Change of Intergranular Corrosion Sensitivity of HR3C Steel Under the Condition of 700 °C Aging

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Abstract: This paper studies the change of intergranular corrosion sensitivity of HR3C steel under the condition of 700 °C aging by using the scanning electron microscope, energy disperse spectroscopy (EDS), and double-loop Electrochemical potentiokinetic reactivation (EPR) method. The results show that the main reason for the intergranular corrosion of HR3C steel after aging treatment is the precipitation of $M_23C_6$ along the grain boundary. The morphology and size of $M_23C_6$ also matters in this regard. At the same time, $M_23C_6$ precipitation also causes corrosion of Cr around it. $M_23C_6$ precipitates at the fastest speed at the beginning of aging, which leads to the rapid increase of intergranular corrosion sensitivity. As aging continues, $M_23C_6$ precipitation becomes gradually stable. After the precipitation of large-sized isolated granules, the intergranular corrosion sensitivity of HR3C steel decreases rapidly and maintains at a low level.

1. Introduction
Ultra-supercritical units have become the main force of thermal power generation because of their unique advantages of energy saving, environmental protection, and high efficiency. They are of great significance in the adjustment of China’s thermal power structure and the improvement of power plant equipment manufacturing. As the temperature and pressure of the unit increase, the materials used in the components need to have higher temperature and corrosion resistance. Against this backdrop, a large number of new ferritic heat-resistant steels and austenitic heat-resistant steels have emerged [1]. Among them, HR3C steel, as one of austenitic heat-resistant steels, boasting high-temperature strength, high-temperature oxidation resistance and corrosion resistance, has become one of the preferred materials for high-temperature components used in ultra-supercritical units (mainly for the high-temperature superheater and the high temperature section of the re heater). HR3C (25Cr-20Ni-Nb-N) steel is a kind of austenitic heat-resistant steel developed by adding Nb and N elements to TP310H steel. HR3C steel components not only have to face the high temperature and pressure, but also the severe corrosion of sodium and potassium sulphate on the fire side. Therefore, its resistance to intergranular corrosion sensitivity during operation deserves high attention. However, little research has been made in this aspect, so this study aims to explore the change of intergranular corrosion sensitivity of HR3C steel [2-4].

Electrochemical potentiokinetic reactivation (EPR), as an electrochemical accelerated corrosion test method, is used in the evaluation of or the research on the intergranular corrosion sensitivity of
austenite, such as the stainless steel and nickel base alloy [5-8] because it can quickly quantify the intergranular corrosion sensitivity of materials. This paper adopts EPR method to study the intergranular corrosion performance of HR3C steel welded joints [9-11] under the condition of 700 ℃ aging, thereby providing a theoretical basis for a wider application of HR3C steel and effective supervision during operation.

2. Test materials and methods

2.1 Test materials
HR3C steel pipe with a supply state of solid solution treatment (ϕ 45 mm×9.6 mm) is supplied by Sumitomo Corporation of Japan. Its chemical composition measured using SPECTROLAB quantitative spectrometer is shown in Table 1. Compared with the standard components [9], there exists a non-standard specified element called Mo, which is mainly for improving the high-temperature strength of the steel [13]; Other components are all basically among the standard ones.

| Standard          | C  | Si  | Mn  | P   | S   | Cr  | Ni  | Mo  | Cu  | Nb  | N   |
|-------------------|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| ASME Code Case2115-1 | 0.04-0.10 | ≤0.75 | ≤2.00 | ≤0.03 | ≤0.03 | 24.00-26.0 | 17.0-23.0 | / | / | 0.20-0.60 | 0.05-0.35 |
| measured          | 0.06 | 0.35 | 1.18 | 0.019 | 0.003 | 25.3 | 19.8 | 0.13 | / | 0.39 | /   |

2.2 Test method
This paper processes the HR3C steel sample using wire cutting method, and then places it in SX2 12-16 box-type resistance furnace for high temperature aging under the air condition. The aging temperature is 650 ℃ and the aging time is 100 hours, 200 hours, 300 hours and 500 hours, respectively. Furnace cooling is adopted in this paper.

