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Evaluation of intergranular corrosion susceptibility of Super304H steel after being aged at 600°C

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Abstract: The susceptibility to intergranular corrosion of as-received and 600°C aging-treated new austenite heat-resistance Super304H steel was investigated by double loop electrochemical potentiodynamic (EPR) test. Experimental results indicated that the as-received Super304H steel possesses lower tendency of intergranular corrosion. With the increase of aging time, intergranular corrosion susceptibility of Super304H steel increases. Intergranular corrosion of Super304H steel occurs due to the precipitation of Cr_{23}C_6 along grain boundaries. At the initial stage of aging, the rapid precipitating behavior of Cr_{23}C_6 leads to the rapid increase of intergranular corrosion susceptibility. The amount of Cr_{23}C_6 precipitates increases with the extension of aging time, and the intergranular corrosion susceptibility of Super304H steel increases accordingly. The extent of intergranular corrosion change is related to the precipitating rate of Cr_{23}C_6 . ()

1. Introduction

Ultra-supercritical (USC) units are the inevitable trend of current thermal power generation, and the development and application of new materials have always been a key technical problem for USC units. Therefore, countries around the world have successively researched and developed a series of new heat-resistant steels which have been successfully applied to the operation of the unit. Super304H steel, developed by Japan's Sumitomo Metals corporation and Mitsubishi Heavy Industries Co., Ltd. is one of the new heat-resistant steels which are widely used at present. On the basis of TP304H, by reducing the upper limit of Mn content, adding about 3% Cu, 0.45% Nb and a certain amount of N, the steel precipitates copper-rich phase, NbCrN, and Nb (C, N) in the service process, and together with M_{23}C_6 produce excellent strengthening effect to improve the creep fracture strength; Meanwhile, by increasing the softening treatment temperature and reducing the solution treatment temperature, finer grains are obtained to improve the steam oxidation corrosion resistance of the steel ^[1-7], mainly used in superheater and reheater parts of USC units. In the boiler of the thermal power unit, heating surface tubes of the superheater and the reheater are arranged in the area where the boiler smoke temperature is relatively high, so the environmental conditions of the pipeline in operation are the worst, and its



side to the fire is severely corroded due to the presence of sodium potassium sulfate. Since the carbon content of Super304H steel is higher than that of TP304H, and its application temperature in the ultra-supercritical boiler is in the range of 600-650 °C, the variation of its resistance to intergranular corrosion sensitivity must be paid attention to during the operation. Therefore, it is urgent to conduct an in-depth study on the intergranular corrosion resistance of Super304H steel under high temperature conditions. In this paper, the electrochemical potentiokinetic reactivation (EPR) method was used to study the variation of intergranular corrosion sensitivity of Super304H steel after being aged conditions at 600 °C, which provided a theoretical basis for the effective supervision of Super304H steel operation.

2. Materials and methods

2.1 Experimental materials

The steel sample was a Super304H steel tube produced by Sumitomo Corporation of Japan, with the specification of $\Phi 45 \text{ mm} \times 9 \text{ mm}$, of which the chemical composition was measured by SPECTROLAB quantitative spectrometer and the results are shown in Table 1. From the measured composition, there is a non-standard stipulated element Mo in the steel, which should be beneficial to improve the high temperature creep rupture strength of the steel and enhance the corrosion resistance of austenitic stainless steel [9]; The other elements are basically within the constituents specified in the standard, except N, which is not detected due to the standard sample.

Table 1 Chemical composition of Super304H steel (mass fraction /%)

Standard	Chemical composition											
	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	Nb	N	B
ASTM	0.07-	\leq	\leq	\leq	\leq	17.00-	7.50-		2.50-	0.20-	0.05-	0.001-
A 213	0.13	0.30	1.00	0.040	0.010	19.00	10.50	-	3.50	0.60	0.12	0.010
Measured	0.10	0.22	0.85	0.033	0.006	18.4	8.56	0.26	2.41	0.48	-	-

2.2 Experimental methods

The sample was placed in a SX2 12-16 box type resistance furnace and aged under air conditions at a temperature of 600 °C, for the aging time of 100 h, 200 h, 300 h and 500 h, respectively, and cooled with the furnace.

