Microstructure Evolution of a Novel Super304H Steel Aged at High Temperatures

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The microstructure evolution of a novel Super304H stainless steel aged at different temperatures was investigated using various analysis methods. The results reveal that the microstructure of the Super304H steel after aging at 973–1623 K consists of the primary γ matrix and a small amount of precipitated phases. Grain size of γ-matrix shows a slow increase when the aging temperature is lower than 1573 K and it increases quickly when the aging temperature is beyond 1423 K. The lattice parameter of γ-matrix varies at different aging temperatures, and this variation corresponds to the phases precipitated or redissolved. The variation of grain size and precipitated phases can affect the performance of the steel when exposing to steam oxidation and be subject to creep at high temperatures.

Keywords: Super304H steel, aging temperature, microstructure, lattice parameter, precipitation

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1. Introduction

Due to the problems of the earth environment such as the increase of carbonic acid gas, improvement of thermal efficiency is required in fossil fired power plants. USC (Ultra super critical) boilers that are operated under the condition of a temperature over 873 K and steam pressure over 24 MPa are expected as one of the higher heat efficiency plants. To meet the critical demands for the boilers, a new austenitic stainless steel Super304H (0.1C-18Cr-9Ni-3Cu-Nb-N) has been developed.¹-³ The Super304H has high strength at elevated temperatures and are required for superheater tubes in fossil fired boilers. The 10⁵ h creep rupture strength at 973–973 K for this steel is more than 20% higher, compared with ASME SA-213 TP347H which has the highest allowable stress among the conventional 18-8 steels. This excellent creep rupture strength is based on finely precipitated particles such as Cu-rich phase, NbCrN, Nb(C,N) and M₆₃C₆.⁴-⁷ However, the properties about this new austenitic stainless steel are mainly provided by manufacturer. The study focusing on the high temperature properties of Super304H is limited in the published literatures.⁸⁻¹¹ In order to use them widely in high-temperature environment, the effect of aging at different temperatures on the properties is investigated. This study aims to investigate the microstructure development of the Super304H steel after being aged at high temperatures. The analysis of microstructure, in particular, precipitates formation at different temperatures provides the more fundamentals for wide application of the steel at elevated temperatures.

2. Experimental

A 15 mm × 12 mm × 7 mm square test specimen was cut from the commercial tube with the specification of φ45 mm × 9 mm that was available from Sumitomo Metal Industries. The chemical composition of this Super304H is shown in Table 1. The measured value was obtained by using quantitative analysis spectrometer.

These specimens were heated respectively in a tube furnace at temperatures between 973–1623 K with soaking time 3.6 ks and then quickly quenched in water. After aging, the samples were ground to remove surface layer for 0.5 mm in order to remove the oxide peels. Then the samples were analyzed by X-ray diffractometry (XRD) with CuKα radiation at 30 kV and 100 mA to identify the phase constitution. The microstructures of the aged samples were observed and analyzed by using an optical microscope (OM) and scanning electron microscope (SEM) equipped with an energy-dispersive spectroscopy (EDS) system. For the OM and SEM observation, the samples were mechanically polished and etched in a solution of aqua regia. For transmission electron microscope (TEM) observation, 3 mm diameter discs were cut from the aged samples and were mechanically ground to a thickness of 150 μm. Final foils for TEM observation were prepared by twin-jet electropolishing in an electrolyte solution. The microstructure of the thin films was observed by TEM using an H-800 instrument at 200 kV.

3. Results and Discussion

Figure 1 shows the OM morphology of the as-received specimen and specimens aged at 973 K, 1373 K, and 1523 K, respectively. It can be seen that the microstructure includes the γ phase and precipitated phases, and the grain size of γ phase is increased with the increasing of aging temperatures. Figure 2 summarized the variation of grain size with aging temperatures. As a comparison, the grain size of as-received base metal also is listed in this figure. This figure indicates that the austenitic grain size of specimen aged at 973 K is almost kept the same value as that in as-received condition. After being aged at 1123–1373 K, the grain size of austenitic matrix shows a slow increase. But the austenitic grain size shows a rapid growth when the aging temperature is increased to 1423–1623 K.

