Research of intergranular corrosion properties of heat affected zone for HR3C steel after aging treatment

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Abstract: The intergranular corrosion susceptibility of heat affeceed zone(HAZ) for HR3C steel after aging at 600℃ was investigated using electrochemical double-loop potentiokinetic reactivation. Experimental results show that HAZ has intergranular corrosion susceptibility after aging at 600℃. At the initial stage precipition of $M_{23}C_6$ along grain boundaries occurs rapidly, which leads to formation of Cr-depleted in the grain boundary and the increase of intergranular corrosion susceptibility. With the increase of aging time, the Ra value of HAZ rapidly increase. Intergranular corrosion of HAZ after aging occur due to the precipitation of $M_{23}C_6$ along grain boundaries, not only the precipitation of $M_{23}C_6$ along grain boundaries caused poor Cr, but the precipitation of $M_{23}C_6$ inside the grains also results in the formation of Cr-depleted zone and subsequent corrosion.

1. Introduction

Energy efficient and environmental friendly, Ultra Supercritical (USC) units have become an important measure to optimize the energy structure, save energy and reduce emissions in China. So far, more than 100 USC units have been put into operation and have grown into the main unit in China's thermal power generation. In addition, China also has the largest number of USC units in the world. With its rapid development, austenitic heat-resistant steels such as HR3C (25Cr-20Ni-Nb-N) see wider application in parts of superheaters and reheaters in the demanding operating environments of the USC boiler[1-4], which may lead to the severe corrosion of sodium and potassium sulphate on the fire side. Worse still, the operating temperature of HR3C steel components is within the temperature range where sodium and potassium sulphate are most corrosive[2]. Therefore, attention must be paid to changes in the sensitivity of HR3C welded joints to intergranular corrosion during operation.

The intergranular corrosion resistance of austenitic stainless steels tends to change when it is heated or welded[5-8], especially in the affected zone. Whether its corrosion resistance after multiple welding thermal cycles is sufficient and how intergranular corrosion resistance changes after high temperature operation are issues worth more attention to ensure safe operation of components. However, there are few studies on the intergranular corrosion performance of HR3C steel [9-11], In addition to this research group without any research report on the intergranular corrosion resistance of HR3C steel welded joints[12]. Therefore, it is of practical significance to conduct studies concerning the

intergranular corrosion resistance of the affected zone of HR3C steel after welding. This paper studies the performance change of intergranular corrosion of the affected zone of HR3C steel after 600°C heating and explores the root causes for intergranular corrosion using the double-ring electrochemical potential reactivation method to facilitate wider application of HR3C steel and selection of proper welding and repairing techniques.

2. Test material and method

2.1 Test material

The HR3C steel pipe was produced by Sumitomo Corporation of Japan, with the specification ofΦ45mm×9.6mm, and its supply state was solid solution treatment.Its chemical composition was measured by the SPECTROLAB quantitative spectrometer, as shown in Table 1. Compared with the standard components, there was a non-standard stipulated element Mo in the steel used to improve the strength of the steel under high temperature [13]; the other elements were basically listed in the standard components, except N, which was not detected due to the sample taken here.

Table 1. Chemical composite of HR3C tube (wt, %)

element	C	Si	Mn	P	S	Cr	Ni	Mo	Nb	N
GB5310-2008	0.04-0.10	≤0.75	≤2.00	≤0.030	≤0.015	24.00-26.0	19.0-22.0	-	0.20-0.6	0.15-0.35
measured	0.06	0.35	1.18	0.019	0.003	25.3	19.8	0.13	0.39	-

2.2 Test method

The HR3C steel pipe was processed into a V-shape groove joint and welded at a fixed position of 45°using GTAW. The welding process parameters are shown in Table 2.

