Effect of solution treatment on pitting behavior of 2205 duplex stainless steel

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Abstract The effect of solution heat treatment on pitting behavior of 2205 duplex stainless steel was investigated by EDS, potentiodynamic polarization and SECM. The contrast experiments were carried out on the original steel. The results demonstrate that for the original sample, when the potential was at the open circuit potential, there were many pitting precursor areas, due to the local breakdown of passive film on the surface, the pitting current fluctuations on the scale of pA. On the contrary, after 1100 °C solution treatment, the passive film was more stable than the original one. Therefore, the solution treatment can markedly improve the pitting resistance of 2205 duplex stainless steel due to the reduction of pitting precursor areas.

1. Introduction

2205 duplex stainless steel (DSS) with a ferrite/austenite has been increasingly used for its attractive combination of mechanical properties and corrosion resistance (Tsai and Chen, 2000; Ezuber et al., 2007). The high corrosion resistance of DSS is due to not only alloying elements such as Cr, Mo and N, but also the microstructure. The best general properties are obtained with approximately equal amounts of austenite and ferrite and the absence of the third phase, which can be formed from ferrite after hot rolling without quick cooling.

There are many reports about the pitting corrosion resistance of DSS (Moura et al., 2008; do Nascimento et al., 2008) and also pointed out that the solution heat treatment could improve the pitting corrosion. However, seldom explanations focus on why the pitting resistance is improved after the change of microstructure. Also there is not enough direct evidence because of the limitation of experimental methods.

Scanning electrochemical microscopy (SECM) represents a powerful scanning probe technique in that it can be used for high-resolution topographic imaging, mapping microscopic variations in the conductivity, and chemical reactivity of solid/liquid interfaces (Bard et al., 1989; Fushimi and Seo, 2001). In the field of corrosion, dissolution of iron, passivity of iron and localized corrosion of stainless steels (Fushimi et al., 1999; Williams et al., 1998; Paik et al., 2000), have been investigated by SECM. Therefore, the local corrosion process due to the solution treatment could be detected by SECM.
In this paper, the effects of 1100 °C solution heat treatment on pitting behavior of 2205 DSS in chloride solution environments were investigated by potentiodynamic anodic polarization, energy disperse spectroscopy (EDS), and scanning electron microscopy (SEM). At the same time, the stability of passive film of 2205 DSS was studied by SECM by detecting the dissolved Fe²⁺ ions emanating from propagating metastable pits.

2. Experimental

The material used in this work was cut from a sheet of 2205 DSS supplied by Avesta Inc., with the chemical composition (wt.%): C 0.014, Cr 22.39, Ni 5.68, N 0.17, Mo 3.13, Si 0.39, Mn 1.38, S 0.001, P 0.023 and Fe balance. The material’s solution heat treatments were held at 1100 °C for 2 h under atmosphere and then cooled quickly in water.

The test solutions employed for the test were 0.1 mol/L NaCl. All the solutions were prepared from reagent grade chemicals and Millipore-Q water. Before each measurement, the solutions were purged with nitrogen gas for 1 h. All the experiments were conducted at the room temperature. Each type of measurement was repeated at least three times.

Electrochemical measurements were performed with a PAR VMP3 potentiostat. All potentials were referred to the saturated calomel electrode (SCE). Before electrochemical tests, the specimens were cathodically cleaned for 20 min at −800 mV sce to remove the primary oxide film. Specimens were immersed in the test solution 1 h prior to each measurement in order to stabilize the open-circuit potential. The potentiodynamic anodic polarization tests were conducted, at a scanning rate of 1.5 mV/s, starting from −800 mV sce and finally moved to the anodic direction. The pitting potentials of austenite and ferrite were defined as $E_{A-pit}$ and $E_{F-pit}$.

SECM experiments were carried out on a M370 electrochemical workstation, including a scanning microprobe with a tip, a 370 scanning control unit, a M236A potentiostat, a M5210 lock-in amplifier and a video camera system. SECM image was performed in a conventional four-electrode electrochemical cell with a Pt microelectrode (10 μm) and a modified glassy carbon (GC) plate as the working electrodes (probe and substrate, respectively), a saturated calomel electrode as reference electrode and a Pt wire as counter electrode. The application of potential and the record of current were done by a M236A potentiostat controlled via SECM.

