Microstructural evolution in S31042 heat-resistant steel after service and the effect on hardness

Xiao Jin¹, Xianxi Xia¹, Baoyn Zhu¹, Yanfen Zhao¹, Peng Duan², Jun Liang³, Jinfeng Du³, Chao Zhou³, Guodong Zhang¹*

¹ Suzhou Nuclear Power Research Institute, Suzhou, Jiangsu Province, 215004, PR China
² Shanghai Minghua Power Technology Co., Ltd., NO. 1687 Changyang Rd, Shanghai 200090, P.R. China
³ CHN Energy New Energy Technology Research Institute Co., Ltd., Future Technology City, Beijing 102209, P.R. China
¹* zhangguodong@cgnpc.com.cn

Abstract—The ultra-supercritical power generation technology with high energy efficiency and low emissions is one of the important ways to solve the current increasingly prominent energy problems in the context of international development requirements for carbon neutrality and the increasingly prominent energy shortage. Because of its excellent resistance to high temperature corrosion and organizational stability, S31042 is commonly employed in the most severe working environment of ultra-supercritical units. Due to its great resistance to high-temperature corrosion and organizational stability, S31042 is commonly employed in the most demanding components of ultra-supercritical units such as high-temperature reheaters and high-temperature superheaters. Various characterisation approaches were employed in this research to reflect the microstructure of S31042 heat-resistant steel in service under various time length conditions, and the hardness of S31042 heat-resistant steel was assessed under the corresponding service conditions. The results showed that the hardness of S31042 increased significantly with increasing service time, from around 160 Hv at the time of non-service to nearly 220 Hv after 75360 hours of service. The continuous distribution of uniformly sized M₂₃C₆ phase on the grain boundaries of S31042 developed toward grain coarsening after service, but the precipitation strengthening effect produced by the nanoscale secondary NbCrN phase appearing in the grains was the main reason for the increase of the hardness value of S31042, according to the microstructure of the material.

1. Introduction
In the backdrop of China national carbon-neutral plan and rising energy tensions, ultra-supercritical power generating technology with high energy efficiency and low emissions is one of the solutions to the country's growing energy crisis. In China, ultra-supercritical units have been in use since 2007, and while these high-parameter units improve thermal efficiency, they also place higher demands on the heat-resistant steel components used in the boilers[1]. S31042 steel (Also known as HR3C) is a new heat-resistant steel developed by Sumitomo Metals Japan on the basis of 25Cr-20Ni heatresistant steel by adding a certain amount of niobium (Nb), nitrogen (N), and other strengthening elements through precipitation strengthening to achieve higher long-term strength under high temperature conditions, the
heat-resistant steel is widely used in supercritical unit superheater and reheater parts because of its great resistance to high-temperature corrosion, organizational stability, and other advantages [2, 3].

As S31042 heat-resistant steel is prepared by adding a range of alloying materials, in long thermal aging conditions, due to the influence of accelerated atom diffusion and other phenomena, a variety of second phase will form in the matrix. Because S31042 steel is an austenitic heat-resistant steel with good organizational stability, its grain organization, chemical composition, and other significant changes do not occur during long service, the main strengthening mechanism affecting S31042’s performance after long service is primarily precipitation phase strengthening[4, 5]. Because S31042 steel is an austenitic heat-resistant steel with good organizational stability, its grain organization, chemical composition, and other significant changes do not occur during long service, the main strengthening mechanism affecting S31042’s performance after long service is primarily precipitation phase strengthening[6, 7]. Several research have looked at how the precipitation of M23C6 and NbCrN phases affects the material’s tensile and impact properties as it ages[8-10].

In actual engineering, the following performance tests must be carried out from the service S31042 tube destructive sample test, influencing the unit’s operation. The practicality of the above tests is poor, especially in the case of a short period of time or insufficient material preparation. Hardness, being one of the few test processes that may be used in service S31042 tube to acquire direct mechanical properties without causing destructive damage to the tube, has considerable application relevance in the actual project. S31042. During the high temperature aging process, the type, amount, and shape of the second phase of S31042 has been verified to alter the material’s hardness value[11, 12]. However, there has been less research on the impacts in real-world settings. The properties of typical precipitation phases of S31042 tube in service, as well as their influence on hardness, are explored in this work utilizing real-world S31042 tube as the research object.