Table 2. Weld parameters

Layer number	Welding current I/A	Welding voltage U/V	Welding speed mm/s	Interlaminar temperature T/°C
1-6	70-90	10-12	20-50	≤150

After passing the internal and external inspections after welding, we processed the sample of HR3C steel in the heat affected zone using the wire cutting method. It was placed in the SX2 12-16 resistance furnace for high temperature aging treatment in the air with temperature of 600 °C and the aging time of 100h, 200h, 300h, and 500h, respectively, before it was cooled in the furnace.

The DL-EPR was used to test the intergranular corrosion sensitivity of HR3C steel in the heat affected zone based on the standard [14]. The size oft he sample was 1 cm × 1 cm × 0.3 cm with a working area of 1 cm^2. The samples of each state were tested at least for 3 times, and the mean of the three effective values was taken as the value of the corresponding state. The test was carried out on a PARSTAT 2273 electrochemical workstation using a three-electrode working system with the reference electrode being a saturated calomel electrode (SCE)and the auxiliary electrode being a platinum electrode. The solution was 0.50 mol/LH_2SO_4 + 0.01 mol/LKSCN, and the pot was used to maintain the temperature at 25 ± 1 °C. During the test, the sample was first immersed in the solution for 10 minutes to obtain a stable corrosion potential; then anode polarization potential scanning was performed at a rate of 1.67 mV/s until a passivation potential of 300 mV (SCE) was reached. After that, reverse scanning was immediately conducted at the same time until the corrosion potential was reached. The double-ring EPR method was used to determine the EPR according to the ratio $R_a=I_r/I_a$ after the activation current Ia and the reactivation current Ir were measured. The higher the R_a, the higher the intergranular corrosion sensitivity (I_r was the maximum anode current for reverse scanning; I_a was the maximum anode current for forward scanning).

The metallographic samples of the HR3C steel in the affected zone were ground and polished after welding; then it was corroded using aqua regia and its microstructure under the SUPRA 55 thermal radiation scanning electron microscope was observed. After the EPR test,the sample was rinsed with water and alcohol, and its morphology after corrosion was observed through the scanning electron

microscope.

3.Test result and analysis

3.1 Intergranular corrosion performance of HR3C steel in the heat affected zone after aging
The reactivation rate R_a of the HR3C steel in the affected zone at different temperatures after 600 °C aging is shown in Figure 3. The R_a value of the HR3C steel in the affected zone under the welding condition was 0.058, greater than 0.05 in comparison with the evaluation standard, which indicated a tendency of intergranular corrosion in the heat affected zone. After aging at 600 °C, the R_a value of the heat affected zone increased.
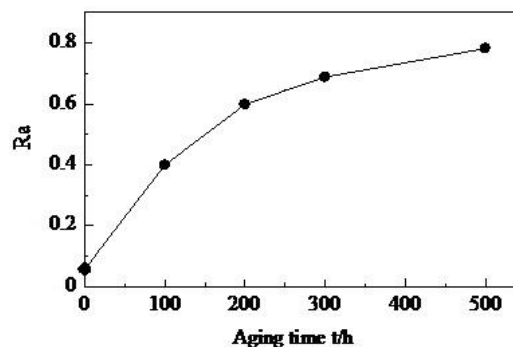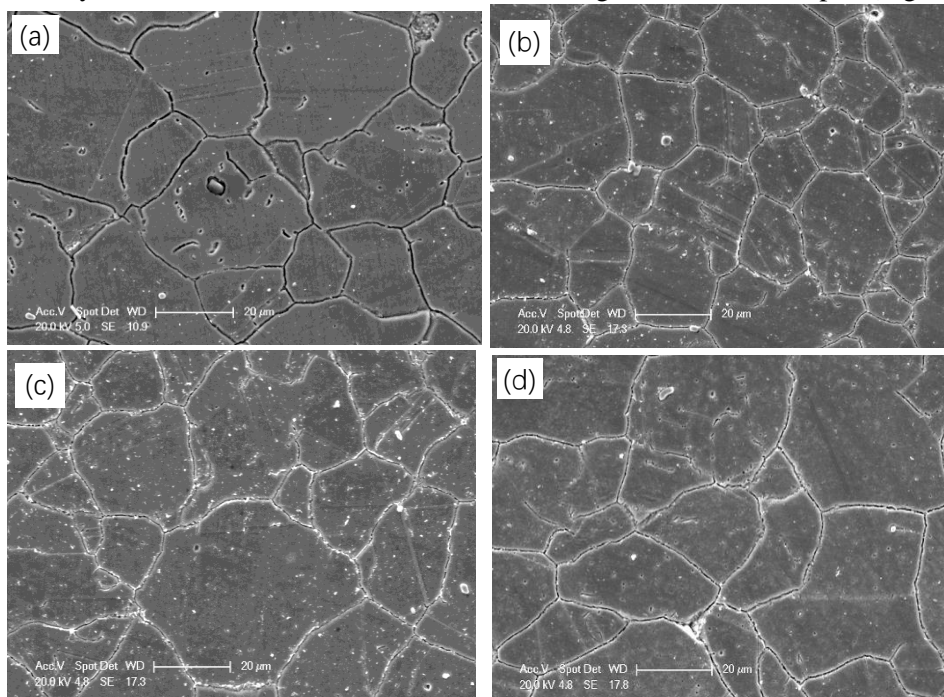

