. The results show that the matrix structure of the steel was stable during high-temperature stress-rupture test without grain growth. Twin boundaries in austenite gradually disappeared with the prolongation of time, which process was accelerated at higher temperatures. The steel hardness sharply increased in the initial stage of high-temperature stress-rupture test due to the second-phase precipitation, and then gradually dropped with time, due to the coarsening of precipitates. The Cu-rich phase and secondary Nb(C,N) with the size less than 50 nm, and $\text{M}_2\text{C}_6$ were the main precipitated phases in the high-temperature stress-rupture test. This allowed the steel under study to retain a high stress-rupture limit due to the precipitation-strengthening effect. The microstructure aging resulted in the formation of $\text{M}_2\text{C}_6$ chain at the grain boundary and coarsening of $\text{M}_2\text{C}_6$ and primary Nb(C,N) in grains. With the coarsening of precipitated phases, hardness and stress-rupture limit of Super304H stainless steel decreased.

1. Introduction

Super304H stainless steel is one of the most economical 18-8-type austenitic stainless steel developed on the basis of the chemical composition of TP304H steel. Moreover, it is widely used as superheater and re heater for supercritical (ultra-supercritical) SC (USC) boiler because of its high-temperature strength and resistance to steam oxidation. The shortage of Super304H tubes became a bottleneck because of increasing worldwide demand to build supercritical (ultra-supercritical) boilers. Since 2003, special steel companies, research institutes, and boiler manufacturers in China are working together toward the localization of Super304H tubes. The Baosteel subsidiary company and a stainless steel company in Taiyuan successively produced Super304H ingot in 2004. Then, some stainless steel manufacturing companies started producing Super304H stainless steel tubes, gradually achieving the production of Super304H stainless steel tubes at home [1].

The first domestic Super304H stainless steel tubes were used as superheaters and re heaters for $2 \times 660$ MW USC boiler in No.3 of one domestic power plant. A few studies reported on the microstructure aging law and the statutes of service for domestic Super304H stainless steel under long-term high-temperature and stress conditions.

In this study, creep rupture specimens of domestic Super304H stainless steel were analyzed to understand the microstructure aging law, which has theoretical meaning and application for ensuring...
China-made ultra-supercritical boiler security and finally spreading the use of the domestic Super304H stainless steel tubes.

2. Experimental setup

The investigated Super304H stainless steel tube of the size of $\Phi 47.6 \times 8.0$ mm was provided by Huzhou steel tube manufacturer in China. After solution treatment at $1150^\circ C \pm 15^\circ C$, it was directly quenched into water. Its chemical composition is given in table 1.

|   | C     | S     | N     | P     | Si    | Cr    | Mn    |
|---|-------|-------|-------|-------|-------|-------|-------|
| 0.095 | 0.0013 | 0.11  | 0.024 | 0.24  | 18.03 | 0.68  |
| Ni  | Mo    | Cu    | V     | Al    | Nb    | B     |
| 9.00 | 0.23  | 2.75  | 0.034 | 0.017 | 0.44  | 0.0028 |

The creep rupture specimens were machined from Super304H steel tube as shown in figure 1. Creep tests were carried out at 600, 650, and $700^\circ C$ from 1 to 13,000 h. As-supplied and as-creep specimens were studied using different technologies. The hardness of all the specimens was measured using FM-800 digital microhardness tester (made by Shanghai Hengyi Company) at a load of 200 g at room temperature. The phase analysis of the specimens was carried out on the D/max2500PC x-ray diffractometer. The microstructure of as-supplied and as-creep specimens was examined using Olympus GX71 optical microscope (OM), FEI Quanta400 scanning electronic microscope, and JEM-200CX transmission electron microscope (TEM). The chemical composition of the precipitates was determined by energy-dispersive X-ray spectroscopy.

![Figure 1. Creep rupture specimens of Super304H steel tube.](image)

3. Results and discussion

3.1. Microhardness

The microhardness test result of as-supplied specimen compared with the standards is shown in table 2. The test had four test points, numbered 1–4. The average value of microhardness was found to be about 180 HV.

| Number | Microhardness (HV) | Average value |
|--------|--------------------|---------------|
| Microhardness (HV) | 180 | 175 | 184 | 181 | 180 |
| ASME SA-213/GB 5310-2008 | ≤230 HV |
Figure 2. Variation in microhardness with rupture time at different temperatures.