Before SECM measurements, the approach curves were measured over the chosen scan area, and the tip was apporched to the sample surface (z-approach curve). Then the tip potential was kept at 0.6 V sce in order to detect the Fe²⁺ ions generating from the sample surface. The scan area is 1000 x 1000 μm. After tests the pitting morphology of the samples was observed by SEM.


3. Results and discussion

3.1. The effect of microstructure and chemical composition

Fig. 1(a) and (b) represents metallographic images of the original state (without solution heat treatments) and solution heat treated samples. The etching solution was concentrated aqua regia solution.

The austenitic phase (A) and ferritic phase (F) are shown in Fig. 1. It clearly shows that the strips of austenitic phase and ferritic phase are distributed alternately, and there is a small amount of other phase particles in the original sample (Fig. 1a). After 1100 °C solution heat treatment, the austenitic phase changed from strips to equiaxed blocks and the amount of other phase particles decreased (Fig. 1b). These results indicate that the solution treatment can influence the distribution of the two phases and the amount of phase particles.

The corresponding composite data of the original samples and solution treated samples are summarized in Table 1. As can be seen from Table 1, for the original sample, Cr, Mo and Si are higher in the ferrite, while Mn and Ni are higher in the austenite. After solution treatment, the contents of Cr, Mo and Ni increased in both the phases due to the decrease of the second phase particles. This demonstrated that the solution treatment can also influence the distribution of Cr, Mo, N and Ni in the phases of 2205 DSS.

The pitting behavior of 2205 DSS is closely related to the composition of ferrite phase and austenite phase. Nitrogen can significantly affect the distribution coefficients of Cr and Mo in the two phases, making these elements transfer from austenite to ferrite phase (Bliznuk et al., 2005). Nitrogen in the two phases is calculated by means of the ThermoCalc computer program. A common way to define the pitting resistance of stainless steel is the pitting resistance equivalent number (PREN). The higher the PREN, the better the pitting resistance is. This parameter strongly depends on the content of three most important elements Cr, Mo and N, according to their influence on pitting:

\[
\text{PREN} = \%\text{Cr} + 3.3\%\text{Mo} + 16\%\text{N}[11].
\]

It is clear that the PREN for each phase could be calculated. The content of important elements, such as Cr, Ni, Mo, and N, in austenite and ferrite phases for the two alloys is shown in Table 1 together with the PREN for the two phases. The results show that the solution treatment markedly improved the value of PREN, indicating that the pitting resistance of the sample enhanced by solution treatment.
3.2. The effect of polarization curves

Fig. 2 shows the potentiodynamic polarization curves of 2205 DSS in the original state and after 1100 °C solution treatment. As can be seen, on the cathodic branch of the curve, hydrogen evolution reaction appears due to water electrolysis. On the anodic part, an important feature of the polarization behavior is the existence of two discrete pitting potentials. The sample is passive when the potential was under 450 mV_SCE. When the potential is higher than 450 mV_SCE, pitting occurred in the austenite phase, while the ferrite remained passive. However, when the potential reached to 1050 mV_SCE, pitting occurred in both austenite and ferrite phases.

The $E_{A-pit}$ for original state and after solution treatment is nearly the same. Therefore, the pitting resistance of 2205 DSS mainly depends on the pitting resistance of ferrite. Hussain (do Nascimento et al., 2008; Hussain and Robinson, 2007; Symiotis, 1990) also confirmed the differences in the stability of the passive films on the two phases of 2205 DSS, and the pits are preferentially nucleated in the $\gamma$/\delta boundaries. These conclusions are all corresponding with the PREN results.

3.3. The stability of the passive film and pitting precursor area

The stability of the passive film is measured by the SECM. Based on the voltammogram characterization of the Pt ultra microelectrode in the testing solution, the probe potential is set at about 600 mV_SCE for maximal collection of the local electrochemical current. $I_c/I_i$ is used as the redox mediator and the tip-interface distance is determined by moving the Pt ultramicroelectrode slowly to the sample surface. In the KI solution, iodide ions in the oxidation reaction occur on the probe. The reaction is as follows:

$$3I^- \rightarrow I_3^- + 2e \quad (3.1)$$

Reactions that occurred on the sample surface are:

$$Fe - 2e \rightarrow Fe^{2+} \quad (3.2)$$

$$Fe^{2+} + I^- \rightarrow I + Fe^{3+} \quad (3.3)$$

According to feedback and generation/collection mode of SECM, the reduced iodide ions will be oxidized again on the probe. When the Pt microelectrode closes to the conductor surface, positive feedback occurs. As the distance increases, the current signal begins to fluctuate. Therefore, the distance between the substrate and the probe is ultimately determined within 10 μm.

