Short Communication

Effect of δ-ferrite on stress corrosion cracking of CF8A austenitic stainless steels in a simulated pressurised water reactor environment

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A B S T R A C T

The effect of δ-ferrite on the stress corrosion cracking (SCC) of CF8A austenitic stainless steels in a simulated pressurised water reactor environment is investigated from the viewpoint of oxidation. In constant-displacement tensile tests, a large number of entangled dislocations are formed in δ-ferrite due to the incompatibility of the slip system between the austenite and δ-ferrite. The activity of the metal atoms in dislocation-entangled nodules is much higher than that in other regions. Therefore, many Fe and Ni atoms break through the barrier of the inner Cr2O3 oxide films and diffuse to react with the Cr2O3 to form non-stoichiometric (Ni,Fe)(Fe,Cr)3O4 spinel-structure oxides, and denser outer Fe3O4 granular oxides. In addition, δ-ferrite–austenite grain boundaries are oxidised preferentially due to the accumulation of a high level of interfacial energy and plastic damage. However, SCC retardation is clearly observed because the presence of δ-ferrite changes the direction of SCC propagation and increases the length of the SCC propagation pathways.

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1. Introduction

Austenitic stainless steels (SS) are usually recommended for fabricating the primary coolant pipes of nuclear power plants because of their excellent mechanical properties, corrosion resistance, and low cost [1,2]. In the manufacturing process of austenitic SS, up to approximately 10 vol% δ-ferrite remains among the austenite grains, distributed as reticulate and isolated grains [3–5]. The δ-ferrite and austenite phases differ significantly in their crystal structure and physical properties [6,7]. Therefore, the strain distribution of the austenite and δ-ferrite becomes extremely inhomogeneous under applied stress [8–10]. Many studies have reported that the existence of δ-ferrite has an adverse effect on the mechanical properties of austenitic SS due to the nucleation of cavities at the δ-ferrite–austenite boundary junctions [5,7].

Stress corrosion cracking (SCC) is a major challenge associated with the service life of austenitic SS during its extended service in a pressurised water reactor (PWR) [11–13].
Effect of $\delta$-ferrite, a residual phase, on the corrosion resistance and stress corrosion resistance of austenitic SS is not clear and has attracted considerable attention. Many researchers have reported that $\delta$-ferrite has a higher SCC resistance than austenite in high-temperature water because of the high precious-metal content. It is recognised that a 3–8% $\delta$-ferrite content could effectively prevent hot cracking and decrease the SCC crack growth rate in austenitic SS welds [14]. However, Du [15] suggested that the 316L SS weld metal with a large fraction of $\delta$-ferrite–austenite phase boundaries is more susceptible to SCC than the base metal with austenite–austenite grain boundaries.

Although many phenomena related to the effects of $\delta$-ferrite on the SCC of austenitic SS have been observed and studied, the mechanisms whereby $\delta$-ferrite affects the SCC of austenitic SS have not been fully clarified. Many factors influencing SCC have been identified, such as stress, environment, and electrochemical potential [16–18]; these factors affect the SCC mainly by changing the phase composition and structure of the protective oxide films formed in the matrix [19–22]. Galvele et al. [23] proposed a model that accurately predicted SCC crack growth based on the microscopic scale of the oxide film evolution, where the parameters related to the types and evolution of oxide films were considered. Therefore, to clarify the effect of $\delta$-ferrite on the SCC of austenitic SS in a simulated PWR environment, it is important that we investigate the composition, structure, and mechno-chemical interactions of the oxide films. The objectives of this work are to enable a detailed description of the evolution of oxide films on CF8A SS in tensile tests in a simulated PWR environment. The interactions between the oxide films and cracks, as well as the effect of $\delta$-ferrite on the SCC growth behaviour, are also addressed.

