Analysis on the microstructure and properties of P92 steel after long-term service at high temperature

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Abstract. SA335-P92 steel is a kind of heat-resistant steel with martensitic lath as matrix and multi alloy composite strengthening, which has excellent high temperature performance. It is used for high temperature components of high parameter units in China for nearly 20 years. Many research institutions have done a lot of research on the properties and characteristics of high temperature aging and creep durability in the laboratory, but there are few researches on the micro-characteristics and properties of P92 steel after long-term service. In this paper, the studies are carried on the P92 steel of high temperature reheat steam pipeline taken from the first group of ultra-supercritical units in China. The microstructure characteristics and properties of the material are systematically studied by means of test methods such as micro metallography, scanning electron microscopy, EDS and mechanical properties. It is concluded that although the P92 steel after long-term service still remains the microstructure of martensitic lath, but the toughness greatly reduces caused by large amounts of large scale precipitates at the original austenite grain boundaries and lath boundaries.

1. Introduction

P92 steel is a kind of martensitic heat-resistant steel with typical alloy of Cr content of 9-12%. With the development of thermal power technology in China, P92 steel has been widely used in ultra-supercritical units. This type of steel was first used in 2006 and has been in service for nearly 100000 hours [Ref.1-2]. P92 steel plays an important role of the safe operation of the units, which is often used in high temperature components such as steam pipe, header, heating surface pipe and so on. So, a lot of researches have studied on the microstructure and mechanical properties of P92 steel [Ref.3-6].

Most researches are carried out based on the materials of nonservice and their high-temperature aging specimens, as a reason of the difficulty in obtaining long-term service materials [Ref.7-8]. These researches show the results that after aging, the strength of P92 steel remain high level, but the plasticity and toughness of this material are greatly reduced which is the results of the ripening of M23C6 and the new generated phase of lavers. So, the question is whether is lab results are completely coinciding with the realities? If not, what occurred on the material after long-term service in the condition of high level of temperature and stress.
This paper carried researches on the changes of microstructure characteristics and properties of P92 steel, which has been in-service at 600 °C for about 50000 hours.

2. Materials and methods

The research materials were taken from the high-temperature reheat pipeline of an ultra-supercritical power generation unit in China, which have been in-service about 50000 hours. The pipeline temperature is about 600 °C, and the pipeline inner pressure is about 25MPa. The pipe specification is OD840mm×THK45mm. In order to compare the difference between non-service P92 steel (abbreviation: NSP) and undergone long-term service P92 steel (abbreviation: ULP), we find a block of new P92 steel to do the same microstructure tests.

Two types of experiments have been carried out, one is the chemical composition analysis and mechanical property test, and the other is microstructure tests. We take the power sample of chemical composition test from the ULP by machining, and use the Cs-902G high frequency infrared carbon sulfur analyzer to get the results. The tensile specimens were taken from the outer and inner layers of the wall thickness, and were tested on the 100kN AG-IC Shimadzu electronic universal material testing machine according the GB/T 228.1-2010 standard. The impact test is according the standard of GB/T229, and the specimens are taken from the outer layer, middle layer and inner layer of the material wall thickness. The specifications of impact specimens are all 10mm (width) ×10mm (height)×55mm (length) with V-notch. After impact tests, we observed the fracture surface by the scanning electron microscope (abbreviation: SEM). The microstructure specimens are taken by wire cutting machine, then ground and eroded by the Nitric acid solution with 4% FeCl3 concentration, and observed on optical microscope and SEM. The precipitates of ULP were further analyzed by Energy Dispersive Spectrometer (abbreviation: EDS). The number of precipitates is calculated and counted by the software of Image Pro Plus 6.0.

3. Test results and analysis

3.1. Chemical composition

Table1 shows the results of chemical composition of ULP. The indexes of specimens and ASME A335 standard are contrasted that the main alloy composition is accord with the standard except Ni element slightly exceeds the standard index. So, it draws the conclusion that P92 steel has good alloy stability after long-term service at 600°C.

| Test/ standard values | C  | Mn  | Si  | Cr  | Mo  | W  | V  | N  | Ni |
|-----------------------|----|-----|-----|-----|-----|----|----|----|----|
| Test values           | 0.11| 0.36| 0.35| 8.86| 0.3 | 1.56| 0.13| 0.03| 0.42|
| Standard values [Ref.9]| 0.07~| 0.30~| 0.30~| 8.5–9.| 0.30~| 1.5–2.| 0.15~| 0.03~| 0.40 |
|                       | 0.13| 0.60| 0.60| 5   | 0.60| 00  | 0.25| 0.07| max |

3.2. Microstructure and precipitates observation

Fig.1 shows the metallographic photographs of NSP (see Fig. 1a) and ULP (see Fig. 1b) with the 200X magnification. The two pictures are all typical tempered lath martensitic microstructure. The martensitic lath of P92 steel remains complete metallographic structure after nearly 50000h in-service at high temperature and high pressure, also there are no creep holes and other microstructure deterioration to be observed.
Fig. 1 Metallography of metal in original state and after long-term service

Generally, the structure aging phenomenon of heat-resistant steel will appear after long-term operation, such as the gradually disappearance of martensitic lath, the extension of grain boundary, the appearance of creep holes on grain boundary and so on. The strengthening mechanism of P92 steel depends on martensitic strengthening, solution strengthening, precipitation strengthening and dislocation strengthening. From the metallographic test results, it can be concluded that the martensitic lath of P92 steel has good stability.

