Microstructural Evolution for Super304H Austenite Steel used in China Plants

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Super304H (18Cr-9Ni-3Cu-Nb-N) austenite steel has high creep strength and has been used as the material of tubes in 600℃ class supercritical power plants in China. Many Super304H materials have run for more than 100,000 hours. Long-time service feature of these austenitic stainless steels has not been understood. An understanding of the long-term microstructural evolution under actually used conditions is a key for the improvement of these heat resistant steels. In this article, creep behavior of Super304H used in China plants was analyzed, microstructural evolution of Super304H materials after different service conditions were studied involving in optical microscope, TEM and SAXS. The results show, $M_{23}C_6$, Cu-rich particles, and σ phase were found to precipitate. A quantitative assessment of microstructure evolution was given during long-term creep.

Introduction

Up to now, the amount of supercritical boilers in China has ranked number one in the world. Many supercritical boilers have run for more than 100,000 hours. Heat-resistant austenitic stainless steel has been used in supercritical boiler materials because it has excellent oxidation and corrosion resistance, as well as mechanical stability at a high temperature. Super304H (18Cr-9Ni-3Cu-Nb-N) is an advanced austenitic stainless steel that is used as superheater and reheater tubes in 600°C class supercritical boilers. These tubes are operating in a high temperature and pressure environment and experience creep regime. The importance of microstructure evolution in influencing creep behaviour has been proposed [**1**]. Futhermore, previous research also has showed that the creep strength of Super304H decreased during long-term thermal exposure due to microstructural changes [**2**]. During high temperature service, microstructural evolution of Super304H austenite steel occurs such as precipitation of new secondary phases [**3,4**], growth of precipitates and dissolution of the coherent twins, which may affect mechanical properties, including creep strength [**5,6**]. An understanding of the long-term microstructural evolution under actual service conditions is a key for the improvement of these heat resistant steels.

However, there are very few studies on Super304H steel actually used in power plants. Most research focuses on creep tests in laboratory. Creep tests were conducted at stresses higher than those expected in service, the microstructure evolution does not have enough time to develop. In this article, microstructural evolution of Super304H steels under actual service conditions was studied. Quantitative microstructure characterization was given, focusing on particle size and phase content of precipitates in Super304H steel.

Experimental

Super304H steels were delivered by different power plants, the materials were subjected to various operation conditions. The operation temperature, and pressure and time conditions are shown in **Table 1**. The Super304H steel that has not been used is named as-received steel (Samples No. 1). Optical micrograph specimens were prepared to investigate the microstructure. The transmission electron microscopy (TEM) was performed to determine precipitates types. Physicochemical phase analysis was conducted to determine precipitates quantities and composition [**7,8**]. Small-angle X-ray scattering (SAXS) was performed to determine particle size of precipitates.

Table 1 Operational parameters of the Supper304H steels delivered by power plants.

Samples No.	Dimension	Operation time /10^4h	Temperature /°C	Pressure /MPa
1 (as-received)	Φ51×9	0	0	0
2	Φ51×9	0.49	605	26.15
3	Φ51×9	1	605	26.15
4	Φ48.3×10	3.8	605	27.46
5	Φ41.3×6	4.6	571	25.4

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Results and discussion

Microstructure

The as-received Super304H steel has a fully austenitic microstructure and coherent twins as shown in **Fig. 1(a)**. Fine and dispersed granular $M_{23}C_6$ and MX type carbides are present in the grains and at grain boundaries (**Fig. 1(a)**). The creep strength of Super304H steel combines some solid solution strengthening by Nb atoms as well as precipitation strengthening by $M_{23}C_6$ and MX phases. Alloying elements, such as C, N, Nb, Cr and Ni, promote the formation of precipitates like Cr-rich $M_{23}C_6$, and Nb-rich MX particles. The addition of Cu promotes the precipitation of fine Cu-rich phase [**9,10**]. The microstructure after thermal exposure for 46,000h at 571℃ and 25.4MPa are shown in **Fig. 1(b)**, the microstructure still retains austenitic morphology, however, new secondary phases precipitate at the grain boundaries, twin crystals have dispersed obviously, the number and size of precipitates increase on the grain boundaries. Large-sized precipitates were observed.