2. Experimental

2.1. Materials and methods

The CF8A SS used in the present study was solution-annealed at 1040 °C for 1.5 h, followed by water quenching. The chemical composition of CF8A SS used in this work was 20.5 wt% Cr, 9.65 wt% Ni, 2.4 wt% Mo, 1.2 wt% Mn, 0.065 wt% C, ≤0.045 wt% P, ≤0.030 wt% S, and 66.06 wt% Fe. The microstructure of the CF8A SS is shown in Fig. 1. About 5 vol.% $\delta$-ferrite is distributed at the austenite boundaries. The typical oxidation behaviour of CF8A SS was evaluated in a simulated PWR environment by performing constant-extension-rate tensile (CERT) tests. Rod specimens of M10 for slow-strain-rate testing (SSRT) were machined according to NACE TM 0274. The solution used was 2.2 ppm (by weight) Li as LiOH, H$_2$O and 1200 ppm B as H$_3$BO$_3$. Pure N$_2$ gas was bubbled through the solution to deaerate it. The solution was heated to 300 °C in stages at approximately 100 °C/h. The specimen was then subjected to a load of 50 MPa until the environmental parameters were stable, and then held in tension at a strain rate of 1 × 10$^{-6}$/s. An interruption test with 30% strain was performed to better observe the oxidation behaviour under tension.

2.2. Characterisation

After testing, field-emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to examine the morphologies and phase composition of the oxide films. A SEM/Focused ion beam (FIB) dual-beam system (FEI Helios Nanolab 460HP) was used to obtain the cross-

Fig. 1 – Optical micrograph of CF8A SS microstructure.

Fig. 2 – SEM images of surface morphologies of oxide films of CF8A SS in simulated PWR at 30% strain. (a) Low-resolution image and (b) high-resolution image of oxide films on $\delta$-ferrite.
sectional TEM samples. The oxides were then analysed by TEM (FEI–Tecnai G2 F30), including selected-area electron diffraction (SAED). The elemental distribution was analysed by energy dispersive X-ray spectroscopy (EDS). High-resolution scanning with a high-angle annular dark-field (HAADF) detector was also performed to characterise the crystal structure of the inner oxide film. A fast Fourier transform (FFT) method was used to analyse the high-resolution images.

3. Results and discussion

Fig. 2a shows the oxide films on the specimen surface, and Fig. 2b is an enlargement of the δ-ferrite shown in Fig. 2a. The δ-ferrite grains can be distinguished by the distribution of the faceted large-particle oxides. These faceted large-particle oxides are densely distributed over the surfaces of the specimens but are most highly concentrated on the δ-ferrite surface. In addition, many microcracks appear on the δ-ferrite surface (Fig. 2b).

To observe the different oxidation behaviours of δ-ferrite and austenite more intuitively, a TEM specimen was captured by FIB at the interface between δ-ferrite and austenite, as marked by the dashed box in Fig. 2. First, a platinum layer was deposited on the selected surface area to protect the oxide film from the influence of the Ga ion sputtering. The deposited area measured 15 × 2 μm. Then, triple prism grooves with a depth of about 5 μm were formed on both sides of the Pt-deposited area by using a focused ion beam (FIB) with Ga-ion sputtering (Fig. 3a). Subsequently, the lamella was cut free from the matrix. Finally, the lamella was Pt-welded on a TEM sample grid and then thinned to 50 nm by Ga-ion sputtering (Fig. 3b).

Cross-sectional TEM images are shown in Fig. 4. The interface between the oxide film and matrix is clearly visible. On the δ-ferrite side, faceted large-particle oxides of approximately 600 nm in diameter can be seen to have leached onto the inner oxide film, and slightly smaller ones can also be observed on the austenite side, agreeing with the SEM morphology observations (Fig. 2). The oxide film thickness on the δ-ferrite surface is about three times greater than that on the austenite surface. The oxide film at the δ-ferrite–austenite grain boundary intrudes into the matrix along the grain boundary, exhibiting an oxide spike morphology. This is due to the existence of a grain boundary and the presence of residual impurity elements at the grain boundary during casting and solidification, which makes the interface energy at the δ-ferrite–austenite grain boundary extremely high. In addition, the different oxidation sensitivities of ferrite and austenite result in the formation of micro-corrosion coupling at the δ-ferrite–austenite grain boundaries. All these factors lead to serious corrosion at the δ-ferrite–austenite grain boundaries.