Figure 2 shows the SEM and backscatter electron microscopy (abbreviation: BEM) results. As the morphology of the SEM photograph of NSP (see picture 2a), ULP has the same convex morphology which is the martensitic lath and grain substructure (see picture 2c). This result corresponds with the conclusion of metallography. In the NSP SEM and BEM figures, a small amount of precipitates are mainly distributed in the austenite grain boundary, as shown in picture 2a. Compared with picture 2a, picture 2c shows that ULP has not only more amount of but also larger size of precipitates which can be observed on the original austenite grain boundary and lath boundary. The atomic number of Cr is 24, while that of W is 74. Due to the difference of atomic number of the main elements in precipitates, the contrast difference in the BEM imaging can be used to clearly identify Laver phase which present as bright and white points [Ref. 10-11]. The BEM picture of NSP presents few white and bright points which probably are chemical compounds of element W or Mo come into being during the manufactory of P92 steel, as shown in Fig. 2b. However, the BEM picture of ULP presents large amounts of white and bright points at the boundaries of grain and martensitic lath, as shown in Fig. 2d.
Fig. 3 is the EDS results of the bright and white points that there are rich element Cr (except element Fe) and a little elements W and Mo in the precipitates of NSP (see Fig.3a), while the rich W and Mo (except element Fe) in the precipitates of ULP (see Fig.3b). The alloy contents in precipitates of P92 steel undergo large changes after long term in-service at high temperature, which the contents of W and Mo change from 3.41% and 1.03% to 13.88% and 3.96% separately. The precipitates in P92 steel which undergone high temperature aging mainly include Lavers phase, M23C6 phase and Z phase [Ref.10]. Generally, Lavers phase is a kind of Fe2W (Mo) metal compound which riches in element W or Mo, and M23C6 is a kind of carbide which riches in element Cr. The EDS results reveal that the bright and white points in Fig.2d have large proportion in ULP which should be Laves phase in the evidence of the rich W and Mo content precipitates, while the dark points in Fig.2b are the main precipitates in NSP which should be M23C6 in the evidence of rich Cr content. Analyzed the results of Fig.2 and Fig.3, a conclusion can be drawn that Lavers phase is the most important change occurred on P92 steel during long-term high temperature in-service and Lavers phase has much faster growing speed than M23C6 as a reason that Lavers phase could not be produced during the steel manufacture. Some studies at laboratories found that Lavers phase has faster growth speed than M23C6 at 650 ℃ aging degree [Ref.12], and another studies found that M23C6 ripening is the main form of precipitation at 750 ℃ aging degree [Ref.10]. The results in this paper are correspond with the former, and the size and number of Lavers phase are more considerable.
The Ipp6.0 software is used to calculate the area proportion and size distribution of precipitates of NSP and ULP which shows that the precipitates total area proportion increases from 3.17% of NSP to 8.28% of ULP, and the precipitates average size increases from 0.034 μm² of NSP to 0.078 μm² of ULP. Figure 4 is the results of the difference comparison of each precipitation size statistics in NSP and ULP. The precipitates number of NSP with size below 0.1 μm² is almost equivalent to that of ULP, while the precipitates number of ULP larger than 0.1 μm² increases significantly after long-term in-service. The analysis results in Fig. 2 and Fig. 3 can infer that the precipitates larger than 0.1 μm² are mainly lavers phase. With the precipitation and growth of lavers phase, on the one hand, the W element in the grain boundary gathers to the grain boundary, which weakens the precipitation strengthening effect of W element. On the other hand, lavers phase is a kind of metal compound with high hardness. Small size Lavers phase can strengthen the grain boundary, while the large Lavers phase size precipitates at the grain boundary will cause grain boundary embrittlement. Both of them will affect the plastic toughness and creep resistance of the material performance is adversely affected.

3.3. Micro-hardness analysis

According to P92 steel manual, the micro-hardness of P92 steel before service is about 210-240HV1. The micro-hardness test results of ULP are shown in Fig. 5. The hardness distribution of the outer layer, middle layer and inner layer of the base metal is relatively uniform, and there is no hardness
reduction phenomenon. The test results meet the requirements of "the base metal hardness is controlled within 185HB-250HB" in the DL/T438-2016 standard [Ref.13].