Figure 2 shows the variation in microhardness of domestic Super304H steel during the creep rupture test. In the initial creep stage (<100 h), the microhardness increased rapidly. Then, it decreased gradually in relation to the second-phase particle precipitation behavior [2]. During the creep rupture test, the atomic activity enhanced and a large number of second-phase particles precipitated from the supersaturated solid because of the action of high temperature and stress. These fine coherent second-phase particles caused effective precipitation strengthening in the initial formation stage [2]. Moreover, the microhardness reached the peak when the second-phase had semi-coherent relation with the matrix. With further prolongation of creep time, the microhardness decreased as the coarse precipitated phase destroyed the coherent relation with the matrix. The microhardness also decreased slowly with the increase in the creep temperature due to the decline in dislocation density and coarsening of the precipitated phase that weakened the effectiveness of precipitation strengthening in the matrix.

The microhardness of as-creep specimens was found to be much higher than that of the as-supplied specimen related to the effectiveness of precipitation strengthening. Although the hardness decreased with the increase in creep time, it steadily remained at a high value after a creep of more than 10,000 h.

3.2. Optical micrograph observation

Figure 3 shows the optical micrograph of domestic Super304H steel. The microstructure of as-supplied specimen was typical austenite. A lot of twin boundaries and some precipitation could be observed. Some twin boundaries are marked with black arrows in figure 3. The average grain size was about 8-9 grade of GB/T 6394-2017.

Figure 3. Optical micrographs of domestic Super304H steel at supply state.
An as-creep specimen had only minor precipitation when the creep time was less than 1000 h at 600°C as shown in figure 4(a). With an increase in the creep time, clearly more precipitation in the matrix was observed as shown in figures 4(b)-4(d), referring to figures 5(a)-5(c). The creep rupture specimens were found to have a clear grain boundary with a large amount of precipitation distribution both in grain and at grain boundaries after 13,198.3 h. The average grain size was about 8-9 grade after a creep of 13,198.3 h.

![Figure 4. Optical micrographs of domestic Super304H steel creep at 600°C at different times: (a) 19.8 h, (b) 1064.8 h, (c) 3172.5 h, and (d) 13,198.3 h.](image1)

![Figure 5. Scanning electron microscopy micrographs of domestic Super304H steel creep at 600°C at different times: (a) 19.8 h, (b) 3172.5 h, and (c) 13,198.3 h.](image2)

Figures 6(a)-6(d) shows that the number of precipitated phases obviously increased after 1200 h at 650°C. The twins disappeared gradually and a large amount of coarse precipitates segregated at the grain boundary after 14,364.1 h. figures 7(a)-7(d) shows that the number of precipitated phases increased significantly at 700°C. Then, after 12,708.9 h, the twin boundaries completely disappeared, and the grain boundary became obscure with the coarsening of the precipitated phase, resulting in a chain-like distribution at the grain boundary. However, the number of precipitated phases decreased
significantly in the grain.

![Optical micrographs of domestic Super304H steel creep at 650°C at different times: (a) 20.7 h, (b) 1287 h, (c) 2950 h, and (d) 14,364.1 h.](image)

**Figure 6.** Optical micrographs of domestic Super304H steel creep at 650°C at different times: (a) 20.7 h, (b) 1287 h, (c) 2950 h, and (d) 14,364.1 h.

![Optical micrographs of domestic Super304H steel creep at 700°C at different times: (a) 20.1 h, (b) 1277.7 h, (c) 3289.9 h, and (d) 12,708.9 h.](image)

**Figure 7.** Optical micrographs of domestic Super304H steel creep at 700°C at different times: (a) 20.1 h, (b) 1277.7 h, (c) 3289.9 h, and (d) 12,708.9 h.

During the creep rupture of domestic Super304H steel, the amount of precipitation increased with prolongation of time but the grain had no obvious growth. With an increase in the creep temperature,
the disappearance of twins was accelerated. This promoted the coarsening of the precipitated phase. Moreover, the amount of the precipitated phases declined. At a creep temperature of less than 650°C, the matrix structure of domestic Super304H stainless steel was stable without grain growth, while the precipitated phase grew slightly. After the long-term lasting beyond 700°C, the microstructure age resulted in the coarsening of the precipitated phase and chain-like arrays at the grain boundary [3].

