Investigation on microstructure of weld metal of HR3C heat resistant steel after service for 50000 hours

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Abstract: This paper studied the microstructure of the HR3C steel-welded metal having serviced for 500 hours via metalloscopy, scanning electron microscopy and Energy Disperse Spectroscopy (EDS). As the result shows, the HR3C steel-welded metal remains the cellular-dendrite structure after 500 hours of service, with the number of its precipitated phases increased and its size enlarged. The M₂₃C₆ carbide is distributed in the strip or lump pattern along the boundaries of afterbirth-like crystals and dendritic crystals, while it is distributed in the form of small particles close to the crystal boundaries. Cu-rich phase, NbCrN- and Nb (C, N)- precipitated phases are highly stable and small, which accounts for the main reason why the HR3C steel welding joint presents high intensity.

1. Introduction

The development of efficient and environmentally friendly clean coal power generation technology is an important guarantee for realizing China's energy development strategy. Ultra-super critical (USC) units have become the main force of China's thermal power generation due to their unique advantages such as energy conservation and environmental protection [1][2]. Since China's first ultra-supercritical unit was put into operation in 2006, more than 100 USC units have been put into operation in China, and some USC units have been running for more than 10 years. Under the long-term service conditions of high temperature, high pressure and steam flue gas corrosion environment of USC unit, the microstructure of boiler component materials will change and degrade the performance of materials [3][4]. At present, HR3C austenitic heat-resistant steel is used in the high temperature superheater and reheater of USC unit in China. It is based on 25-20 (AISI310) steel, which limits C content, adds Nb and N elements, and uses dispersion to precipitate. The fine NbCrN and Nb carbon and nitrogen compounds and M₂₃C₆ are strengthened [1].

The rapid heating and cooling characteristics of the welding process make the weld metal structure super-saturated coarse cell dendrites. Under the service conditions of the unit, the precipitation metal will precipitate and precipitate and change, which will affect the performance of the material. The existing researches show that [5-9], HR3C steel structure has been aging after high temperature service,
so it is of great practical significance to study the microstructure of HR3C steel weld metal after high temperature service to ensure the safe and stable operation of the unit. There have been no reports on the structural changes of HR3C steel weld metal after high temperature service. This paper takes HR3C steel weld metal after 50,000 hours in a power plant as the research object, analyzes the change of metal structure of HR3C steel weld after service, analyzes the shape, size and distribution characteristics of precipitated phase, and studies the metal structure change of weld metal of HR3C steel, provides technical data for metal supervision and condition maintenance of welded joint parts.

2. Experimental materials and methods
The HR3C steel welded joint parts used in the test were taken from the high temperature section of the high temperature superheater of a 1000 MW ultra-supercritical unit in a power plant. The steam pressure of the high temperature superheater was 26.25 MPa, the outlet temperature was 605 °C, and the HR3C steel specification was Φ 50 mm × 10 mm. The cumulative running time was about 50,000 hours. The chemical composition of HR3C steel and its welding materials was measured by SPECTROLAB quantitative spectrometer as shown in Table 1. Compared with the standard components, there is a non-standard stipulated element Mo in the steel, which is mainly to improve the high temperature strength of the steel [10]; the other elements are basically not included in the standard specified components except N.

|                | C  | Si | Mn | P  | S  | Cr | Ni | Mo | Cu | Nb | N   |
|----------------|----|----|----|----|----|----|----|----|----|----|-----|
| GB5310         | 0.04-0.10 | ≤0.75 | ≤2.00 | ≤0.030 | ≤0.015 | 24.0-26.0 | 19.0-22.0 | /  | /  | 0.20-0.6 | 0.15-0.35 |
| HR3C           | 0.06 | 0.35 | 1.18 | 0.019 | 0.003 | 25.3 | 19.8 | 0.13 | /  | 0.39 | /   |
| #T-HR3C        | 0.05 | 0.28 | 1.55 | 0.011 | 0.003 | 27.4 | 19.9 | 0.84 | 2.24 | 0.40 |     |