The SAED images in Fig. 4b–d are from positions 1–3 in Fig. 4a. Fig. 4b, c shows that the matrices have face-centred cubic (FCC) and body-centred cubic (BCC) structures, confirming them to be austenite and δ-ferrite, respectively. The SAED image shown in Fig. 4d reveals that the faceted large-particle oxides are Fe₃O₄. The fast Fourier transform (FFT) of the high-resolution TEM (HRTEM) image of position 4, shown in Fig. 4e, suggests that position 4 oxides have a spinel structure. Fig. 4f–i shows an EDS mapping analysis of the area enclosed by the white box in Fig. 4a. The oxides contain all the major elements such as Fe, Cr, and Ni. The faceted, large-particle oxides in the outer layer are rich in Fe. Regarding the elemental content, as determined by TEM-EDS, it is confirmed that the position 4 oxide has a non-stoichiometric spinel structure, specifically, (Ni,Fe)₉(Fe,Cr)₂O₄.

The growth mode of the oxide film is closely related to the chemical activity of the substrate metal atoms. In our previous studies, we found that a Cr₂O₃-based passive film preferentially grows due to the greater affinity between Cr and high-temperature water as compared to the other major components (Ni and Fe) [24]. In addition, the growth mode of the oxide film is closely related to the chemical activity of the substrate metal atoms. The main contribution to the activation of the metal atoms is dislocation multiplication and movement during deformation [25,26]. According to the transition state theory in chemical kinetics, it is necessary to jump a certain barrier when the reactant is transformed into a product. For a metal matrix without plastic deformation, the oxidation rate can be expressed as: [27]

\[
\dot{J} = k \alpha \exp \left( -\frac{\Delta G_{\text{f}}^{\#}}{RT} \right)
\]

where \( \dot{J} \) denotes the current density on the surface of the sample, \( \Delta G_{\text{f}}^{\#} \) is the difference between the standard Gibbs free energy of the reaction state and the excess state of the reaction, \( \alpha \) denotes the concentration of the reactants involved in
With the local plastic deformation of δ-ferrite, the potential at dislocation entanglement deviates from the equilibrium potential, resulting in a potential difference ($\psi$) between the regions without dislocation entanglement. According to the relationship between the standard Gibbs free energy $G_e^0$ and $\psi$ of the 1-mol electrons:

$$G_e^0 = \mu_e + F\psi$$  \hspace{2cm} (2)

where $\mu_e$ is the chemical potential of the electrode without plastic deformation. Because the increase in the activation Gibbs free energy of oxidation reaction is only part of $F\psi$, this fraction is expressed in $\beta$. The difference between the standard Gibbs free energy of transition state and reaction state after plastic deformation is as follows:

$$\Delta G_p^{\#} = \Delta G_e^{\#} + \beta F\psi$$  \hspace{2cm} (3)

By substituting Eq. (3) into (1), the current density in the plastic deformation region is given by:

$$j = Fk\exp(-\frac{\Delta G_p^{\#}}{RT})\exp(\frac{\beta F\psi}{RT})$$  \hspace{2cm} (4)

Therefore, the corrosion rate increases with the plastic deformation, and a large amount of oxide is formed in the plastic deformation zone.