Figure 1 Change of R_a of HAZ for HR3C steel versus aging time

Figure 2 shows the corrosion morphology of the HR3C steel in the heat affected zone after EPR tests. Under the welding condition, the affected zone showed obvious intergranular corrosion characteristics. Corrosion grooves appeared in the austenite grain boundary when corrosion pits appeared in the crystal (Figure 2a). After aging at 600 °C for 100 hours, almost all grain boundaries were corroded to some extent with more intragranular corrosion pits. As aging time increased, the grain boundary was further corroded with even more intragranular corrosion pits (Figure 2c, d).
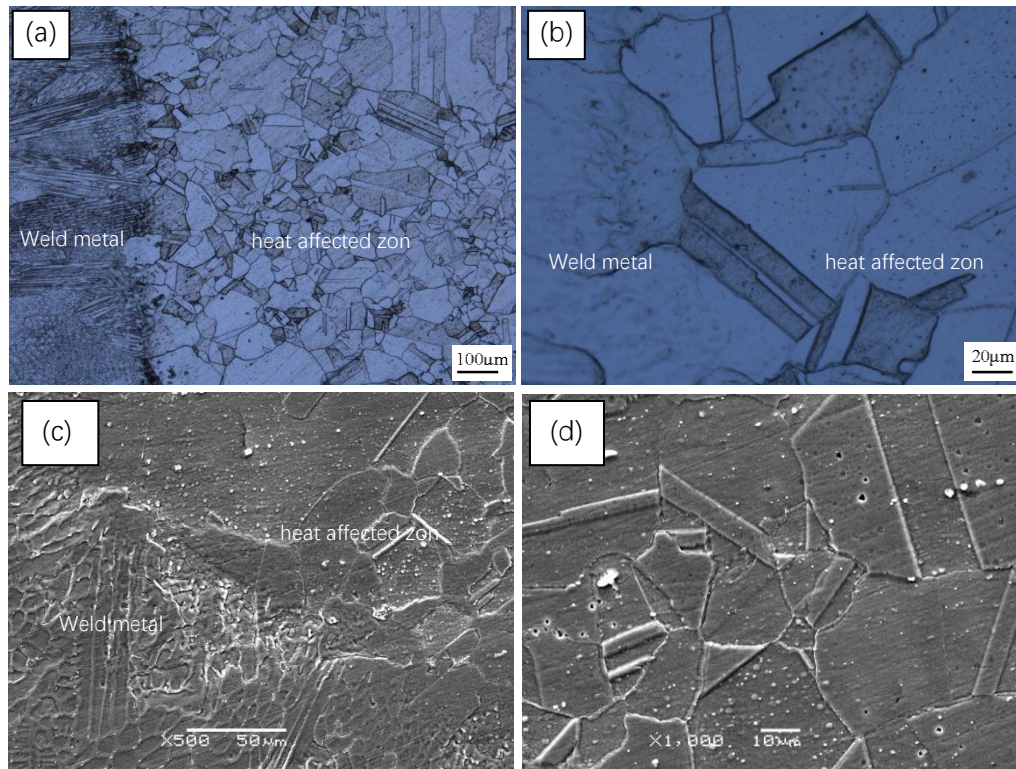