The EPR sample was processed to $1 \times 1 \times 0.3 \text{ cm}$, with the working area of 1 cm^2 , and the working surface was ground and polished. The electrochemical apparatus was PARSTAT 2273, adopting a three-electrode working system with a saturated calomel electrode (SCE) as reference electrode and a platinum electrode as the auxiliary electrode, and the test solution is $\text{H}_2\text{SO}_4(0.50 \text{ mol/L}) + \text{KSCN}(0.01 \text{ mol/L})$, using an electric thermostatic water bath to keep the testing environment temperature at $25 \pm 1 \text{ }^\circ\text{C}$. During the experiment, the sample was immersed in the solution for 10 min to obtain a stable corrosion potential, and then the anode polarization potential scan was performed at a rate of 1.67 mV/s . After scanning to the passivation potential of 300 mV (SCE), reverse scanning was immediately conducted to the corrosion potential at the same scan rate. The double-loop EPR method measures the activation current I_a and the reactivation current I_r , of which ratio $R_a = I_r / I_a$ was used as the criterion of EPR. The higher the reactivation rate R_a , the higher the sensitivity of intergranular corrosion, while I_r is the maximum anode current during reverse scanning, and I_a was the maximum anode current during the frontal scanning.

The metallographic samples were etched with aqua regia. The micromorphology was observed on a JSM-6380LA scanning electron microscope, while the morphology of the etched samples was observed on a SU-70 thermal field emission electron microscope. The phase compositions of each sample were determined by D/max-rc X-ray diffractometer with the specific parameters: Cu target as

the target material, the scanning range of 20° - 90° , the acceleration voltage of 45kV, the current was of 100mA, and the scanning speed of 2° / min, continuous scanning by stepping 0.020° .

3. Experiment results

3.1 EPR experiment results

The polarization curve of Super304H steel as-received is shown in Fig. 1, where R_a is 0.003, less than the lower limit of 0.01 in the standard ^[10], so the original base material has no obvious intergranular corrosion tendency.

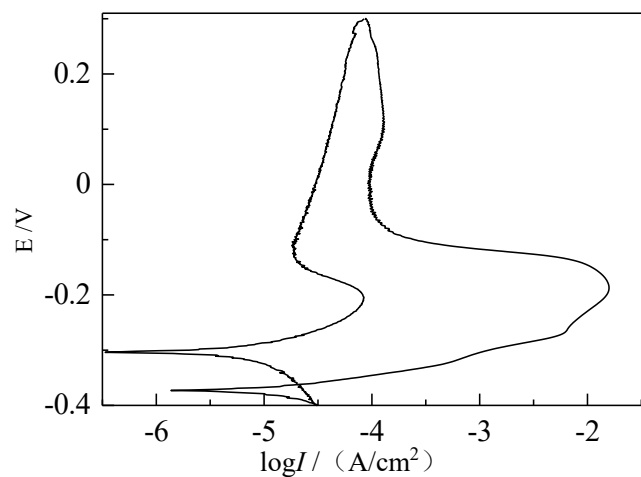


Fig.1 Curves of EPR for Super304H steel as-received

After being aged at 650°C for different times, R_a of each sample are shown in Fig. 2. With the aging time extension, the value of R_a increase rapidly, and the growth rate of R_a becomes slower after the aging time exceeds 300h.