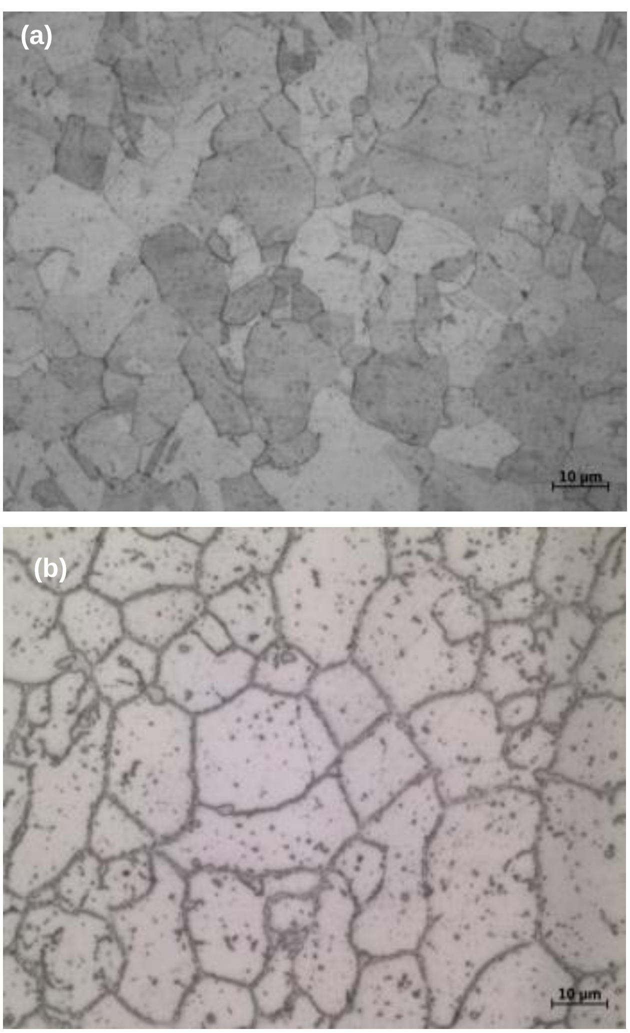

Fig. 1. Microstructure of Super304H steel, (a) as-received sample, (b) sample after thermal exposure for 46,000 h at 571℃ and 25.4MPa.

Transmission electron microscopy investigations

Fig. 2 shows the TEM micrographs of as-received Super304H steel. Microstructure of as-received Super304H shows that twin crystals in the grains (**Fig. 2(a)**), a high dislocation density is observed inside subgrains, and these dislocations are pinned by some fine and dispersed precipitates. $M_{23}C_6$ precipitates (M-Cr, Fe) were observed in austenite grains, see **Fig. 2(b)**. Fine NbC particles precipitated pinning dislocations **(Fig. 2(c))**. High alloy steels are strengthened by these mechanisms including solution hardening, precipitation or dispersion hardening, dislocation hardening, and boundary or sub-boundary hardening [**11**]. However, creep strength of Super304H comes predominantly from precipitation hardening.

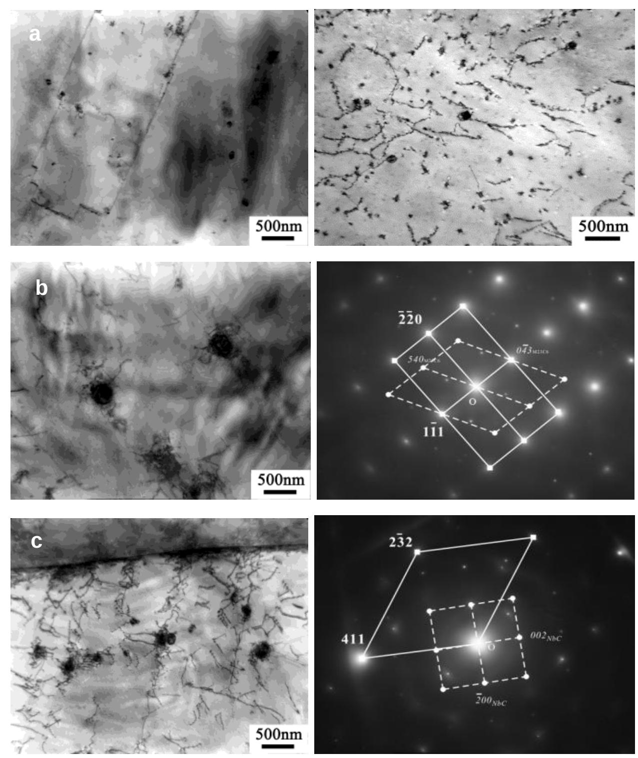

Fig. 2. Transmission electron micrographs of as-received Super304H steel (a) twin crystals and a high dislocation density, (b) $M_{23}C_6$ precipitates in the grains, (c) MX precipitates in dislocation.