2. Experimental

The heat-resistant steel used in this study is a commercial S31042 tube supplied by Sumitomo Metals of Japan, which is in actual service in an ultra-supercritical unit of a power plant with a design maximum operating temperature of about 665°C and a design maximum operating pressure of about 27 MPa, and the S31042 tube was taken as a sample in service for 0 hours, 15501 hours, 35564 hours, and 75360 hours, respectively.

Table 1 displays the chemical composition of S31042 sample tubes in various service length states, as well as the alloying element requirements of GB/T 5310-2017 for S31042 tubes.

| Element         | C      | Si     | Mn     | P      | S       | Cr     | Ni     | Nb     | N       |
|-----------------|--------|--------|--------|--------|---------|--------|--------|--------|---------|
| 0 h             | 0.056  | 0.45   | 1.13   | 0.017  | 0.005   | 24.91  | 18.91  | 0.38   | 0.24    |
| 15501 h         | 0.054  | 0.43   | 1.13   | 0.021  | 0.008   | 24.89  | 19.24  | 0.42   | 0.22    |
| 35564 h         | 0.047  | 0.46   | 1.15   | 0.018  | 0.005   | 25.80  | 19.31  | 0.43   | 0.21    |
| 67705 h         | 0.049  | 0.42   | 1.12   | 0.015  | 0.004   | 24.89  | 19.51  | 0.39   | 0.23    |
| GB/T 5310-2017  | 0.04-  | ≤0.015 | ≤0.03  | ≤0.075 | ≤2.00   | 24.00- | 19.00- | 0.2-   | 0.150-  |
|                 | 5310-  |        |        |        |         |        |        |        |         |
|                 | 0.1    |        |        |        |         | 26.00  | 22.00  | 0.6    | 0.350   |

Various characterization techniques, such as Scanning Electron Microscopy (SEM), Electron Backscatter Diffraction (EBSD), Back-Scattered Electron (BSE) and Transmission Electron Microscopy (TEM), were used to obtain microstructural information of S31042 tubes in different service states in order to study the microstructural changes during the long service time and their influence on the hardness of S31042 in the corresponding state. A Vickers hardness tester was used to examine the hardness of S31042 tubes in various service conditions, and the impact of typical microstructural evolution on hardness changes was discussed. Samples were wire cut on S31042 tubes with varying service lives and polished with 400#, 800#, 1200#, and 2000# sandpaper, respectively, before being electrolytically polished in 10% perchloric acid alcohol (polishing conditions were constant pressure of 20 V at room temperature). A Tescan mir3 scanning electron microscope and an FEI G20 transmission
electron microscope were used for SEM, EBSD, and TEM. S31042 tubes in the corresponding condition were polished at the same time and then submitted to hardness testing.

3. Results and Discussions

Solid solution strengthening, precipitation strengthening, dislocation strengthening, and fine grain strengthening are the main strengthening mechanisms of austenitic heat-resistant steel[13]. In the preparation of S31042 heat-resistant steel, Nb, N, and other strengthening elements were added, resulting in the addition of the Fe matrix to the matrix lattice distortion, resulting in a solid solution strengthening effect. Simultaneously with the addition of these strengthening elements, instrumentation chamber in high temperature long-term service conditions, these strengthening elements are easy to precipitate from the Fe matrix, resulting in the formation of second-phase particles, resulting in second-phase strengthening, such second-phase may take the form of carbon/nitride, intermetallic compounds, etc. One of the most important techniques to reinforce austenitic heat-resistant steel S31042 is by second-phase strengthening. According to earlier studies, there is also dislocation strengthening and fine grain strengthening in austenitic heat-resistant steel[9, 14-16], under service simulation morphologies such as long-time creep, the microstructure of S31042 remained stable, with no substantial grain size changes or plastic deformation. As a result, dislocation strengthening and fine grain strengthening methods are thought to have limited strengthening effects on S31042 over long-term operation and do not generate major S31042 property changes. The typical microstructure of S31042 heat-resistant steel is austenite and precipitation phase. The austenite phase does not change much under long-term high temperature conditions of the organization, affecting its mechanical properties of the microstructure is mainly reflected in the evolution of the precipitation phase[11].