![Image of micro-hardness results](image)

**Fig.5 Micro-hardness of P92 steel after long service**

### 3.4. Analysis of mechanical properties

The tensile specimens are cut from the outer layer and the inner layer (NCL / WCL) from the wall thickness. The test results are shown in Table 2. The minimum yield strength and tensile strength of ULP is separately 498 MPa and 678 MPa, which are all higher than the minimum standard value in ASTM SA335. The elongation after fracture of the base metal can reflect the material plasticity. The maximum and minimum elongation value of test specimens are 19.5% and 19.1%, which are all lower than the lowest value specified in ASTM SA335 which is 20%. The results show that the strength of P92 steel does not decrease obviously after long-term in-service, but its plasticity significantly reduces and becomes lower than the standard index.

| Specimens number | Tensile strength Rm/MPa | Yield strength Rp0.2/MPa | Elongation A/% | Reduction Z/% |
|------------------|------------------------|--------------------------|----------------|--------------|
| NCLS1            | 687                    | 519                      | 19.5           | 54           |
| NCLS2            | 684                    | 503                      | 19.2           | 53           |
| WCLS1            | 693                    | 525                      | 19.1           | 54           |
| WCLS1            | 678                    | 498                      | 19.3           | 54           |
| Standard indexes [Ref.9] | 660-720                | 480-540                 | ≥20            |              |

P92 steel as supplied has smaller grain size, stronger fine grain strengthening effect and higher impact absorption energy by nucleation element, rapid cooling and TMCP (thermal control rolling process). According to GB / T229-2007, standard 10 × 10 × 55 (mm) impact specimens were taken from the outer layer, middle layer and inner layer of the material. The test results are shown in Fig. 6. In ASTM A335, the reference value of impact toughness of P92 steel as supplied is 140J. The highest value of shock absorption energy is 29J and the lowest value is 20J, which is far lower than the reference value in the standard. The results show that the impact toughness of P92 steel decreases obviously after long-term service.
Fig. 6 Test results of shock absorption energy of P92 steel after long service

Fig. 7 is the fracture morphology of impact specimen. The macroscopic imagine of impact fracture surface is even, and there is not obvious plastic deformation which has typical macro morphology characteristics of brittle fracture, as shown in Fig. 7a. The fracture initiation zone is located at the narrow range of the "V" notch root of the impact specimen, where a large number of dimples formed by plastic crack propagation can be observed, as shown in Fig. 7b. The extension zone has a river pattern, which is composed of small cleavage surfaces connected by tearing ridge, as shown in Fig. 7c. There are a large number of dimples on the tearing ridge, and the most is smooth cleavage surfaces. The whole quasi cleavage fracture surface in the expansion area is relatively flat, and the local cleavage surface has the characteristics of inter-granular fracture. Dense micro-cracks can be seen in the terminal zone, forming approximately parallel ridge lines, which are generated at the final stage of fracture, as shown in Fig. 7d.
c. Expansion area with 1000X magnifies d. Terminal fault area with 1000X magnifies

Fig. 7 Impact fracture morphology of P92 steel after long service

The cleavage surface and dimple of the impact fracture are further observed at greater enlargement by SEM, as shown in Fig. 8. It is observed that a large number of precipitates are mainly distributed in the grain boundary and within the crystal, as shown in Fig. 8a. The precipitates in the crystal are arranged in a directional manner, which should be precipitated along the lath boundary. Granular precipitates can be seen in the crack sources of cleavage surface. Granular precipitates are also observed in dimples, as shown in Fig. 8b. The above results show that the precipitation has a certain correlation with crack initiation and propagation, which is the main reason for the decrease of material toughness.

a. Cleavage surface b. Dimple zone

Fig. 8 Backscattering morphology of precipitates on fracture surface

4. Conclusions

The mechanical properties and precipitate characteristics of P92 steel for high temperature reheat steam pipeline of million ultra-supercritical units have been changed after service for about 50000 hours.

(1) After long-term service at high temperature, the microstructure of P92 steel is still remain tempered martensitic lath with clear lath morphology. There are a lot of intermetallic compound precipitates at the original austenite grain boundary and lath boundary.

(2) Compared with the original state, the amount and size of precipitates in P92 steel after long-term service at high temperature have changed significantly. The amount of precipitates with the size of 0.1 ~ 0.5 μm² increases obviously, but there is no significant difference in the amount of precipitates below 0.1 μm². The precipitates of these large particles are mainly Lavers phase.
After long-term service at high temperature, P92 steel still has high tensile strength and yield strength, the reduction of area slightly decreases, but the impact toughness of the material decreases obviously. The fracture surface shows obvious brittle fracture characteristics, and a large number of brittle precipitates found in cleavage surface and dimple have an important impact on the reduction of impact toughness.

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