The HR3C steel is welded by manual non-polar argon arc welding (GTAW), the groove type is “V”, and the groove is shown in Figure 1. The HR3C steel pipe was placed at a fixed position of 45°. The welding material was selected from the matching wire #T-HR3C provided by Sumitomo Corporation of Japan, the specification was φ =2.4mm, the welding procedure specification was; the welding voltage was 10-12V, and the welding current was 70-90A. Multi-layer multi-pass welding method is used. During the welding process, the temperature between the layers is monitored by the far-infrared thermometer to be no more than 150 °C, and the welding is completed internally and externally.

![Fig.1 Schematic diagram of HR3C steel welding groove](image-url)

Metallographic samples of HR3C steel welded joints after welding and after 50,000 hours of service were prepared and etched with aqua regia and ferric chloride aqueous hydrochloric acid solution respectively. The metallographic structure of the samples was observed by Olympus GX41 metallographic microscope. The microstructure and fracture morphology of the sample were observed under ZEISS-SUPRA55 field emission scanning electron microscope, and the chemical composition of the precipitated phase was analyzed by its own energy spectrometer.
3. Experimental results and analysis

3.1. Microstructure of HR3C steel welded weld metal

The metal structure of HR3C steel welded joints is cellular crystal or cellular dendrites. As shown in Figure 2, there are a small amount of precipitated phase in the weld metal structure of HR3C steel under welding conditions, and its shape is granular or strip-like. The grain boundaries are intermittently distributed, while the number of precipitated phases in the dendrites is relatively fewer (Fig. 2b).

The energy spectrum analysis of the welded weld of HR3C steel is shown in Figure 3. The precipitation phase in the weld metal structure of HR3C steel under welding condition is mainly rich in elements such as Cr, Fe and Nb, accompanied by the crystallization process of weld metal. Nb carbonitrides precipitate on the dendritic boundaries, and the morphology is dominated by strips. Combined with the welding material composition, welding metallurgy characteristics and preliminary research results of HR3C steel, the precipitation phases in the weld metal structure of HR3C steel are mainly Nb(C,N), M23C6 and Cu-rich phase.

![Metallographic structure of HR3C steel weld metal under welding conditions and after 50,000 hours of service](image)

![Results of energy spectrum analysis of welded joints of HR3C steel](image)
3.2. Microstructure change of HR3C steel weld metal after 50,000 hours of service
After 50,000 hours of service, the weld metal of HR3C steel is still a typical cell dendritic form, and the number of precipitated phases in the structure is large, as shown in Figure 4. Due to the loose arrangement of atoms at the cell boundary and the large number of lattice defects, the precipitated phase is easy to nucleate and grow [11], which is continuous strip or irregularly large granular. The dendritic boundary in the solidification substructure of the weld is also an important place for the nucleation of the precipitated phase. The precipitated phase at the dendrite boundary is mainly distributed in strips. In the precipitated phase inside the cell crystal and dendrites, in addition to the large initial precipitated phase formed during the solidification process, a large number of small granular precipitates are precipitated during long-term high-temperature service.

![Fig.4 Metal microstructure of HR3C steel weld metal after 50,000 hours of service](image)

