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Localized Corrosion of Thermally Aged Cast Duplex Stainless Steel for Primary Coolant Pipes of Nuclear Power Plant

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Abstract

Localized corrosion of cast duplex stainless steel Z3CN20.09M, which used widely in primary coolant pipes of nuclear power plants, has been investigated after thermally aged at 400℃ for 100, 300, 1000 and 3000h by making use of electrochemical method. Double loop electrochemical potentiodynamic reactivation (DL-EPR) and potentiodynamic polarization tests were used for assessing intergranular corrosion (IGC), pitting and general corrosion resistance, respectively. The experimental results showed that the general corrosion resistance of Z3CN20.09M did not change almost with increase of thermal aging time, however, IGC and pitting corrosion resistance decreased. In the polarization curves, the peak anodic current density of general corrosion was not found to change almost with increase of thermal aging time, but DL-EPR results showed that the value of Ir/Ia increased. The deterioration in localized corrosion resistance of thermally aged specimen was directly related to the precipitation of alpha prime phase in ferrite by spinodal decomposition.

Keywords: Cast duplex stainless steel; thermal aging; pitting and intergranular corrosion; primary coolant pipes; nuclear power plant

1. Introduction

Duplex stainless steels (DSSs), which constitute both ferrite and austenite dual phase, are widely used in oil, chemical, petrochemical, marine and nuclear power industries, as they are characterized by high

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strength, good toughness, very outstanding corrosion resistance in general and excellent resistance to stress corrosion cracking and corrosion fatigue in particular [1-3]. However, DSSs are inherently susceptible to thermal embrittlement at elevated temperatures. It is well known that DSSs will be normally suffered from thermal aging embrittlement when they are exposed to longer time at elevated temperature aging (<550℃). In general, the thermal aging of cast duplex stainless steels suffered at temperatures between 300 and 550℃ often causes an increase in hardness and tensile strength. Of course, the thermal aging causes normally a decrease in ductility, Charpy impact energy and J_{IC} fracture toughness of the material [4-6]. The main reason of that is due to the spinodal decomposition from ferrite into fine α' chromium rich precipitates and Cr-depleted matrix [5-9]. α' phase is harder than ferrite and will decrease steel's toughness. For the change of microstructure, the corrosion resistance of aged DSS will be degraded to some extent, especially for localized corrosion resistance [10-13].

Primary coolant pipe is a key component of nuclear power plant (NPP) and usually made from cast duplex stainless steels, for example Z3CN20.09M DSS. The mechanism of thermal aging of Z3CN20.09M DSS has been made by researchers [14-16], but there are no reports about corrosion behavior of aged Z3CN20.09M. In the present work, the effect of thermal aging time on corrosion behavior of Z3CN20.09M DSS was investigated and the aim of this study is trying to establish the relationship between thermal aging and localized corrosion behavior of above material.

2. Material and experimental procedures

The as-received specimen was commercial type Z3CN20.09M cast duplex stainless steel, and its chemical composition (wt %) is listed in table1. The as-received specimens were aged at 400℃ for from 100 h to 3000 h following air cooling. After aging treatment the samples were cut into 10mm × 10mm × 3mm size for electrochemical tests, and then burnished to 2000 # by emery paper and polished to 0.5μm finally using diamond abrasive paste for preparation of next etch and electrochemical etch test.

The polarization tests were used to evaluate general and pitting corrosion resistance of the aged samples. The working electrodes were prepared by spot welding a lead wire onto one side of each sample and then mounted by epoxy resin. The reference electrode was a saturated calomel electrode (SCE) and a Pt foil was used as the auxiliary electrode. The electrolyte solutions were used 0.5M/L H_2SO_4 and 3.5 wt% NaCl respectively for general and pitting corrosion resistance tests.