3.3. X-ray diffraction analysis
Figure 8 shows the x-ray diffraction (XRD) patterns of the as-supplied specimen. The as-supplied specimen was mainly composed of the γ-matrix and the Nb(C,N) phase. The XRD patterns of as-creep specimens at 600°C, 650°C, and 700°C, respectively, are shown in figures 9-11. At different temperatures, the main precipitation phases were γ-matrix and Nb(C,N) for specimens’ creep time of about 20 h (in the short term). The figure shows that the precipitation-phase composition of specimens in the short-term creep was consistent with that of the as-supplied specimen. The difference in the precipitation phase composition during creep was noticed between short-term creep and long-term creep (>10,000 h). This could be due to the precipitation of M23C6.

3.4. TEM analysis
As shown in figure 12, granular particles were observed along the austenite boundaries or in the grain in as-creep specimens after long-term creep at different creep temperatures. The electron diffraction pattern analysis proved that they belonged to M23C6. The TEM analysis indicated that the chain-link
precipitates were granular $M_23C_6$ in the form of the chains. The size of $M_23C_6$ particle ranged from 80 to 250 nm, increasing with the increase in the creep temperature. Figure 13 shows that Nb(C,N) precipitates were formed inside the grains. The secondary Nb(C,N) was fine, and the size range was from 30 to 50 nm. With the increase in creep temperature, more and more Nb(C,N) precipitated, but they were very stable during the creep time. Figure 14 shows the distribution of nano-sized particles in as-creep specimens during the long-term creep at different creep temperatures. Determined by the energy dispersive spectrum analysis EDS as shown in figure 14(d), nano-sized particles had a high Cu content. This confirmed that these nano-sized precipitates were the Cu-rich phase. The average size of the particles ranged from 10 to 30 nm. It was stable and increased slightly during the creep process. The microstructure analysis by TEM showed that the Cu-rich phase and secondary Nb(C,N) precipitates distributed uniformly with high density in grains were the main strengthening phase that caused the strong hardening effect.

Figure 12. TEM micrographs of $M_23C_6$ in domestic Super304H steel after long-term creep: (a) at grain boundary of 600°C /13,198.3 h sample; (b) in the grain of 600°C /13,198.3 h sample; (c) at grain boundary of 650°C /14,364.1 h sample; (d) in the grain of 650°C /14,364.1 h sample; (e) at grain boundary of 700°C /12,708.9 h sample; (f) in the grain of 700°C /12,708.9 h sample; and (g) diffraction pattern for $M_23C_6$.

Figure 13. TEM micrographs of Nb(C,N) in domestic Super304H steel after long-term creep: (a) 600°C/13,198.3 h; (b) 650°C/14,364.1 h; (c) 700°C/12,708.9 h; and (d) diffraction pattern of Nb(C,N).
Figure 14. TEM micrographs of ε-Cu in domestic Super304H steel after long-term creep: (a) 600°C/13,198.3 h; (b) 650°C/14,364.1 h; (c) 700°C/12,708.9 h; and (d) EDS spectrum of the Cu-rich phase.

3.5. Scanning electron microscopy analysis
Scanning electron microscopy (SEM) micrograph and EDS of specimens after long-term creep at different creep temperatures are shown in figure 15. Figure 15(a) is the SEM micrograph of the as-supplied specimen. The microstructure of the sample was characterized by an equiaxed austenite with a few coarse particles randomly distributed in grains or partially at grain boundaries. Also, some small particles were distributed in grains and at grain boundaries. The EDS indicated that these particles consisted of NbC and primary Nb(C,N). These randomly distributed coarse particles belonged to the Nb-rich MX-type inclusions directly formed during solidification [4]. However, the scattered small particles were primary Nb(C,N).

Figure 15. SEM micrographs and EDS spectra of domestic Super304H steel after long-term creep: (a) supply state, (b) 600°C/13,198.3 h, (c) 650°C/14,364.1 h, (d) 700°C/12,708.9 h, (e) EDS spectra of the white blocks in part a, and (f) EDS spectra of precipitates.