(a) and (b) metallographic organization; (c) and (d) SEM organization

3.3. Analysis of precipitation phase of HR3C steel weld metal after 50,000 hours of service
The preliminary research results show that [5,12-14], the precipitation phases in the weld metal structure of HR3C steel are mainly Nb(C,N), M₂₃C₆ and Cu-rich phase, combined with HR3C steel and welding material chemistry in Table 1. Composition, long-term high temperature service after HR3C precipitation phase composition and weld metallurgy characteristics, after long-term high-temperature service, HR3C steel weld metal precipitation phase components are mainly NbCrN, Nb (C, N), M₂₃C₆ and Cu-rich phase. The energy spectrum of the precipitated phase in the weld metal structure of HR3C steel after 50,000 hours of service was analyzed. The results are shown in Figure 5 and Table 2. The bulky phase precipitates in the cell boundary are mainly Cr, Fe, and Mo, while the Ni content is small, and the bulk precipitate phase is M₂₃C₆ carbide. A certain amount of fine granular precipitates is precipitated near the cell grain boundaries, mainly M₂₃C₆ type carbides and Nb compounds. Since a large amount of M₂₃C₆ carbides are precipitated on the grain boundaries, a large amount of Cr, Nb and other elements are consumed. It is difficult to diffuse the elements such as Cr...
and Nb at the grain boundary to reach the area leading to the vicinity of the grain boundary, and the growth rate of the element is limited. Therefore, the size of the precipitated phase particles is small.

![Fig.5 Analysis of the phase energy spectrum of HR3C steel weld metal after 50,000 hours of service](image)

Figure 6 shows the distribution of the scanning elements of the EDS surface of the weld metal of HR3C steel after 50,000 hours of service, and the long or large precipitates at the cell boundary and the dendritic boundary are M\textsubscript{23}C\textsubscript{6} type carbides rich in Cr and Fe. A large precipitated phase poor in Fe and Ni elements is mainly a Nb chemical compound of Nb and Mo. The precipitated phase having a large internal size in the crystal grain is mainly a Cr-rich M\textsubscript{23}C\textsubscript{6} type carbide, and a small-sized granular precipitated phase is a Nb compound.
HR3C steel is a supersaturated solid solution in the supply state. The heating and cooling speeds in the welding process are relatively fast, which makes the solidification and crystallization speed of the weld metal fast. On the one hand, the grain boundary, dendritic boundary, etc. in the crystal structure of the weld metal Lattice defects are higher density, on the other hand, it can cause solute atoms to segregate at grain boundaries, dendritic boundaries, etc. (such as Nb, Mo, etc.), while the weld metal is also subjected to residual tensile stress after solidification, accompanied with the solidification of molten pool crystallization and precipitating a Nb compound along the dendrite boundary and is distributed in a strip shape.

Since the welded joint structure of HR3C steel is also a supersaturated solid solution, $M_23C_6$ is rapidly precipitated under the service conditions of the unit. The austenite grain boundary and the cell dendritic boundary of the weld metal are the main point for its first nucleation [14] [15], as the service time increases, the number of precipitated phases increases, the size grows and is connected to each other, which will adversely affect the performance of HR3C steel. The composition of the weld metal contains Cu alloying elements. The solid solubility of Cu in $\gamma$ decreases sharply with the decrease of temperature, and the precipitation of Cu-rich phase has no incubation period, which can be supersaturated during welding cooling and multiple welding thermal cycles. The middle part of the matrix was analyzed. Nb (C, N) has high stability. During the solidification process of weld metal, Nb segregates and accumulates at the cell dendritic boundary. Nb (C, N) precipitates at the dendrite boundary, and Nb (C, N) has a small solid solubility in austenite and a short incubation period, and can also be analyzed from the middle of the supersaturated matrix during the welding thermal cycle. NbCrN (Z phase) is a composite nitride of Nb and Cr. Its particle size is small and its growth is slow, mainly in the crystal [16] [17]. Cu phase, NbCrN and Nb (C, N) are also precipitated during service, but their stability is high, the precipitation phase is hard to grow, and the size is relatively small, which
will help to improve the high temperature strength of HR3C steel.

4. Conclusion
   (1) After 50,000 hours of service, the weld metal of HR3C steel is still in the form of cellular dendrites, and the number of precipitated phases in the structure is obviously increased and the size is obviously increased.
   (2) $M_23C_6$ carbides are distributed in the form of long strips or large blocks at the cell boundary and dendritic boundaries, and are distributed in the form of fine particles near the grain boundaries. The Cu-rich phase, NbCrN and Nb (C, N) precipitates have higher stability and smaller size, which is the main factor for maintaining high strength of HR3C steel.

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