TEM micrographs after thermal exposure for 38,000 h at 605℃ and 27.46MPa are shown in **Fig. 3**, which consist of $M_{23}C_6$ carbides, MX carbonitrides, Cu-rich precipitates. Boundaries between grains are mainly decorated with $M_{23}C_6$ carbides (**Fig. 3(a)**). The MX carbonitrides precipitated finely (**Fig. 3(b)**), MX precipitates are stable, nano-sized NbC precipitates were observed, and a reduced dislocation density is observed within subgrains compared with the as-received steel (Fig. 2a). After aging, Cu-rich phase precipitates dispersedly inside grains (**Fig. 3(c)**), the fine Cu-rich particles that precipitated inside the grains improved the strength of Super304H steel. In addition, Sigma phase was observed after long time operation

(**Fig. 3(d)**), the size is bigger than other precipitates. Sigma phase precipitation leads to the depletion of Cr in the matrix, causing property changes. Rich-Cr sigma phase formation could cause a loss of long-term creep strength. TEM micrographs of other thermal exposure samples are similar and are no longer given here.

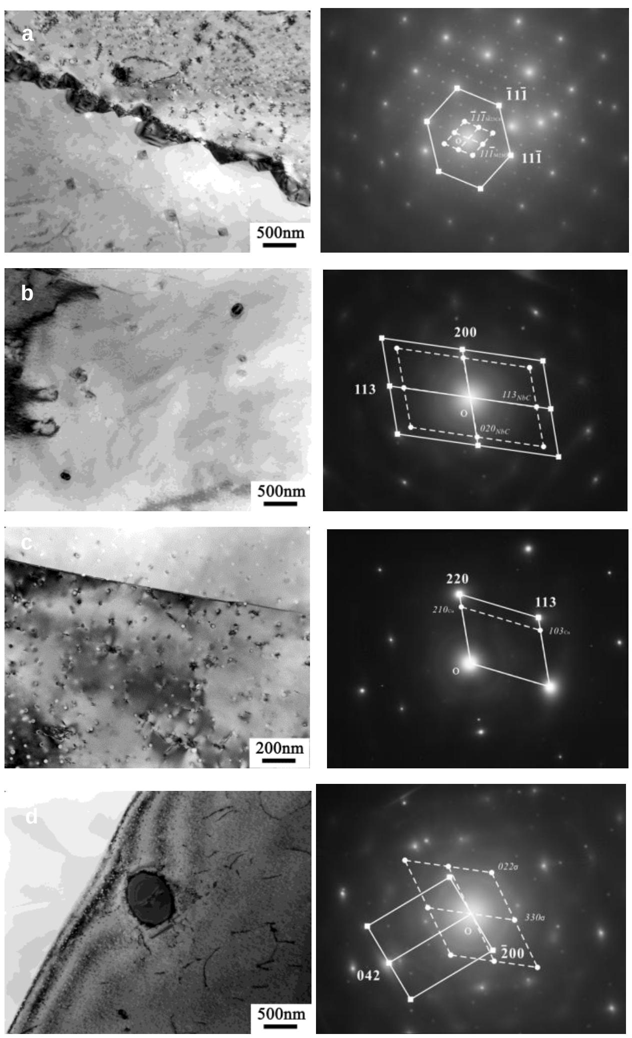

Fig. 3. Transmission electron micrographs of the Super304H steel after thermal exposure for 38,000 h at 605°C and 27.46MPa, (a) $M_{23}C_6$ precipitates at the grain boundaries, (b) MX precipitates in the grains, (c) Cu-rich phase precipitates, (d) σ phase precipitates.

Quantitative microstructural characterization

Content of precipitates in different thermal exposure samples was quantified, total amount of precipitates, the content change of $M_{23}C_6$, MX and sigma phase are shown in **Table 2**. The Cu-rich phase has not been detected due to the small size and content. The Cu-rich phase is very stable and keeps in nano-size after long time aging (**Fig. 3(c)).** Total amount of precipitated phase, $M_{23}C_6$, MX and sigma phases content increase with exposure times at the same temperatures, secondary phases precipitate continuously due to the diffusion at higher temperature, in accord with the observed microstructure. Mass percentage of $M_{23}C_6$ accounting for the total amount of precipitated phase decreases with thermal exposure times, mass percentage of M(CN) is almost unchanged, mass percentage of sigma phases increases in long-term exposure steels. Sigma phase could not be detected after thermal exposure for 46,000 h at 571°C, because of relatively low temperature and lesser content.

