Microstructure of P92 Steel for Main Steam Pipeline of Ultra Supercritical Units after 50,000 h Service

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Abstract: The microstructure of P92 steel used in the main steam pipeline of ultra-supercritical unit after 50,000 h service was studied by means of metallographic microscope, scanning electron microscope, energy dispersive spectroscopy and X-ray diffraction. The results show that the microstructure of P92 steel is still lath martensite after 50,000 hours of service at high temperature, but the martensite recovers. There are many large-sized M23C6 and Laves phases in the structure, and the aging phenomenon is obvious. The compound of bismuth is small in size and difficult to grow during service, which is beneficial to the improvement of creep rupture strength of P92 steel. The initial particle size of M23C6 and Laves phase is small, which is beneficial to improve the high temperature strength of the material. With the extension of service time, the size of M23C6 and Laves phase increases, which promotes the creep cavity and reduces the creep rupture strength of the material.

1. Introduction

Since the construction of the first batch of 1,000MW ultra-supercritical units in 2005, the number of 1,000 MW ultra-supercritical units put into operation in China has exceeded 100. With the rapid development of ultra-supercritical units, there has been an upsurge in research on the use of heat-resistant steel by scientific and technical workers. Especially after long-term high-temperature service, whether the microstructure and properties of the first-used steels in China are degraded and can continue to be used. Conditions have become the focus and hotspot of research.

P92 steel is a kind of fine-grained and toughened ferritic heat-resistant steel developed for the development of ultra-supercritical units. It is developed on the basis of P91 steel by adding 1.5%~2% of W element instead of some Mo element and adopting ultra-pure smelting, controlled rolling and microalloying technologies. It is mainly used in super-supercritical unit headers, main steam and reheating steam pipes [1-3]. The main steam pipe of P92 steel runs in the harsh environment of high temperature and high pressure, and its microstructure is bound to change. Therefore, it is of great practical significance to study the evolution of P92 steel under high temperature conditions. Compared with the study of high temperature aging [4-6] and permanent creep [7-9] under laboratory conditions, the research on the microstructure and properties of P92 steel pipeline under actual service conditions...
is less [10-12]. Based on the previous research [13-16], this paper cuts the P92 steel main steam pipe serving 50,000 h, studies the changes of matrix microstructure and precipitated phase of P92 steel, discusses the influence of microstructure changes on material properties, and provides theoretical basis for unit maintenance and metal supervision.

2. Test Materials and Methods
P92 steel used in the test is taken from the main steam pipeline of 1000MW ultra-supercritical unit after service for 50,000h. The specification is $\Phi 370\text{mm} \times 60\text{mm}$. The chemical composition of P92 steel is tested by quantitative spectrometer.

| material | C (wt, %) | Si (wt, %) | Mn (wt, %) | P (wt, %) | S (wt, %) | Cr (wt, %) | Ni (wt, %) | Mo (wt, %) | Cu (wt, %) | Nb (wt, %) | W (wt, %) | V (wt, %) | N (wt, %) |
|----------|-----------|------------|------------|----------|----------|-----------|-----------|-----------|-----------|-----------|---------|---------|---------|
| GB5310   | 0.07-     | $\leq$ 0.30- | $\leq$ 0.30- | $\leq$ 0.020 | 0.01     | 9.50      | 0.40      | 0.60      | /         | 0.04-    | 1.50-   | 0.15-   | 0.030-  |
| measured | 0.12      | 0.51       | 0.016      | 0.005    | 8.62     | 0.20      | 0.40      | 0.11      | 0.05      | 1.79      | 0.20    | -       |

The metallographic samples of P92 steel were prepared and etched with FeCl$_3$ hydrochloric acid aqueous solution. The metallographic structure was observed by Olympus GX41 metallographic microscope. The microstructure of the microstructure was observed on the SUPRA 55 field thermal emission scanning electron microscope. The major alloy elements of precipitated phase were tested with energy spectrometer. Electrolytic extraction of precipitated phase in P92 steel structure after service, the electrolyte is zinc chloride hydrochloric acid methanol solution. After drying, the phase composition in each sample is determined by D/max-rc X-ray diffractometer. The specific parameters are: the target is a Cu target, the scanning range is $20^\circ$-$100^\circ$, the acceleration voltage is 45kV, the current is 100mA, the scanning speed is 2°/min, and the step is 0.020° continuous scanning.

3. Test Results

3.1 Microstructure changes
The metallographic structure of P92 steel before and after service is observed under metallographic microscope. The matrix structure of P92 steel is lath martensite under the condition of supply. The size of lath bundle is closely related to the size of lath. After 50,000 h of high temperature service, the matrix structure of P92 steel still has a clear lath martensite morphology, but the martensite lath has recovered and formed a substructure. After long-term high-temperature service, there are more precipitation phases in the grain boundary and lath boundary due to the continuous precipitation and aggregation of the precipitation phase.

Figure 1 Metallographic structure of P92 steel before and after service

The microstructure of P92 steel after 50,000 h service is observed under scanning electron microscope. As shown in Fig. 2, there are a small number of fine granular precipitates in the grain boundary and martensite strip boundary in the state of supply (Fig. 2a). Due to the continuous
precipitation, aggregation and growth of the precipitated phase, the number and size of precipitated phases increases increase continuously. The large-scale precipitated phase is mainly distributed at the grain boundary and lath boundary (Fig. 2b).