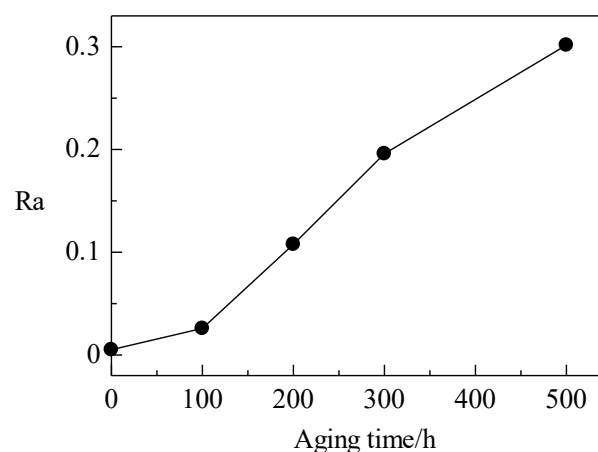
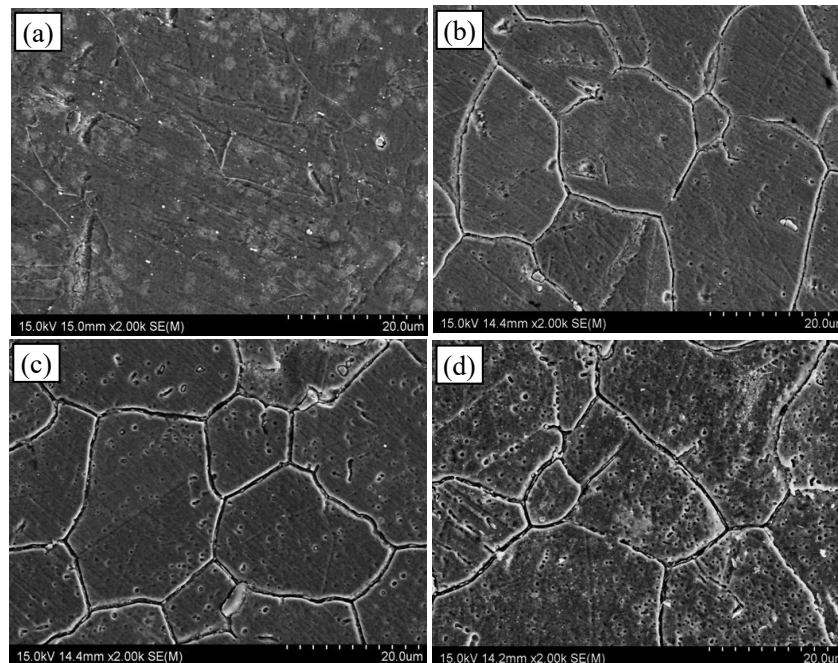


Fig.2 The variation of R_a of Super304H steel under different aging times

3.2 Corrosion morphology observation

After the EPR experiment, the corrosion morphology of the sample is shown in Fig. 3. The original parent metal grain boundary has only slight signs of corrosion, and the grain boundary is basically intact. When the sample is aged at 600°C for 100h, part of the grain boundaries are corroded, and a

certain width of corrosion grooves appear on the grain boundary. As the aging time extends, the proportion of the corrosion grain boundary increases, and the corrosion width also gradually enlarges. A small number of corrosion pits also appear inside the austenitic grains at 500 h, but the depth of the corrosion pits is shallow.