The existence of these Nb-rich MX coarse particles damaged the matrix continuum because of incomplete dissolution in the matrix due to low softening temperatures or inadequate holding time during the tube manufacturing process. In the deformation process, the original crack was formed between these coarse particles and the matrix. However, it had few coarse NbC particles randomly distributed in the imported Super304H stainless steel. Therefore, as a matter of fact, it was necessary
to control the manufacturing process to reduce the content of coarse NbC particles in domestic Super304H steel.

Figures 15(b)-15(d) shows that M23C6 carbide mainly precipitated at grain boundaries, and primary Nb(C,N) and few M23C6 precipitated within the grain after long-term creep. The secondary Nb(C,N) phase and Cu-rich phase particles were too tiny to be detected by SEM as the size of these particles was less than 50 nm.

The as-creep specimens of domestic Super304H stainless steel with the increase in the creep temperature resulted in coarse precipitates and a decrease in the number of precipitates. The key features of domestic Super304H stainless steel microstructure after long-term aging were the accumulation and arraying of M23C6 in the form of chains at grain boundaries, in addition to the coarse M23C6 and primary Nb(C,N) particles in grains.

The sizes of precipitates in domestic Super304H steel creep at different creep temperatures are summarized in Table 3. The table clearly shows that the size of the primary Nb(C,N) particles that grew slightly was in the range of 300-500 nm during the creep process at 600°C. After long-term creep at 650°C, the average diameter of primary Nb(C,N) particles increased quickly from 500 nm to 1 μm, and the M23C6 particles coarsened obviously in the course of the creep process. However, M23C6 particles coarsened significantly under the creep condition at 700°C for long-term creep. The size of M23C6 particles was in the range of 600 nm to 1 μm.

### Table 3. Size of precipitates in domestic Super304H steel creep at different temperatures.

| Precipitate | Size of precipitate |
|-------------|---------------------|
|             | 600°C | 650°C | 700°C |
| Primary Nb(C,N) | 300–500 nm | 1 μm | 1 μm |
| M23C6       | ≤200 nm | 200–600 nm | 600 nm–1 μm |

### 4. Discussion

#### 4.1. Mechanical properties during the creep process

The hardness of domestic Super304H steel rapidly changed from 180 HV of the as-supplied specimen to 300 HV in the initial stage of high-temperature stress-rupture test due to the second-phase precipitation. Moreover, it was found that the higher the creep temperature, the shorter the processing time.

The microstructure of domestic Super304H stainless steel specimens analyzed by XRD analysis, TEM, SEM, and energy spectrum analysis showed that the Cu-rich phase, secondary Nb(C,N), and M23C6 were the main precipitated phases during the high-temperature stress-rupture test. These precipitates maintained higher hardness and strength compared with the as-supplied specimen due to their precipitation-strengthening effect.

However, the hardness and strength were subject to a slight decrease caused by the decline in the strengthening effect of the solution or the effectiveness of precipitation strengthening, in addition to the drop in the dislocation density with the increase in the creep time. The decline in the strengthening effect of the solution was due to the migration of alloy elements. Besides, the decline in the effectiveness of precipitation strengthening was due to the coarsening of the secondary-phase particles. Moreover, the higher the creep temperature, the lower the hardness and strength. Compared with the as-supplied specimen, the hardness of as-creep specimens was maintained at a high value after a creep of more than 10,000 h.

#### 4.2. Microstructure evolution during the creep process

The matrix structure of domestic Super304H stainless steel was stable austenite with high-dislocation density during the high-temperature stress-rupture test without grain growth. The average grain size was about 8-9 grade after a creep of 13,000 h. Twins in austenite gradually disappeared with the
prolongation of time, and the disappearance was faster with increasing temperature. The amount and the size of precipitates also increased with the prolongation of time. Rather, the amount of precipitates comparatively slowly increased with the increase in creep temperature. After the long-term creep, a lot of coarse precipitates arrayed in the form of a chain at the austenite grain boundary, leading to the aging of microstructure.