Fig. 4 shows the size of MX and $M_{23}C_6$ precipitates in as-received and in long-term service steels. Most $M_{23}C_6$ particle size is within 36-60nm, mean size is about 109 nm in the as-received steel (**Fig. 4(a)**). A frequency density increases in the greater than 60nm size of $M_{23}C_6$ carbides was observed in long-term service steel, mean size is about 120 nm (**Fig. 4(b)**). This quantitative result shows the coarsening of $M_{23}C_6$ precipitates.

MX mean size is from about 100.9nm in the as-received steel to about 102.1 nm in long-term service steel (**Fig. 4(c)** and **Fig. 4(d)**). The coarsening rate of $M_{23}C_6$ is significantly higher than that of the MX phase. The particle size of MX did not change significantly before and after service. This shows that the MX phases are relatively stable before and after service.

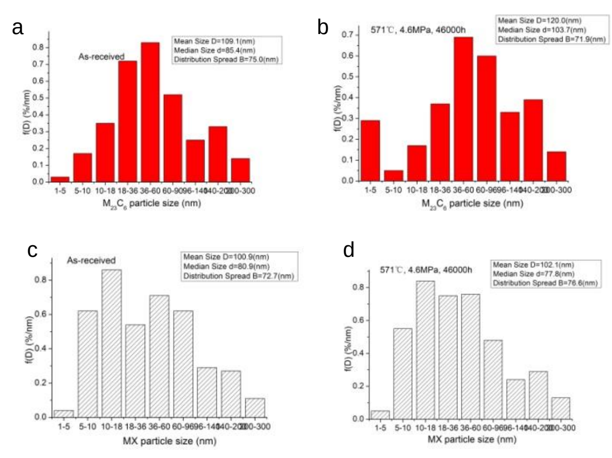

Fig. 4. Histogram of particle size distribution (a) $M_{23}C_6$ as-received steel, (b) $M_{23}C_6$ after thermal exposure for 46,000 h at 571°C and 25.4MPa, (c) MX as-received steel, (d) MX after thermal exposure for 46,000 h at 571°C and 25.4MPa.

Table 2. Content of precipitated phase in Super304H steels.

Samples No.	Total amount of precipitated phase	$M_{23}C_6$		M(CN)		σ	
		Phase content	Mass percentage (%)	Phase content	Mass percentage (%)	Phase content	Mass percentage (%)
(605°C, 26.15MPa,4900h)	1.47	1.055	71.769	0.415	28.2319	—	—
(605°C, 26.15MPa, 10000h)	1.61	1.062	65.963	0.478	29.689	0.07	4.348
(605°C, 27.46MPa, 38000h)	1.823	1.067	58.530	0.543	29.786	0.213	11.684
(571°C, 25.4MPa, 46000h)	1.918	1.483	77.32	0.435	22.68	—	—

Conclusion

The microstructure of as-received Super304H steel consistes of fully austenite and coherent twins with higher dislocation density, $M_{23}C_6$ and MX were the main precipitates. After long time service, the dislocation density within subgrains reduced, twin crystals dispersed, Cu-rich phase and sigma phase were found. Quantitative results show, the total amount of precipitated phase increased after long time exposure. Mass percentage of $M_{23}C_6$ accounting for the total amount of precipitated phase decreased, mass percentage of MX phase was unchanged, mass percentage of sigma phase increased in long time service steels. Compared with the as-received steel, the size of $M_{23}C_6$ increased, and the size of MX did not change in long time service steels.

In the future, it is more important to develop the technology of lifetime prediction. For this purpose, it is necessary to quantify microstructure of material used at high temperature for long time actual service.

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Conflicts of interest

"There are no conflicts to declare".

Keywords

Microstructural evolution, austenite steel, supercritical boiler.

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Authors biography

Dr. Che Chang, received doctorate in materials science from Beihang University in 2005, then became a post-doctoral scholar in the department of thermal engineering, Tsinghua University. Now she works as a senior engineer in China Special Equipment Inspection Institute. Research field focuses on high temperature properties of advanced heat-resistant steels and superalloys, microstructural evolution, phenomenological understanding of creep and fracture processes, as well as failure analysis and life prediction of component materials.

Graphical abstract

Microstructural evolution of Super304H tubes after different service conditions were studied involving in optical microscope, SEM, TEM and SAXS. The results show, $M_{23}C_6$, MX, Cu-rich particles, and σ phase were found to precipitate. A quantitative assessment of microstructure evolution was given during long-term exposure, focusing on the particle size and number density of particles in Super304H steel.