EPR test is carried out according to the requirements of BS ISO 12732-2006 [14]. The sample is 1 cm×1 cm×0.3 cm with a working area of 1 cm². All other surfaces are sealed with paraffin and are welded with wire on the opposite of the working surface, and the working surface is ground and polished. The samples of each state are tested at least three times, and the average of three effective values is taken as the value measured in the test. The EPR test is performed on a PARSTAT 2273 electrochemical workstation using a three-electrode working system in which the reference electrode is a saturated calomel electrode (SCE), the auxiliary electrode is a platinum electrode, and the solution is 0.50 mol/L H₂SO₄ + 0.01 mol/L KSCN. The electric-heated thermostatic water bath maintains the temperature at 25±1 ℃. The test procedures are: first, immerse the sample in the solution for 10 minutes to obtain a stable corrosion potential; second, perform the anode polarization potential scan at a rate of 1.67 mV/s; third, immediately conduct reverse scanning at the same rate after reaching a passivation potential of 300 mV (SCE). The double-loop EPR method measures the activation current \( I_a \) and the reactivation current \( I_r \), and an reactivation rate (\( R_a = I_r/I_a \)) is used as the criterion of EPR. The higher the \( R_a \), the higher the intergranular corrosion sensitivity. \( I_r \) is the maximum anode current during reverse scanning, while \( I_a \) is the maximum anode current for forward scanning.

After the test, immediately rinse the sample with water and alcohol, and observe the morphology after corrosion using a SU-70 thermal field emission electron microscope. In order to observe the micro-structure of HR3C steel after aging, it is necessary to grind and polish the HR3C steel metallographic sample, corrode it with aqua regia, observe its micro-structure using JSM-6380LA scanning electron microscope, analyze the spectrum using its own energy spectrometer and obtain the composition of the major alloying elements.
3. Experimental results

3.1 Change of intergranular corrosion sensitivity

$R_a$ of HR3C steel after 700 °C aging is shown in Figure 1. $R_a$ of the supplied HR3C steel is 0; within the first 100 h of 700 °C aging, $R_a$ rapidly increases to the peak, and then it decreased rapidly with the aging time; finally, it remains at a low level after 300 hours.

![Variation of $R_a$ of HR3C versus aging time](image)

The corrosion morphology of aging HR3C steel after EPR test is shown in Figure 2. During the first 100 h, HR3C steel has significant corrosion at the boundaries of and inside the austenite crystal. A large amount of corrosion occurs in the crystal, and the etching trench at the grain boundary is relatively wide (Figure 2a, b). As aging continues, the number of etch pits in the crystal is gradually reduced. After 500 hours, the grain boundary corrosion is relatively wider, while the number and size of corrosion pits inside the crystal are significantly reduced (Figure 2c, d).

(a) and (b) 100 hours; (c) and (d) 500 hours

![Corrosion morphology after EPR tests of Super304H steel aging treated at 700°C with different aging times](image)
3.2 Micro-structural changes

The micro-structure of HR3C steel after aging at 700 °C for different time periods is shown in Figure 3. After aging, the structure of HR3C steel is still γ-matrix and precipitation phase with no obvious change in the austenite grain size. After 100 hours aging, there is a large amount of precipitated phase in the grain boundary and inside the crystal. Most of the precipitated phase on the grain boundary is in the shape of the chain, and some is in the shape of fine granular. As aging continues, and the number and size of precipitated phase in the crystal increases, and the size of the spheroidal precipitates on the grain boundary continues to grow. After 500 hours, the isolated granular precipitates appear on the grain boundaries.

![Fig.3 Microstructures of HR3C aging treated at 700°C for different aging times](image)

The composition of the precipitated phase in the HR3C steel structure after 500 hours aging is measured using an energy spectrometer, as shown in Figure 4. The precipitated phase is distributed in a discontinuous chain shape or an isolated granular shape on the grain boundary, and the components are mainly Cr, Fe, Ni alloy elements. According to the chemical composition and metallurgical characteristics of HR3C steel [1], the large-scale precipitation phase at the grain boundary is mainly $\text{M}_2\text{C}_6$. The precipitates inside the crystal are dispersed with a relatively smaller size. In the
backscattered image, the precipitates with higher gray level are mainly Nb compounds rich in Cr, Fe, Ni and Nb alloy elements, while smaller precipitates with lower gray level in the crystal are the $M_{23}C_6$.