A double loop electrochemical potentiodynamic reactivation (DL-EPR) test was used for assessing the intergranular corrosion (IGC) resistance. The DL-EPR tests were initiated after nearly steady-state open circuit potential (E_{oc}, ~400mV) and then developed potential sweep in anodic direction at 0.83mV/S until the potential of 400mV (vs. SCE) was reached. The scan was reversed in the cathodic direction until the E_{oc} at the same scan rate. The electrolyte was 0.5M H_2SO_4 + 0.02M/L KSCN solution. The loss of intergranular corrosion resistance (or degree of sensitization – DOS) was evaluated by measuring the ratio of maximum current density in the reverse scan I_r to maximum current density in the active scan I_a. The higher I_r/I_a value, the more susceptive to IGC of DSSs also.

It is noteworthy that all polarization tests mentioned above were carried out at 30±1℃ in order to make the results comparable.

Table 1 Chemical composition of Z3CN20.09M cast duplex stainless steel (wt %).

C	Si	Mn	P	S	Cr	Ni	Cu	Co	Nb+Ta	B	Mo	N	Ti
0.024	1.09	1.11	0.023	0.0039	20.16	9.06	0.031	0.026	0.066	0.0001	0.26	0.033	0.0027

3. Results and discussion

3.1. General corrosion

Figure.1 shows the anodic polarization curves of thermally aged and un-aged specimens in 0.5M/L H_2SO_4 solution. All tested specimens show the same corrosion current density I_{corr} of 10^{-5} Acm^{-2} and corrosion potential E_{corr} of 330 mV. This means that the same general corrosion resistance of specimens under different thermal aging time treatment was indicated. The potentiodynamic tests results showed that there was no influence of thermal aging on the general corrosion resistance of Z3CN20.09M DSS in the 0.5M/L H_2SO_4 solution. Although the microstructure of specimens has changed obviously with increase of thermal aging time from 100 h to 3000 h at 400℃[15-16], the general corrosion resistance of specimens has no variation remarkably maybe due to general corrosion resistance is not susceptibility to microstructure but depends strongly on alloy elements.

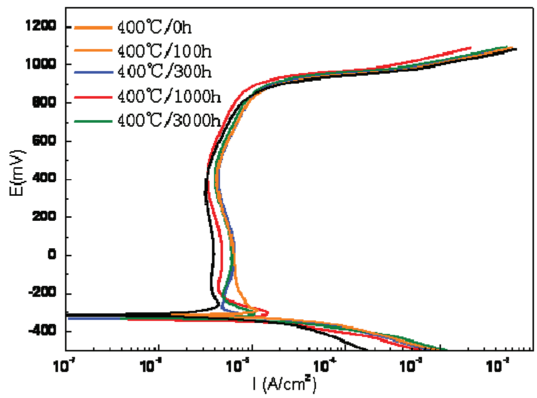


Fig.1. Polarization curves of general corrosion test in 0.5M H_2SO_4.

3.2. Pitting corrosion resistance

The pitting resistance equivalent number (PREN) was often used as a guide to the tendency of stainless steels to pit and it is given as (wt-%Cr) + 3.3(wt-%Mo) + 16 (wt- %N) [17]. However, PRE can only be used to assess the pitting resistance of well-annealed materials. Various precipitate phases due to welding or aging treatments, for example, would adversely affect the pitting resistance of a material. Certain phases can be sites for preferential initiation of pits, whereas others can cause depletion of chromium, nitrogen, and molybdenum to initiate pits in the depletion zones. Clearly, the difference of pitting corrosion resistance of thermally aged specimens can not be indicated by PREN due to the same alloy elements of all specimens, however it can be concluded from the polarization curves (as shown in Figure 2) of the pitting corrosion test in a solution containing 3.5wt% NaCl and micrographs of pits (as shown in Figure 3) after pitting corrosion tests. The pitting potential (E_p) was defined at the potential where the anodic current density exhibited a sharp and sustained increase from the background passive current density. A stable pit starts growing and developing at above E_p where the current increases sharply from the passive current level. It is generally considered that materials exhibiting higher values of E_p are more resistant to pitting corrosion. In Figure 2, the aged DSS showed a lower pitting potential compared with un-aged sample. Moreover, E_p has decreased with an increase in thermal aging time and reached the lowest value at aging time 3000 h as shown in Figure.3. So, the longer thermal aging time, the worse corrosion resistance of Z3CN20.09M. The results can be confirmed by the small pit micrographs of thermally aged specimens after tests shown in Figur.4. It can be seen that the number of pits has increased with aging time (from 100 h to 3000 h). These pits will be formed pitting corrosion source in the subsequent process. Apparently, the pitting corrosion resistance of the specimen aged for 3000 h was very poor. Figure.5 shows the pits morphology of specimens thermally aged for (a) 100 and (b) 1000h after pitting corrosion. In can be seen that the pits originated from ferrite and grown along it finally from this picture. And the number and size of pits has increased with thermally aging time. So, the effect of thermal aging treatment on the pitting corrosion resistance of Z3CN20.09M is adverse.