3.1. Microstructure of S31042 heat-resistant steel before aging

Figure 1 show the microstructure morphology of S31042 steel before serviced, Figures 1(a) and 1(b) the SEM and BSE morphologies of S31042 steel, respectively. The matrix structure in the unserviced S31042 samples is austenite grains with twin grains, there is no second phase on the grain and twin boundaries, and there are a few white particles inside the matrix, as shown in the images. Previous research has revealed that these second phases are Nb-rich phases, which are undissolved Nb-rich particle strokes in the manufacturing of S31042 heat-resistant steel, and that the number of such second phases is tiny and has no major effect on the S31042 steel qualities [5]. The EBSD reconstruction of the unsaved S31042 is shown in Figure 1(c). The S31042 matrix grain boundaries are black with large angle grain boundaries (mis-orientation > 10°) and almost no red small angle grain boundaries (mis-orientation between 2°-10°) visible in the figure, and the grains are in an obvious fully annealed state, indicating that the material was completely annealed during the preparation process and that there is no residual plastic deformation during rolling or cold-drawing.
Fig. 1 Microstructure of S31042 before service: (a) SEM map; (b) BSE map; (b) EBSD map

3.2. Microstructure of S31042 heat-resistant steel after aging

Figure 2 shows the SEM morphology of S31042 and the BSE morphology of the relevant areas under various service time conditions. After service, a variety of second phases occur in the grain boundaries and matrix of S31042 steel, and the density of second phases in S31042 increases dramatically with increasing service time, as shown in the figure. Figures 2(a) and 2(b) show the microstructure of S31042 steel after 15501 hours of service, and it can be seen that the second phase of S31042 steel has an obvious continuous distribution on the grain boundary. According to previous studies, these precipitated phases are $\text{M}_{23}\text{C}_6$ phases [17], as shown in Figure 3. This continuous distribution of $\text{M}_{23}\text{C}_6$ on the grain boundary is the root cause of the rapid decrease in impact power of S31042 steel at the beginning of thermal aging [17]. Furthermore, there are a few coarse particles inside the grains, and it can be seen in the BSE morphology diagram that these coarse particles are Nb-rich phase particles, i.e. Nb-rich phase particles observed in the unserved S31042, this structure has a stable state over time and its size does not change significantly [6,14]. Figures 2(c) and 2(d) show the microstructure morphology of S31042 after 35564 hours of service, revealing that, similar to the grain boundary structure of S31042 after 15501 hours of service, a continuous distribution of $\text{M}_{23}\text{C}_6$ structure exists inside the grain near the grain boundary, and a small amount of nano size $\text{M}_{23}\text{C}_6$ particles and needle-like secondary Z phase (NbCrN phase) exist inside the grain near the grain boundary. Figure 2(e) and Figure 2(f) microstructure morphology of S31042 after 75360 hours of service, showing that the number of precipitated phases increased significantly after 75360 hours of service, while the characteristics of $\text{M}_{23}\text{C}_6$ particles on the grain...
boundaries were significantly different compared to the previous period, the size of $M_23C_6$ particles on the grain boundaries of the previous samples were essentially equal, but coarsening significantly.