![Secondary electron image](image1)

![Backscattered-electron image](image2)

(a) Secondary electron image; (b) Backscattered-electron image

Fig. 4 Energy spectrum analysis of precipitated phase in HR3C steel after 500 hours aging

4. Analysis and discussion

The intergranular corrosion of austenitic stainless steel is an electrochemical process. The austenite grain boundary, different from the crystal in the intrinsic composition and structure, forms a multi-electrode system. When the Cr content near the grain boundary is lower than the limit required for passivation (12% Cr), a chromium-depleted region in the grain boundary will emerge. An activation-passivation short-circuit galvanic corrosion cell taking the crystal grain as the cathode and the grain boundary as the anode is formed, resulting in severe anodic dissolution in the chromium-depleted region, and that is how intergranular corrosion occurs [15, 16]. The double-loop EPR method takes $H_2SO_4$ as the passivating agent to form a passivation film on the surface of stainless steel. KSCN is used as the depolarizing agent during reactivation, which causes the rupture of the passivation film covering the sensitized grain boundary and the decrease of the current density. Since the grain and unsensitized grain boundaries are in a passive state, $Ra$ can be used as an indicator to reflect the sensitivity of intergranular corrosion of austenitic stainless steel.

HR3C steel under the state of supply is a supersaturated solid solution, which will precipitate during the aging process. According to the precipitation kinetic curve of $M_{23}C_6$ [17][18], the diffusion coefficients of C and Cr atoms at 700 °C are relatively large and the precipitation rate of $M_{23}C_6$ is relatively fast. In the first 100 hours of aging, $M_{23}C_6$ is mainly precipitated along the $\gamma$ grain boundary and the non-coherent twin boundary. The diffusion of Cr atom is not quick enough to supplement the grain boundary, resulting in a sharp depletion of Cr in this area. The intergranular corrosion sensitivity increases rapidly and the $Ra$ value rises to the peak. As aging continues, the number of size of $M_{23}C_6$ precipitation on the grain boundary increase. The supersaturation of the matrix decreases, and the precipitation rate of $M_{23}C_6$ slows down. In addition, the diffusion rate of Cr atoms remains the same,
and the amount of Cr at the grain boundary increases. In this way, the intergranular corrosion sensitivity of HR3C steel decreases rapidly, and $Ra$ rapidly drops to a lower value. After 300 hours, the rates of $M_2\text{C}_6$ precipitation and Cr diffusion achieve a balance, and the sensitivity of intergranular corrosion is stabilized at a low value. When the $M_2\text{C}_6$ precipitation is stable, the precipitation phase on the grain boundary grows into larger isolated granular due to Ostwald ripening. Inside the crystal, $M_2\text{C}_6$ and Nb compounds also precipitate mainly in the form of fine particles. The boundary with large-sized Nb compound particles is also the place for $M_2\text{C}_6$ to precipitate rapidly. $M_2\text{C}_6$ inside the crystal grains also causes chromium depletion in the surrounding area, thus leading to corrosion.

5. Conclusion

(1) In the HR3C steel under 700 °C aging condition, $M_2\text{C}_6$ rapidly precipitates along the crystal with an increasing number, which leads to a rapid increase of intergranular corrosion sensitivity. As aging continues, the precipitation of $M_2\text{C}_6$ gradually becomes stable and grows into larger and isolated particles. After that, the intergranular corrosion sensitivity of HR3C steel is stabilized at a low level.

(2) The main reason for the intergranular corrosion of HR3C steel after aging treatment is the precipitation of $M_2\text{C}_6$ along the grain boundary. The morphology and size of $M_2\text{C}_6$ also matters in the regard. At the same time, $M_2\text{C}_6$ precipitation also causes corrosion of Cr around it.

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