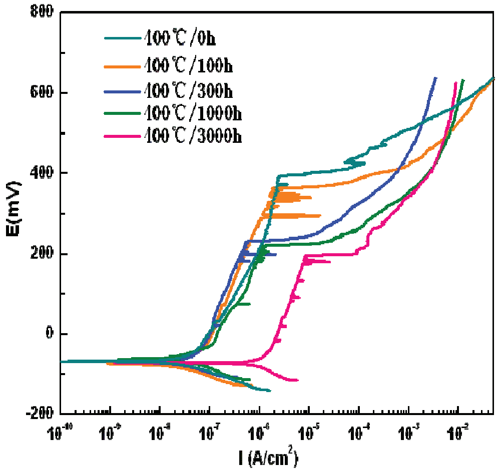


Figure.2. Polarization curves of pitting corrosion of thermally Aged specimens test in 3.5wt% NaCl.

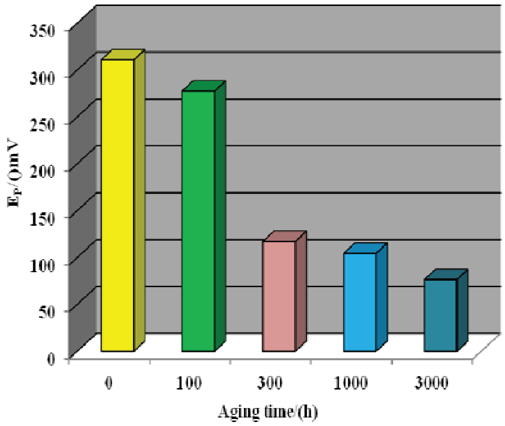
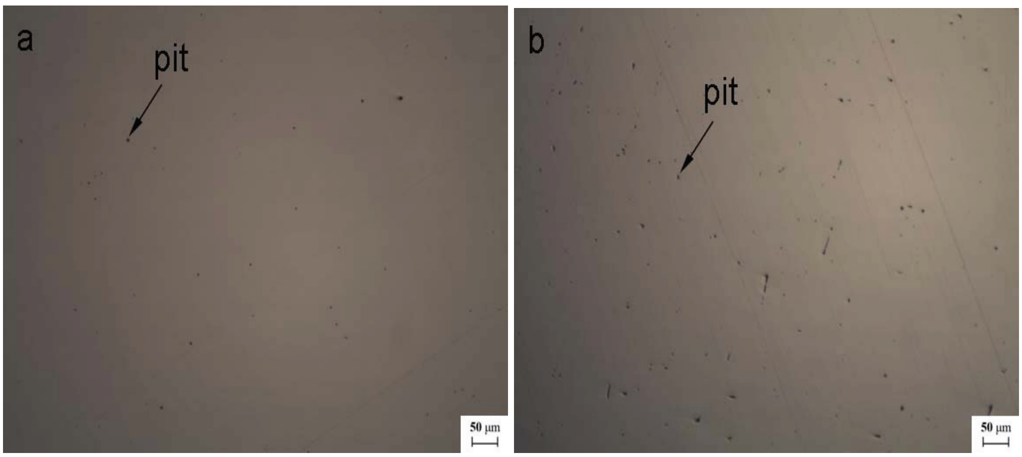


Figure.3.Pitting potential of thermally aged specimens test in 3.5wt% NaCl.