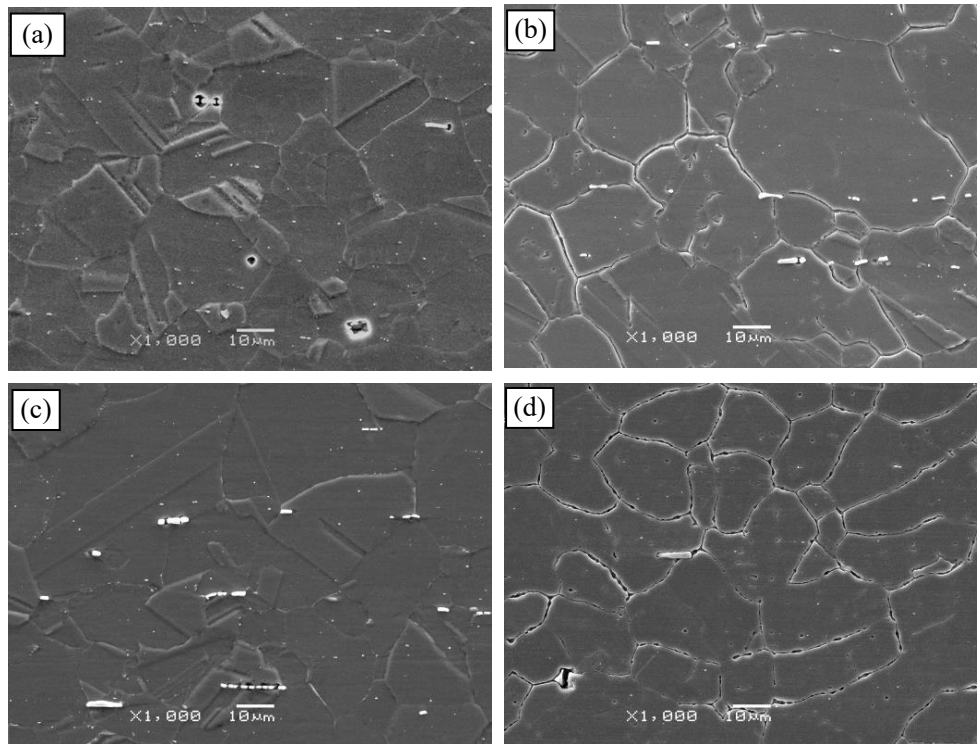
(a) Original base material; (b) 100h; (c) 300h; (d) 500h

Fig.3 Corrosion morphology of Super304H steel after being aged at 600°C for different time

3.3 Microstructure observation

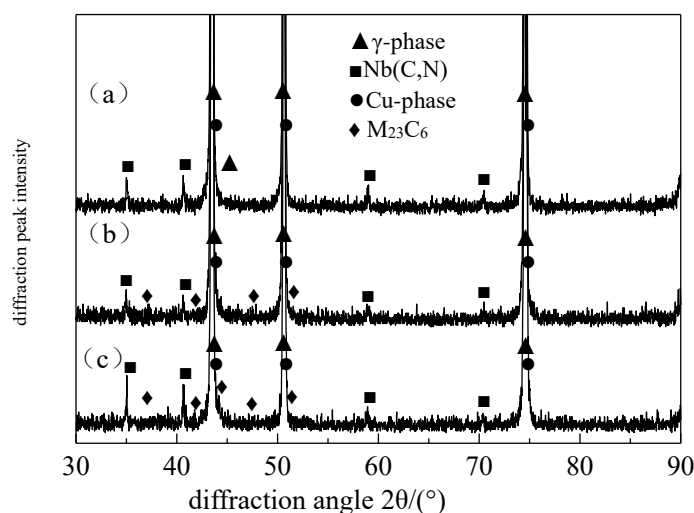
The microstructures of Super304H steel as-received and after being aged at 600 °C are shown in Fig. 3. The microstructures are all γ + precipitated phases, and the number, shape and distribution of the precipitated phases change with time.

The precipitated phases in Super304H steel as-received are mainly Nb(C,N) and Cu-rich phase. There are two kinds of Nb(C,N): one is a shape of strip and block, with a directional distribution due to deformation during the forming process, and due to the high temperature stability this morphology and distribution can be maintained in the structures which are aged for different time; The other is a fine spherical Nb(C,N) of dispersive distribution, a product precipitated during the solution treatment and the aging process ^[11,12]. After aging at 600 °C for 100 h, a small number of thin-strip or fine-grained precipitated phases precipitate on the γ grain boundary, and the number of precipitated phases in the crystal has no significant variation compared those as-received; After 200h, the number of precipitated phases in the crystal gradually increases, at this time, the morphology of the precipitated phase in the grain boundary has been distributed in small particles, and the number has enlarged; At 300 h, the precipitated phase on the γ grain boundary is mainly in the form of granules, strips and blocks. The precipitated phase particles on some grain boundaries are linked to each other and the sizes are also increased. Further extension of the aging time enlarges the number and size of the precipitated phases.