![Figure 2 SEM organization of P92 steel before and after service](image)

(a) availability status; (b) after service for 50,000 h

Figure 2 SEM organization of P92 steel before and after service

3.2 Precipitation Phase Change

(1) X-ray diffraction results

According to the previous research results, the precipitated phase in P92 steel is mainly M$_{23}$C$_6$ carbide and a small amount of MX type carbonitride [17]. The X-ray diffractometer was used to analyze the results of electrolytic extraction of P92 steel after 50,000 hours of service. See Figure 3 for the extraction of the compound in the powder. In addition to the M$_{23}$C$_6$ phase, a large amount of Laves phase is precipitated in the extraction powder. According to the chemical composition of P92 steel, Nb compound should also exist in the structure, which is believed to be less precipitated, fine particles, electrolytic extraction filtration and other reasons and cannot be analyzed.

![Figure 3 XRD pattern of weld metal extracts in service for 50,000 hours](image)

(2) Energy spectrum analysis results

The energy spectrum of the precipitated phase in P92 steel after 50,000 hours of service was analyzed. The results are shown in Fig. 4 and Table 2. The large-sized precipitates on the grain boundary and the lath boundary are mainly rich in Fe, Cr, C and W elements, and some contain a large amount of Mo element. Combined with X-ray diffraction analysis results (Fig. 3), it can be seen that the bulky precipitates rich in W and Mo are mainly Laves phases. Fig. 4(b) is the backscattered image of Fig. 4(a). Since the atomic number contrast of different elements in the precipitated phase is different, the brightness exhibited in the backscattered image is also different. Since the atomic ratio of Mo and W is higher than Cr. Large, the Laves phase is bright in the backscattered image. While the M$_{23}$C$_6$ precipitated phase is gray, the bright granular precipitate in the figure is the Laves phase, and the grayish precipitate is M$_{23}$C$_6$.
4. Analysis and Discussion

The supply state of P92 steel is normalized + high temperature tempering treatment. The base structure is tempered lath martensite and a small amount of retained austenite. The martensite lath is uniform and fine in size. There are fine granular precipitated phases inside and between the martensite laths. There is a fine granular precipitate phase, and the precipitate phase is mainly \( \text{M}_2\text{C}_6 \) phase. After 50,000 hours of service at high temperature, the shape of the martensite lath of P92 steel is still clear. But the number of precipitated phases in the structure is obviously increased and the size is obviously increased. In addition to the \( \text{M}_2\text{C}_6 \) carbide, there are many Laves phases with larger sizes. \( \text{M}_2\text{C}_6 \) (M is Cr, Fe) has a complex cubic structure, which is easy to be first nucleated and precipitated at higher energy such as grain boundary and lath boundary. Ostwald ripening is prone to grow and coarsen during service. The Laves phase structure is \((\text{Fe, Cr})_2(\text{Mo, W})\), which is mainly precipitated at the grain boundary, and has a small size at the initial stage of precipitation, and is continuously precipitated and grows with the extension of service time. At the beginning of service, the fine \( \text{M}_2\text{C}_6 \) and Laves phase can prevent the recovery of lath martensite and dislocation, and improve the high temperature creep rupture strength of P92 steel to some extent. With the extension of service time, \( \text{M}_2\text{C}_6 \) and Laves phase are continuously precipitated. When grown up, the coarsening of \( \text{M}_2\text{C}_6 \) is controlled by the volume diffusion mechanism, while the Laves phase is affected by the grain boundary diffusion mechanism. The coarsening rate is obviously faster than that of \( \text{M}_2\text{C}_6 \) [18], and the larger size of \( \text{M}_2\text{C}_6 \) and Laves phase is weaker than the matrix. Promote the formation of creep voids, which are easy to become creep crack sources under stress. In addition, the precipitation of Laves phase causes the decrease of Mo and W content in the matrix, which affects the high temperature creep resistance of P92 steel. Nb compounds have high stability, are not easy to grow during service, can effectively pin dislocation, and have a solid solution strengthening effect, which is beneficial to improve the creep rupture strength of P92 steel.

After 50,000 hours of service, the aging phenomenon of P92 steel is obvious, which is bound to cause changes in material properties and needs to be paid attention to by technical supervision. At the same time, the performance of P92 steel should be further studied, and the change of P92 steel after long-term high temperature service should be mastered to promote ultra-supercritical. The unit is safe.
and stable in operation and healthy development.

5. Conclusion
(1) After service for 50,000 h, the matrix structure of P92 steel is still martensite lath, but the morphology is still clear. The number of precipitated phases increases and the size increases. The precipitates of the species are mainly $M_23C_6$, Laves phase and strontium compounds.

(2) After aging, P92 steel has obvious aging phenomenon. The larger $M_23C_6$ and Laves phase and weaker matrix are easy to form a creep crack source, which will adversely affect the performance of the material. However, the bismuth compound is in service. It is not easy to grow, which is conducive to the improvement of creep rupture strength.

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