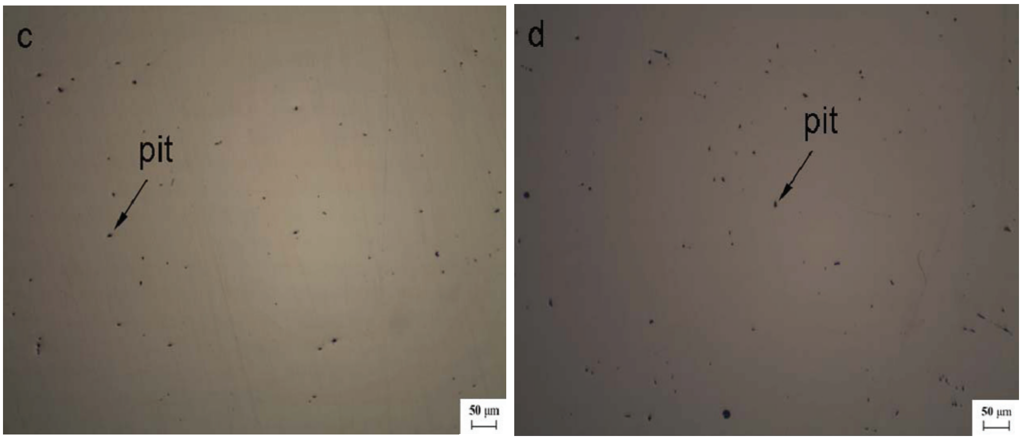


Figure.4. Micrographs of pits of specimens aged for (a) 100h, (b) 300h, (c) 1000h and (d) 3000h at 400 ℃after polarization tests in 3.5wt% NaCl.

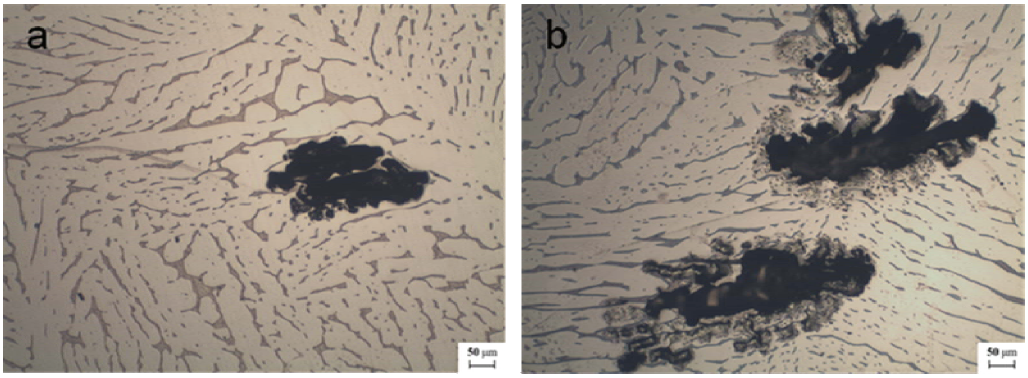


Fig.5. Pits morphology of specimen thermally aged for (a) 100h and (b) 1000h at 400 ℃ after pitting corrosion.

3.3. Intergranular corrosion resistance

Figure.6 shows the result of DL-EPR tests for the specimens thermally aged at 400℃ for 100, 300, 1000 and 3000 h respectively. Figure.7 shows the I_r/I_a versus aging time behavior. The DOS of each aged specimen was evaluated by the ratio I_r/I_a. It can be seen that very low DOS values of the specimens were got at every aging time as shown in Figure.7. The value of I_r/I_a, however, was increased markedly with aging time increase, and the maximum value of I_r/I_a has been obtained when thermal aging time was 3000h. No remarkable evaluation of microstructure for the samples thermally aged at 400℃ for less than 3000h was found on the DOS, because the Cr-rich α' precipitate phase formed by spinodal decomposition from ferrite is very fine with a size of nanometer scale and the amount of α' is few when aged below 3000 h, so the effective Cr-depleted zone in the material can not be formed by α' phase. Although the absolute value of DOS is lower, the results indicated the tendency of IGC of aged specimens. It means that intergranular corrosion resistance of material has been deteriorated practically by the α' phase in ferrite.