(a) under welding condition; (b) 100h; (c) 200h; (d) 500h
Figure 2 Corrosion morphologies of HAZ for HR3C steel after being aged at 600°C

3.2 Microstructural change of HR3C steel in the affected zone after 600 °C aging
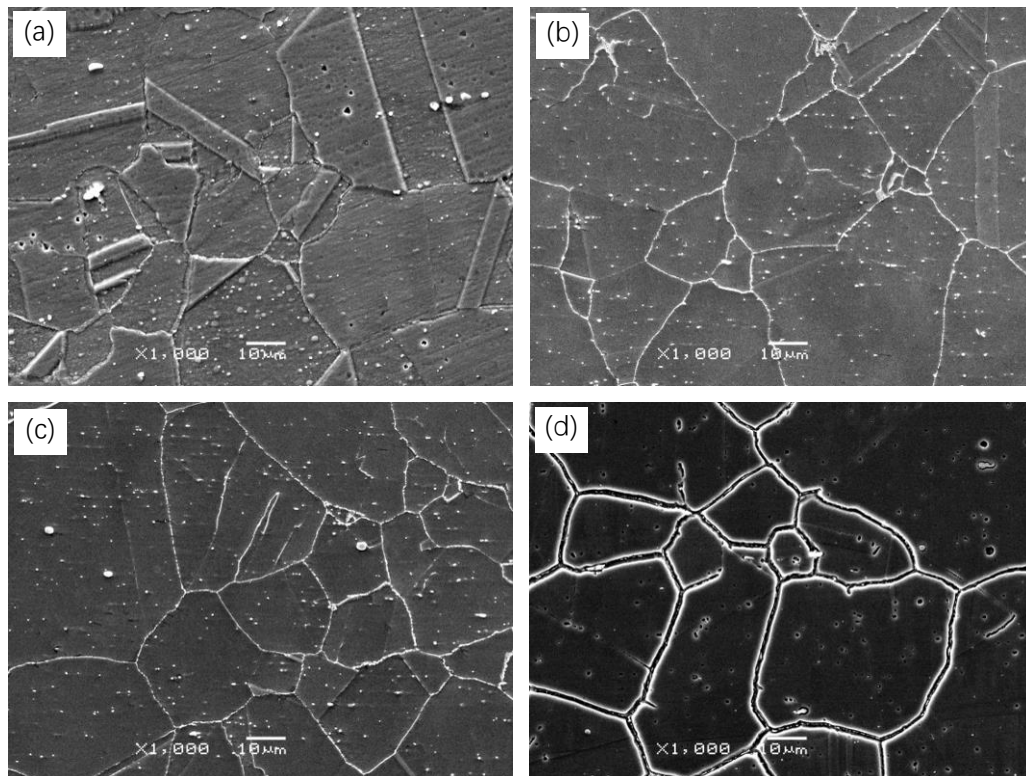The points in the heat affected zone of HR3C steel experienced different welding thermal cycles. The size of the grain near the welding zone grew bigger (Fig. 3). And there are some twin in the structure. while the precipitated phases away from the welding zone increased in number.