Fig. 3 displays the SECM three-dimension images of the original and solution treated samples in 0.1 M NaCl solution at the open-circuit potential. The images show clearly different current levels in different active areas. The topography seems somehow rough and a number of peaks projecting into the anodic direction of spatial extent a few micrometers, died down in a short time. And most of them lasted less than the time in which they can complete a line scan.

In the test solution, chloride ions will be adsorbed on surface film, undermining the integrity of passive film and leading to the nucleation of pits. Nucleation of pits can hardly be detected by conventional electrochemical measurements, but it can be easily detected by SECM. The current peaks in Fig. 3 are related to such nucleation of pits occurring on the samples. The peaks (González-García et al., 2004) in the images are the areas, where the oxide film is broken. There can be no tip reaction of the simultaneously dissolving Cr$^{3+}$ or Ni$^{2+}$. The only possible reaction at the tip is therefore the oxidation of Fe$^{2+}$ to Fe$^{3+}$ on the SECM tip. Fe$^{2+}$ was released from the dissolving point on surface, where it may be a pit precursor.

As is shown in the Fig. 3(a) and (b), the amount of the current peaks on the original sample is more than that after solution treated. This indicated that the protective property of the passive film on the original sample is weaker than that after the solution treated sample.

Fig. 3(c) and (d) provide images obtained after immersing for 1 h in test solution. Obviously, the background currents tend to be flat. The current peaks in Fig. 3(d) is less than that in Fig. 3(c), indicating that the solution treatment markedly enhanced the pitting resistance of the sample, this also indicated that with the immersion time being prolonged, the destruction of chloride and the reparation of the passive film constantly happened and reach a new state.

The deleterious tertiary phases, such as sigma, chromium carbides and nitrides, exist as a chromium depleted zone, which inclines to be corroded first. When deleterious phases

![Figure 4](image-url)
are worn away, the passive film on the metal surface has not yet dissolved, leading to the even deeper corrosion at the chromium depleted zone (Kajimura et al., 1995). But, after the solution treatment, the deleterious phase dissolved and also the chromium depleted zone disappeared.

Generally speaking, at the open-circuit potential, the passive film is stable in the chloride solutions with low concentration. However, the SECM results, which showed that the presence of chloride ions in the electrolyte gives rise to surface heterogeneities, disagree with the above statement. These may be due to the inhomogeneous absorption of Cl$^-$ ions. The Cl$^-$ ions incline to be adsorbed at the defective places, like cracks and dislocations. The Cl$^-$ ions adsorbed on the surface or incorporated into the passive film can be detrimental to film stability, leading to the initiation of pitting.

3.4. Surface morphology

Fig. 4 shows the surface morphologies of the samples after electrochemical tests. Due to the less protective ability of the passive film, there are more pits on the original samples than after solution treatment.

However, it can be seen that the number of pits on the treated sample is less, the size of the pits is much bigger than that on the original sample. This indicates that pitting inclines to develop at the point where pits have already happened, that is, exaggerate the existing pits instead of forming new pits on the treated sample.

4. Conclusions

(1) The alloy element content in the ferrite and the austenite is not the same in the original state and treated state. The 2205 DSS after solution treatment has a higher pitting resistance than the original state.

(2) SECM clearly detected the effect of solution treatment on the pitting corrosion of 2205 DSS. The results showed that at the open circuit potential, more current peaks, corresponding to the pitting precursors, were observed on the original sample. After the solution treatment, the amount of current peaks markedly decreased. It demonstrated that the solution treatment enhanced the pitting corrosion resistance of 2205 duplex stainless steel.

(3) There are more pits on the original samples than the solution treatment sample, though the pits are bigger on the latter surface. The explanation is that pitting inclines to develop at the point where pits have already happened on the treated sample, instead of forming the new pits as happened on the original sample.

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References