(a) Original base material; (b) 100h; (c) 300h; (d) 500h
Fig.4 Microstructure of Super304H steel after being aged at 600°C

The sample was analyzed by X-ray diffraction, and the results are shown in Fig. 5. Super304H steel before being as-received was subjected to solution treatment, and the precipitated phase in the structure was Nb(C, N) and Cu-rich phase. Since M₂₃C₆ was almost dissolved completely during the softening treatment, it was too late to precipitate during the rapid cooling process in the solution treatment, so a supersaturated γ solid solution was formed. After the aging at 600 °C, precipitation of precipitated phase occurred in the supersaturated γ solid solution. At this time, in addition to Nb(C, N) and Cu-rich phase, M₂₃C₆ type of carbide was newly precipitated in the structure.



(a) The as-received state; (b) 100h; (c) 500h
Fig.5 X-ray diffraction patterns of Super304H steel after being aged at 600°C

4. Analysis and discussions

Electrochemical corrosion theory believes that grain boundary corrosion is an electrochemical process^[13]. Since the precipitation of Cr_{23}C_6 along the γ grain boundary at a certain temperature consumed a lot of Cr near the grain boundary, if Cr could not be replenished from the grains inside to the grain boundary in time, the Cr content near the grain boundary would be lower than the limit required for passivation, forming a galvanic corrosion cell with the crystal grains as the cathode and the grain boundary as the anode, which resulted in intergranular corrosion in the Cr-poor grain boundary region.

X-ray diffraction analysis showed that there was no Cr_{23}C_6 in the microstructure of Super304H steel as-received, and the reactivation rate Ra in the EPR experiment was 0.003, much lower than the lower limit specified in the standard, which illustrated no obvious intergranular corrosion tendency in the as-received state. From the SEM topographies after corrosion, the γ grain boundary is basically complete, and only slight signs of corrosion appear in some grain boundaries. It can be considered that even if Cr_{12}C_6 was precipitated in the structure, its quantity was little. In the structure of Super304H steel as-received, all M_{23}C_6 were dissolved, so there is no obvious tendency of intergranular corrosion.

After aging at 600 °C, M_{23}C_6 began to precipitate rapidly at the beginning of aging. At this time, the precipitated M_{23}C_6 were mainly distributed along part of the grain boundaries due to their relatively small amount, and the shapes were fine strips or granules, which caused a certain lack of Cr on part of grain boundaries. During the EPR experiment, part of grain boundaries were corroded to form corrosion grooves, which led to an increase in the reactivation rate Ra; However, due to the relatively low aging temperature, the atomic diffusion coefficient was comparatively small, and the precipitation of M_{23}C_6 did not increase significantly. As a result, the precipitated phases on the grain boundaries were mainly of interrupted distributions, and the deficiency of Cr was not very serious, which brought about a small increase in Ra; With the extension of aging time, due to the slowly increase of the precipitation of M_{23}C_6 , and the deficiency of Cr on the grain boundaries was gradually enhanced, reflecting that Ra tended to increase gradually. In the meantime, fine-grained M_{23}C_6 were also precipitated in a small amount position of the crystal, which also caused deficiency of Cr on the particle boundaries, but the finer the precipitated phase, the weaker degree of the deficiency of Cr.

5. Conclusions

(1) When Super304H steel was aged at 600 °C, the precipitation speed and the distribution pattern on the grain boundaries of Cr_{23}C_6 were all changed with the extension of the aging time.

(2) During the aging process of Super304H steel, the precipitation increases of Cr_{23}C_6 s led to the continuous enhance of intergranular corrosion sensitivity. Cr_{23}C_6 not only precipitated along the crystal causing Cr deficiency and intergranular corrosion, but also precipitated inside the crystal, also resulting in Cr deficiency around it and corrosion.

Author introduction

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