The particle distribution in the as-supplied specimen consisted of coarse NbC and small primary Nb(C,N). The size of these coarse particles was more than 1 μm. They were randomly distributed and belonged to the Nb-rich MX-type inclusions directly formed during solidification. The existence of these coarse particles violated the matrix continuum because of incomplete dissolution in the matrix during the tube manufacturing process. Therefore, as a matter of fact, it was important to reduce the content of coarse NbC particles in domestic Super304H steel by controlling the manufacturing process.

During the creep of domestic Super304H steel, the predominant precipitates were M$_{23}$C$_6$ carbide, Cu-rich phase, and secondary Nb(C,N) phase. A large amount of Cu-rich phase and secondary Nb(C,N) phase distributed dispersively in the austenite matrix and tended to grow slightly. The size of the Cu-rich phase ranged from 10 to 30 nm, and the size of secondary Nb(C,N) phase ranged from 30 to 50 nm after the long-term creep. The Cu-rich phase and secondary Nb(C,N) precipitates distributed uniformly with high density in the matrix formed the main strengthening phase, which caused strong hardening effect. The Cu-rich phase played the most important role in the strong hardening effect.

The size of M$_{23}$C$_6$ precipitates increased with the prolongation of creep time. Besides, it increased faster with the increase in the creep temperature. The coarse M$_{23}$C$_6$ distributed at grain boundaries in the form of a chain wrecked the continuity of the grain boundary and formed the crack and cavities at the grain boundaries, leading to a decline in the creep strength and plasticity of domestic Super304H steel.

Primary Nb(C,N) particles grew gradually in the as-supplied specimen. With the increase in creep time, the dispersion strengthening contributed by primary Nb(C,N) phase weakened. The decline in hardness and strength of the matrix mainly resulted from the weakening of the dispersion strengthening due to the coarsening of M$_{23}$C$_6$ and primary Nb(C,N) phase.

The key features of the domestic Super304H microstructure after long-term aging were accumulation and arraying of M$_{23}$C$_6$ in the form of a chain at grain boundaries, besides the coarse M$_{23}$C$_6$ and primary Nb(C,N) particles in the grain.

5. Conclusions
The microstructural evolution and variation of mechanical properties of Super304H stainless steel under high-temperature and long-term creep conditions can be summarized as follows:

- During the creep process of Super304H stainless steel, the matrix structure was stable austenite with high dislocation density without grain growth. The average grain size was about 8–9 grade. Twins in austenite gradually disappeared with the prolongation of time, and the disappearance was faster with increasing temperature.

- The hardness of Super304H stainless steel rapidly increased in the initial stage and then decreased gradually with the prolongation of creep time, which was considered in relation to the secondary-phase precipitation, growth, and coarsening.

- The particles in the as-supplied specimen were coarse NbC and small primary Nb(C,N). During the creep process of Super304H stainless steel, the predominant precipitates were M$_{23}$C$_6$ carbide, Cu-rich phase, and secondary Nb(C,N) phase. The existence of coarse NbC particles violated the matrix continuum and reduced the strength as it did not completely dissolve in the matrix. Therefore, reducing the content of coarse NbC particles in the manufacturing process is beneficial.

- A large amount of Cu-rich phase and secondary Nb(C,N) phase was distributed in the austenite matrix and tended to grow slightly during the creep process. The size of these precipitates was less than 50 nm. The Cu-rich phase and secondary Nb(C,N) precipitates were
distributed uniformly with high density in the matrix, which formed the main strengthening phase causing the strong hardening effect. Moreover, the Cu-rich phase played the most important role in the strong hardening effect.

- The key features of domestic Super304H microstructure after long-term aging were the accumulation and arraying of M$_{23}$C$_6$ in the form of a chain at grain boundaries, in addition to the coarse M$_{23}$C$_6$ and primary Nb(C,N) particles within the grain. The coarse precipitates led to a decline in creep strength and plasticity.

The microstructure and mechanical properties of domestic Super304H stainless steel were remarkable when creep for 13,000 h at less than 650°C. Then, the grain boundaries were weakened after a creep at 700°C, which resulted from the accumulation of coarse precipitates. The increase in the working temperature accelerated the aging process. Therefore, it is essential to control the working temperature to less than 650°C to avoid component damage by overheating.

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