Fig. 2 Microstructure of S31042 with different aging time: (a) 15501h-SEM map; (b) 15501h-BSE map; (c) 35564h-SEM map; (d) 35564h-BSE map; (e) 75360h-SEM map; (f) 75360h-BSE map
Figure 3(a) and (b) shows the TEM morphology of S31042 after 75360 hours of service, and Figure 3(c) shows diffraction images of $M_23C_6$ on grain boundaries in Figure 3(a), the precipitates on the grain boundary of S31042 were confirmed to be $M_23C_6$ particle. From the picture, it can be seen $M_23C_6$ particle with chain-like distribution on grain boundaries, but the size of every particles are different. The secondary Z-phase and nano size $M_23C_6$ particle interacting with a large number of dislocations can be seen in the matrix near the grain boundaries. The enormous number of nano size Z-phase and $M_23C_6$ particles in S31042 helps to improve the material strength in general. The existence of nano size particles can affect the stress field near the particles and hinder the migration of dislocations, resulting in an increase in the strength and rheological stress of S31042, as seen by an increase in mechanical parameters such as tensile qualities. The bypassing mechanism and the tangential mechanism are the two mechanisms that interact with dislocations in the second phase\cite{18}. The magnitude of the second phase is the key to distinguishing the two mechanisms. The Orowan bypassing mechanism is primarily responsible for the strengthening process after the size of the second phase particles exceeds a specific scale value. When the particle size of the second phase reaches around 1.5 nm to 6 nm, the critical value of the dislocation bypassing mechanism is reached\cite{4}. Figure 4 shows that the secondary Z-phase and nano size $M_23C_6$ particles in S31042 exceed this critical size limit, indicating that the strengthening mechanism is primarily the Orowan mechanism, in which the secondary Z-phase and nano size $M_23C_6$ particles in S31042 interact with the matrix dislocations via a bypassing mechanism, increasing material strength.

![Fig. 3 TEM morphology of S31042 with 75360 hours of service: (a) TEM map; (b) TEM map; (c) diffraction images of $M_23C_6$ on grain boundaries in Figure 3(a)](image-url)
3.3. Hardness changes during service of S31042

Figure 4 shows the hardness S31042 heat-resistant steel with different service time. From the picture, it can be found that the hardness of S31042 steel without service is close to 160 Hv, as the service time increases, the hardness value increases significantly, when the service time reaches 75 360 hours, the hardness has reached to 220 Hv. In comparison to the non-service sample, the hardness of S31042 steel rose by more than 30%. M23C6 phase and Z phase are the most important precipitation phases of S31042 during lengthy service, and the precipitation strengthening effect caused by the intracrystalline nano size M23C6 phase and secondary Z phase is the most essential explanation for S31042’s change in hardness.

The strength equation (1) for precipitation strengthening is as follows [19]:

\[ \Delta \tau = \alpha Gb/\lambda \]  \hspace{1cm} (1)

Where \( \Delta \tau \) is the reinforcement increment in S31042 steel due to precipitation strengthening, \( \alpha \) is a constant, \( G \) is the matrix's shear modulus, \( b \) is the dislocation Berger vector, and \( \lambda \) is the average distance between the second phases.

And the following equation (2) can be used to express it [20]:

\[ \lambda = d(1-f^{1/3})/f^{1/3} \]  \hspace{1cm} (2)

where \( d \) is the second phase's average diameter and \( f \) is the second phase's volume proportion.

The strength increment produced by precipitation strengthening is inversely proportional to the \( d \) of the second phase under the condition that the number of second phase is known, i.e., the smaller the size of the second phase, the more noticeable the strengthening impact on S31042. Previous research has demonstrated that the secondary Z-phase is responsible for S31042's superior creep capabilities at high temperatures, delivering a 10 times stronger strengthening effect than M23C6 particles [9].

4. Conclusion

The following conclusions were reached by testing and analyzing the microstructure of S31042 samples with 15501 hours, 35564 hours, and 75360 hours of non-service and service, respectively, by testing and analyzing the material in different states with the hardness values under the corresponding conditions:

1. The M23C6 phase at the grain boundary of S31042 heat-resistant steel evolved from a continuous distribution and uniform size to a continuous distribution of the M23C6 phase at the grain boundary but not uniform size after a lengthy period of service. At the same time, nano size secondary NbCrN and M23C6 phases can be seen around the service samples' large-angle grain boundaries, and the longer the service period, the more precipitated phases there are in the samples.