Figure 3 shows the micro-morphology of precipitates for samples aged at different temperatures. The shape of precipitated phases include the lath-like and fine spherical, as shown in Fig. 3(a). After being aged at 1123 K for 3.6 ks, it
can be observed more precipitated phases which distributed in the interior of grain and grain boundary. The precipitated phases along the grain boundary show the lath-like, and those in the interior of grain show a spherical shape. With the increasing of the aging temperature, the size and amount of precipitated phases increase continuously. However, the amount of precipitated phases begins to decrease when the aging temperatures exceeds 1273 K. When the sample was aged at 1523 K, the size of lath-like precipitated phase shows the increasing tendency, but the amount of fine spherical phase decreased obviously. Figure 4 is the statistical results of the area ration of the precipitated phases and matrix based on the gray of SEM micrograph, which can be used to estimate the amount changing of precipitated phases during different aging temperatures.

Figure 5 shows the X-ray diffraction profiles of the as-received Super304H and the samples aged at 973 K, 1123 K, 1273 K, 1423 K and 1523 K for 3.6 ks, respectively. It can be sure that the peaks with the highest intensity correspond to the $\gamma$ phase for all the samples. But for some precipitated phases, it is difficult to index these phases due to their lower intensities or overlapping. Therefore, TEM observation and selected area diffraction were used to confirm the precipitated phases. Figure 6 shows the TEM bright field images and selected area diffraction about the specimen after being aged at 1123 K. Two kinds of precipitate were confirmed. One is $M_{23}C_6$ whose lattice parameter is 1.064, as shown in Fig. 6(a) and (b). The EDS result indicated that this precipitate particle included the Cr and Fe elements, and the Cr is the major metal element. Therefore, the $M_{23}C_6$ precipitated phase in this study.

Table 1 Chemical composition of Super304H (mass%).

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>Nb</th>
<th>N</th>
<th>B</th>
</tr>
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<tbody>
<tr>
<td>(1)</td>
<td>0.07–0.13</td>
<td>≤0.30</td>
<td>≤1.00</td>
<td>≤0.040</td>
<td>≤0.010</td>
<td>17.00–</td>
<td>7.50–</td>
<td>–</td>
<td>2.50–</td>
<td>–</td>
<td>2.00–</td>
<td>–</td>
</tr>
<tr>
<td>(2)</td>
<td>0.10</td>
<td>0.22</td>
<td>0.85</td>
<td>0.033</td>
<td>0.006</td>
<td>18.4</td>
<td>8.56</td>
<td>0.26</td>
<td>2.41</td>
<td>0.48</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Note: (1) provided by Sumitomo; (2) measured value.

![Figure 1](image1)

**Fig. 1** OM morphology of the samples aged at different temperature for 3.6 ks (a) as-received, (b) 973 K, (c) 1373 K and (d) 1523 K.

![Figure 2](image2)

**Fig. 2** Variation of austenite grain size of Super304H after being aged at different temperature for 3.6 ks.

![Figure 3](image3)

**Fig. 3** Variation of austenite grain size of Super304H after being aged at different temperature for 3.6 ks.

![Figure 4](image4)

**Fig. 4** Variation of austenite grain size of Super304H after being aged at different temperature for 3.6 ks.
than 96°, it can be distinguished with γ phase only when the diffraction angle is higher than 96°. Therefore, the peaks of Cu$_3$Ni phase are not marked in this figure. In Fig. 5, it can be seen the trendy about the type of precipitated phases. When the specimen is heated at 973 K, the Cr$_{23}$C$_6$ begins to precipitate although its peaks are very weak. With the increasing of aging temperature, it almost disappears when the aging temperature is up to 1423 K. This indicates the Cr$_{23}$C$_6$ phase is precipitated at a lower aging temperature and re-dissolved at a higher temperature. When the aging temperature is as 1523 K, a new NbCrN phase is detected as shown in Fig. 5. At this temperature, other precipitated phases almost disappear.