(a) Metallographic photograph×100;   (b) Metallographic photograph×500;
(c) SEM photograph ×500;   (d) SEM photograph ×1000
Figure 3 Microstructure of HAZ for HR3C steel under welding condition

However, due to the short duration of the high temperature, fast cooling rate, and the state of supersaturated solid solution, the precipitated phase also changed during high-temperature aging. The precipitation phase change in the affected zone after aging at 600 °C is shown in Figure 4. The precipitated phase mainly dispersed in the crystal as fine particles while fine granular, strip-like and large-sized strips were dispersed at the grain boundary. After aging for 100hours, the larger strip-shaped precipitated phase appeared at the grain boundary(Figure 4b). As the aging time lengthened, the number of large strip-shaped precipitates increased. They were linked to each other, almost covering the entire austenite grain boundary (Figure 4d).

(a) welding condition; (b) 100h; (c) 300h; (d) 500h

Figure 4 Microstructure of HAZ for HR3C steel after aging at 600°C

The result of preliminary research shows that the structure of the affected zone of HR3C steel under the welding condition comprised a single austenite structure and a precipitated phase. The XRD analysis shows that the precipitated phase is mainly composed of $M_{23}C_6$ and Nb (C, N).

4. Analysis and discussion

Corrosion electrochemical studies pinpointed that the intergranular corrosion of austenitic stainless steel is an electrochemical process. Because the Cr content near the austenite grain boundary is lower than the limit of passivation (12% Cr), the chromium-depleted zone of the grain boundary is formed, leading to an anode-activated-passivated short-circuit galvanic corrosion cell with the crystal grain as the cathode and the grain boundary as the anode. In this way, severe anodic dissolution in the chromium-depleted zone of the grain boundary is generated, thereby resulting in intergranular corrosion [15,16]. According to the precipitation kinetics curve, $M_{23}C_6$ quickly precipitated at a temperature of 600 °C, and it precipitated along the γ grain boundary and non-coherent twin boundary in the initial aging time. As the aging time prolonged, the number of precipitated phases on the grain boundary increased. Since a large amount of Cr near the grain boundary was consumed as the $M_{23}C_6$ precipitated along the austenite grain boundary, insufficient Cr led to a smaller amount of Cr near the grain boundary than the limit, thus forming the galvanic corrosion cell with the grain boundary as the anode and grain as the cathode, thereby causing intergranular corrosion in the Cr-depleted zone in grain boundary.

The available state of HR3C steel is a supersaturated solid solution. Due to rapid heating and cooling, the affected zone is also in the state of supersaturated solid solution with precipitated phase appearing in the affected zone during aging at 600 °C. Due to the influence of the welding thermal cycle, a large amount of $M_{23}C_6$ precipitated in the affected zone under the welding condition[12]. Therefore, the heat affected zone showed a tendency of intergranular corrosion in the welding state. After aging at 600 °C, $M_{23}C_6$ in the affected zone continuously precipitated with both a low precipitation rate and diffusion coefficient of Cr because the aging temperature of 600 °C was

relatively low. As a result, the value of R_a continuously increased. In the initial aging, $M_{23}C_6$ mainly precipitated along the austenite grain boundary and the non-coherent twin boundary in the form of small-size precipitated phase. Some depleted Cr appeared at the grain boundary; after the EPR test, deep corrosion grooves also appeared there, leading to an increase of the value of R_a. As the aging time prolonged, the precipitation of $M_{23}C_6$ phase and the degree of depleted chromium on the grain boundary both increased steadily, leading to an increase of the R_a value. From the corrosion morphology, it can be seen that there were a certain number of corrosion pits in the austenite crystal. That is to say, $M_{23}C_6$ not only crystallized out along the crystal and led to Cr depletion, but also precipitated inside the crystal and caused Cr depletion around the particles, which exacerbated corrosion.

5. Conclusion

  (1) Under the welding condition, the affected zone of the HR3C steel shows a tendency of intergranular corrosion. The R_a value and the sensitivity of intergranular corrosion both increase during the aging process at 600 °C.

   (2) The precipitation of $M_{23}C_6$ phase along the crystal is the root cause for intergranular corrosion in the heat affected zone of the aging HR3C steel. Meantime, the precipitation of $M_{23}C_6$ in the crystal also causes corrosion around it.

Author brief introduction:

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