2. S31042 heat-resistant steel's hardness value rises with service time, from around 160 Hv before service to about 220 Hv after 75360 hours. The precipitation of a large number of nano size second phases and the associated strengthening, particularly the secondary Z-phase strengthening effect, is the key to S31042’s considerable rise in hardness.
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References
[1] J. Z. Wang, Z. D. Liu, H. S. Bao, et al. (2015) Study of steel and alloys for ultra-supercritical power plant in China. Iron and Steel, 50(8): 1-9.
[2] Y. H. Yao, J. X. Dong, X. S. Xie, et al. (2010) Research development of new austenitic heat-resistant steel HR3C. World Iron & Steel, 2: 42-49.
[3] T.J. Li, F.G. Liu, C. X. Fan, et al. (2010) Study on Aging Embrittlement of New Type Austenitic Heat Resistant Steel HR3C Used in USC Boiler, Material & Heat Treatment, 39(14): 43-46.
[4] Q.L. Yong. (2006) Second Phase in Steel, Metallurgical Industry Press, Beijing.
[5] J. Z. Wang, Z. D. Liu, H. S. Bao, et al. (2013) Effect of Ageing at 700 °C on Microstructure and Mechanical Properties of S31042 Heat Resistant Steel, Journal of Iron and Steel Research International, 20(4): 54-58.
[6] Y.Y. Fang, J. Zhao, X.N. Li. (2020) Precipitates in HR3C steel aged at high temperature, Acta Metallurgica Sinica, 46(7): 844-849.
[7] Y.Y. Fang. (2010), Precipitation in Advanced Heat-resistant Austenitic Steel HR3C, Dalian University of Technology, Dalian.
[8] X. Yang. (2017) Microstructure aging, property degradation and residual creep life evaluation of high-Chrome martensitic heat-resistant steel, Yanshan University, Qinghuangdao.
[9] Y. Yang, L. Zhu, Q. Wang, et al. (2014) Microstructural evolution and the effect on hardness and plasticity of S31042 heat-resistant steel during creep, Materials Science and Engineering: A, 608: 164-173.
[10] B.S. Du, Y.Z. Wei, Z.W. Zhang, et al. (2014) Microstructure and properties of HR3C steel used in ultra-supercritical units after 42000 h exposure to elevated temperature, Transactions of Materials and Heat Treatment, 35(12): 84-89.
[11] W. Bin. (2013) Investigation on Optimization of Microstructure and Mechanical Properties of S31042 Austenitic Heat-resistant steel, Northeastern University, Shen Yang.
[12] Z. Zhang, Z. Hu, H. Tu, et al. (2017) Microstructure evolution in HR3C austenitic steel during long-term creep at 650°C, Materials Science and Engineering: A, 681: 74-84.
[13] J.S. Pan, M.B. Tian, J.M. Tong. (2011) Foundation of Material Science, Tsinghua University Press, Beijing, pp:156.
[14] B.Wang, Z. D. Liu, S. C. Cheng, et al. (2014) Microstructure Evolution and Mechanical Properties of HR3C Steel during Long-term Aging at High Temperature, journal of Iron and Steel Research International, 21(8): 765-773.
[15] A. Zielinski. (2014) Austenitic steels for boiler elements in USC power plants, Journal of Achievements in Materials and Manufacturing Engineering, 57(2): 68-75.
[16] M. Farooq. (2013) Strengthening and degradation mechanisms in austenitic stainless steels at elevated temperature, Royal Institute of Technology(KTH), Stockholm Sweden.
[17] Z.F. Peng, R. Wen, C. Yang, et al. (2015) The relationship between the evolution of phase parameters of grain boundary M_{23}C_6 and embrittlement of HR3C super-heater tubes in service, Acta Metallurgica Sinica, 51(11): 1325-1332.
[18] S.H. Bhadeshia, S.R. Honeycombe. (2016) Steels Microstructure and Properties, Fourth ed., Matthew Deans, Oxford.
[19] K. Maruyama, K. Sawada, J.I. Kot, et al. (2001) Strengthening mechanisms of creep resistant tempered martensitic steel, ISIJ International, 6(41):641-653.
[20] Y. Prawoto, N. Jasmawati, K. Sumeru, et al. (2012) Effect of Prior Austenite Grain Size on the Morphology and Mechanical Properties of Martensite in Medium Carbon Steel, Journal of Materials Science & Technology, 28(5): 461-466.