Analysis of the precipitated phase changes for Super304H heat resistant steel during shot time aging at 800℃

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Abstract. For analyzing the change trend of Super304H heat resistant steel precipitated phases, this article adopts the method of high temperature aging to simulate the material conditions during actual working environment. Super304H steel aged under 800 ℃ for short time 10 h, 20 and 30 h. And analyzed SEM morphology, precipitate phase statistics, composition changes of the original sample and the samples after aging. The results showed that the number of precipitated phase increased first, then decreased and then increased with the prolong of aging time, while the average size and area fraction of precipitated phase increased all the time. In the precipitated phase, Cr continued to increase while Ni decreased.

1. Introduction
In order to improve the efficiency of power generation and reduce pollution emission of coal-fired power plants, it is an effective development direction to improve the parameters of power plant boilers. However, the development of high-parameter power plant boilers has put forward higher requirements for materials, which are required to have good high-temperature strength, oxidation resistance, high-temperature creep strength and welding performance[1-2]. Super304H steel is a kind of fine austenitic heat resistant steel developed by sumitomo metal corporation and finalised heavy industries[3-4]. By adding Cu, Nb and N, the material can precipitate Cu rich phase, M₂₃C₆, MX and Z phase to produce precipitation strengthening effect[5-6]. In order to study the variation trend of precipitated phase of Super304H heat resistant steel, the samples with different aging time were simulated by high temperature and short time aging method, and the number, size and composition of the precipitated phase were analysed by SEM and EDS, in order to understand the change of precipitated phase during the aging process of Super304H steel and guide the practical application of the material.

2. Test materials and procedures
Super304H heat-resistant steel used in this test is the steel tube used for the boiler superheater of thermal power plant. The size of the steel tube is up to φ45 * 9mm, and the chemical composition is shown in table 1. Sample line bar samples into 5 * 5 * 20 mm, after surface treatment clean, the samples were aged at 800 ℃ in the high temperature furnace respectively for 10h, 20h and 30h. SEM was used to observe the changes of precipitated phases, and EDS was used to measure the changes of chemical composition of precipitated phases.

It can be seen from table 1 that the composition of Super304H steel used in the test meets the ASME standard, and the harmful elements such as S and P of the original sample are well controlled.
Therefore, it can be inferred that the mechanical properties of the original steel sample of Super304H used in the test can reach the engineering application.

**Table 1.** Composition of Super304H (mass fraction %)

| Element | C  | Cr  | Ni  | Cu  | Nb  | N   | Si  | Mn  | S   | P   | Fe  |
|---------|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Content | 0.09 | 18.20 | 9.62 | 2.77 | 0.41 | 0.10 | 0.25 | 0.42 | 0.03 | 0.04 | Bal |

3. Test results and analysis

3.1. Analysis of SEM morphology of the samples

The SEM morphology observation results of the original sample and Super304H heat-resistant steel samples after high temperature aging are shown in Figure 1.

![SEM morphology test results of the samples](image)

It is generally believed that Super304H steel benefits from fine grain strengthening and precipitation strengthening. The fine grain metal at room temperature has higher strength, hardness, plasticity and toughness than the coarse grain metal. This is because the plastic deformation of fine grains can be dispersed in more grains due to external forces, and the plastic deformation is more uniform and the stress concentration is less. In addition, the smaller the grain size, the larger the grain boundary area, the more zigzag the grain boundary, the more unfavorable crack expansion. The mechanism of precipitation strengthening is that the second phase particles in the metal materials are precipitated out from the supersaturated solid solution, which causes the strain, and thus leads to the
reinforcement of the metal lattice. The atoms that form the second phase tend to pile up in groups, and they remain coherent to the parent phase.[7-8]

According to the results in Figure 1, the grain size of the original Super304H sample was the smallest, and the size of the precipitated phase was very small and a large quantity of the precipitates phases, which could provide the effect of fine grain strengthening and precipitated phase strengthening, and guarantee the excellent mechanical properties of the original material and the strength of creep fracture resistance. After 10h of aging, the grain size of the sample was larger than that of the original sample. After aging for 20h, the precipitated phase grew further, and the precipitated phase connected growth bars appeared in some places. At the time of aging for 30h, the integrated mass of the grains was precipitated and shed, and the phase distribution inside the grains was also precipitated, showing serious aging of the material.

3.2. Statistical results of precipitated phase of the sample

For further analysis of precipitation changes of Super304H steel ageing at 800 ℃along with aging time, using ImageJ software to analysis the quantity of precipitates, average size of the precipitated phase per unit area, precipitation phase area percentage (total characterization of precipitated phase), and the result is shown in figure 2.

![Graphs showing statistical analysis of precipitated phases](image)

(a) number of precipitated phases  
(b) average size of precipitated phases  
(c) area fraction of precipitated phase

**Figure 2. Results of statistical analysis of precipitated phases**

As can be seen from the results in Figure 2, the number of precipitated phase per unit area shows a trend of decrease followed by increase and then decrease, while the average size and area fraction of the precipitated phase show a trend of continuous increase. Therefore, it can be speculated that with the increase of aging time, the original sample will show the optimal mechanical performance, while...
the mechanical performance of the sample will not change much after 10h and 20h of aging, and the mechanical performance will decline sharply after 30h of aging.

3.3. Chemical component analysis of precipitated phases
The original sample and the precipitated phase composition of the sample after high temperature aging were analyzed by EDS attached with SEM. The EDS analysis pictures are shown in Figure 3. The results are shown in Figure 4.

![Figure 3](attachment:Figure3.png)

(a) aging for 10h  
(b) aging for 20h  
(c) aging for 30h

**Figure 3.** Pictures for EDS analysis

![Figure 4](attachment:Figure4.png)

(a) mass fraction of Cr  
(b) mass fraction of Ni

**Figure 4.** Analysis results of the precipitated phase composition of the sample
Chromium in high performance and heat resistant steel can significantly improve strength, hardness and wear resistance, but at the same time reduce plasticity and toughness. Chromium also improves the oxidation resistance and corrosion resistance of steel. Nickel increases the strength of steel while maintaining good plasticity and toughness. Nickel has a higher corrosion resistance to acid and alkali, rust prevention and heat resistance at high temperature.[9-10]

As shown in Figure. 4, Cr in the precipitated phase showed a trend of continuous growth with the extension of aging time, while Ni showed an opposite trend. This indicates that with the increase of aging time, the precipitated phase is mainly transformed into M$_{23}$C$_6$ type precipitated phase and precipitated along the grain boundary, which will lead to decreased creep fracture strength of the material and intergranular corrosion.

4. Results
1) Super304H steel at 800 °C high temperature aging after 10h, 20h and 30h, the precipitated phase quantity reduction first, then increases, and then decreases. And precipitated phase size and area fraction increased all the time.
2) Super304H steel after 800 °C high temperature aging, the Cr in precipitation phases increased while Ni show the opposite trend.

5. References
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