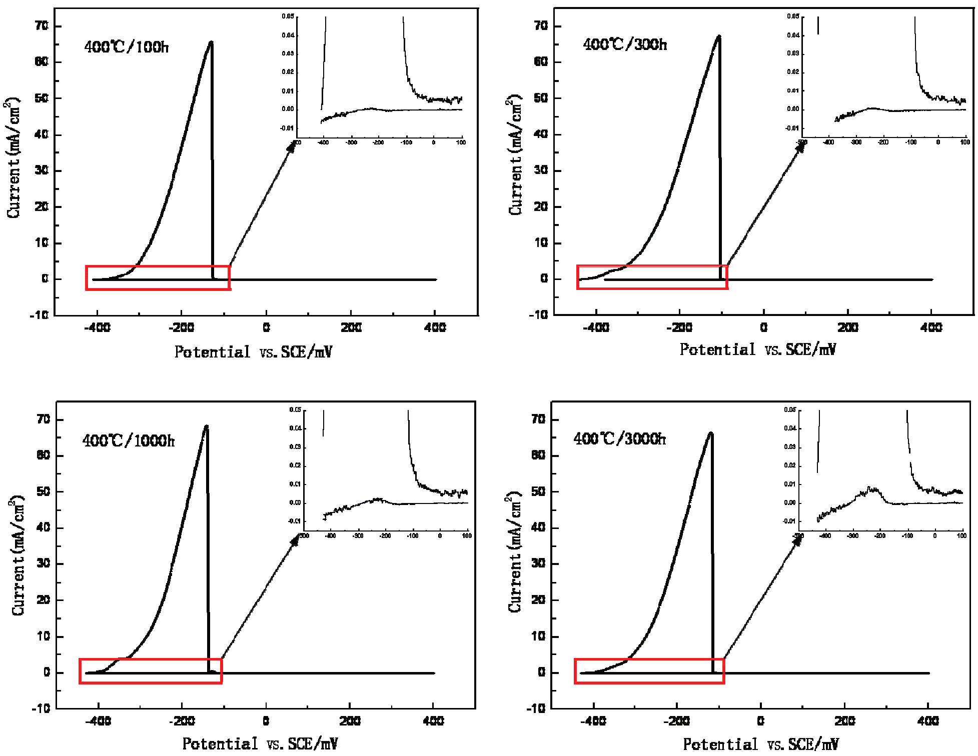
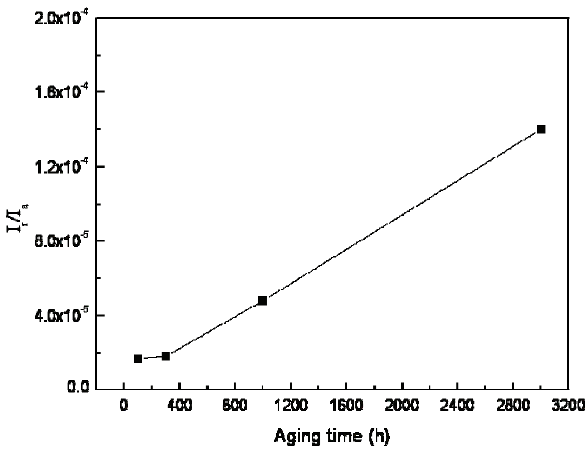


Fig.6. DL-EPR test results of different aged specimens.



Fig,7. The DOS of different aged specimens.

4. Conclusions

1) The general corrosion resistance of Z3CN20.09M had not been affected by thermal aging treatment at 400℃ for 100h to 3000h.

2) With the increase of thermal aging time at 400℃ the pitting corrosion resistance of Z3CN20.09M decreased markedly due to the precipitation of α' phase in ferrite and increase of the amount of that.

3) The results of DL-EPR tests showed that the intergranular corrosion resistance of Z3CN20.09M decreased with the increase of thermal aging time. Although the absolute DOS value was low, the tendency of effect of thermal aging treatment on IGC was obvious.

Acknowledgements

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