The variation of lattice parameter of γ phase at different aging condition is shown in Fig. 7, which is calculated from main peak of γ phase based on the X-ray diffraction data. It can be seen the lattice parameter of as-received base metal has a bigger value, it begins to decrease with the increasing of aging temperature and it reaches the minimum at 1123 K. Although many conditions can affect the lattice parameter, the variation of lattice parameter of γ phase is thought to be caused mainly by the solid solution of some elements, because all the samples were heat treated at similar condition only the temperature is different. The sample at as-received condition is solution treated and some elements (such as C, N and Nb, Mo) solid dissolved in the γ matrix, the lattice parameter of as-received base metal has a bigger lattice distortion. After being aged at 973 K, some C, N and Nb precipitated from γ matrix and formed Cr$_{23}$C$_6$ and Nb(C,N) phases, this will result in the decreasing of lattice parameter for γ matrix. When the aging temperature is up to 1123 K, the amount of precipitated phases has a maximum value and corresponded to the minimum value of lattice parameter for γ matrix. Continue to increase the aging temperature, some precipitated Cr$_{23}$C$_6$ phase begins to re-dissolve and some C atoms are solid dissolved in the γ matrix, then the lattice parameter of γ matrix increase again. According to the X-ray and TEM results, the precipitated Cr$_{23}$C$_6$ phases almost
disappeared when the aging temperature is higher than 1323 K. The lattice parameter of matrix almost returns to the initial stage of as-received condition. When the aging temperature is above 1323 K, although the amount of precipitated Nb(C,N) is increasing, the total amount of precipitated phases is limited, so the lattice parameter of matrix at this aging temperature only has a slight changing. When the aging temperature is above 1423 K, the lattice parameter of matrix increase again due to the Ostwald ripening. When the specimen is aged at 1623 K, the alloy elements in steel almost re-dissolve in matrix, so the lattice parameter reaches maximum value.

According to the analyses above, the Super304H shows the good thermal stability when the specimens are aged treatment below 973 K, the austenite matrix still keep the fine microstructure. This could be attributed to the dispersively distributed Nb(C,N) and Cu-rich phase, which can effectively pin dislocations, subgrain boundaries and impede the movement of boundaries. So the recrystallization of the alloys is retarded in the process of ageing. However, the austenite grains of Super304H also begin to grow when the aging temperature is above 973 K, especially higher than 1423 K. In the previous reports,3) the excellent high temperature steam oxidation resistance of Super304H is benefit from the fine austenite grain. In order to keep the high temperature steam oxidation resistance of Super304H, the service temperature should be limited under 973 K to avoid the grain coarsening. At the same time, it also is noticed that there are lots of Cr$_2$3C$_6$ precipitates along the grain boundary when the specimen is aged at 1123 K, this will weaken the creep rupture strength of Super30H. Therefore, it should avoid this temperature range during manufacturing process of Super304H parts, such as welding and heat treatment.

4. Conclusion

The microstructure of Super304H is consisted by $\gamma$ phase and small amount of precipitated phases when it is aged at 973–1623 K for 3.6 ks and the Super304H shows excellent thermal stability at high temperature. Grain size of $\gamma$-matrix is grown slowly when aging temperature is lower than 1373 K and it increases quickly when the aging temperature is beyond 1423 K. The Cr$_2$3C$_6$, Cu$_3$3Ni, Nb(C,N) and NbCrN precipitated phases appears at different aging temperatures. The lattice parameter of $\gamma$-matrix shows some changing at different aging temperatures, and this variation corresponds to the phases precipitated or redissolved.
REFERENCES