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**Fig. 4** – (a) STEM-HAADF image of cross-section of δ-ferrite–austenite interface of CF8A SS at 30% strain in PWR environment, (b)–(d) SAED images from positions 1–3 in (a), (c) FFT of high-resolution images of oxides of position 4. (f)–(i) EDS mapping of O, Fe, Cr, and Ni of framed area in (a). (j–k) Bright-field TEM images corresponding to labeled squares in (a).
With an increase in the strain, the austenitic phases exhibit planar slip characteristics (Fig. 4k) because of their low stacking-fault energies. However, the contribution of the planar slip bands to the potential energy of the metal matrix is limited, with the increase in the anodic current being caused mainly by dislocation tangles and pile-up groups. The BCC δ-ferrite has fewer slip systems than the FCC austenite [28]. The difference in the slip behaviour of the austenite and δ-ferrite leads to a dislocation pile-up on the austenite side of the δ-ferrite–austenite boundary. In addition, it has been clearly established that the strength of the ferrite phase is lower than that of the austenite phase [29]. Therefore, the incompatibility of the easy-slip systems in the austenite and δ-ferrite causes the cross-slip of dislocations emitted from the boundary into the δ-ferrite grains by forming dislocation tangles at high plastic strains (Fig. 4j). Because of the dislocation tangles, the activities of the metal atoms in the core region of the dislocation tangles are much higher than those in other regions. Therefore, many Fe and Ni atoms break through the barrier of the inner Cr₂O₃ oxide films and diffuse to react with the Cr₂O₃ to form non-stoichiometric (Ni,Fe)(Fe,Cr)₂O₄ spinel-structure oxides (Fig. 4f-1). Mathieu et al. [30] also found that Cr₂O₃ becomes a spinel oxide as a result of the transportation of Fe and Ni into the Cr₂O₃ oxide layer with long-term oxidation. Huang et al. [31] calculated the potential–pH diagram at 300 °C in a ternary Fe–Cr–Ni system and reported that spinel oxides (Ni,Fe)(Fe,Cr)₂O₄ form more easily than Cr₂O₃ with an increase in the passive potential. However, the formation of a protective Cr₂O₃ oxide film is central to the corrosion resistance of SS [32,33]. Metal cations diffuse outwards while anions diffuse inwards, where, without the protection of the Cr₂O₃, they would react and lead to the constant corrosion of the SS. However, the fracture strain of the oxide film is much smaller than that of the metal matrix, thus forming micro-cracks as a result of the tensile process (Fig. 2b), and these micro-cracks become the channels through which the corrosive medium enters the matrix.

The diffusion rate of various ions in Cr-rich oxides has been determined as Fe²⁺ > Ni²⁺ > Cr³⁺ [34,35]. As the most common element, Fe²⁺ diffuses to the surface of the specimen and reacts with the solution to form faceted large-particle Fe₃O₄, which is deposited on the surface of the specimen as a result of the following reaction:

\[3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\]  

(5)

In addition, the oxide film/matrix interface has some discrete nickel-rich points, which is due to the lower diffusion rate of Ni in spinel oxides than that of Fe.

The results of a previous analysis revealed that the local δ-ferrite metal atoms are highly active because of the formation of dislocation tangles, leading to the formation of dense oxides on the surface of the δ-ferrite, which is also the basis for distinguishing δ-ferrite and austenite from the surface oxidation film. However, Ma et al. [36] found that the oxide particles in δ-ferrite had a lower density and smaller size than those in austenite, in a study of exposure tests of 308L SS in simulated primary water. This inconsistency with the preferential oxidation of δ-ferrite identified in this study arises from the lack of a load in the exposure tests. Therefore, the plastic deformation caused by the mechanical load causes the preferential oxidation of δ-ferrite on the surface of austenitic SS.

Upon the completion of the stress corrosion tests, the gauge segments of the specimens were cut along their axial directions to observe the distribution of δ-ferrite in the SCC propagation pathways. The typical relationships between the δ-ferrite and SCC are shown in Fig. 5. During the CEKT tests, the SCC initiated in the austenite grains first extends to the neighbouring δ-ferrite (Fig. 5a). Once the SCC reaches the δ-ferrite, the cracks generally do not pass through the δ-ferrite, but instead propagate along the δ-ferrite–austenite boundaries (Fig. 5b). This is due to the δ-ferrite having fewer slip systems and a higher modulus of elasticity relative to the austenite, which results in the accumulation of strain damage at the δ-ferrite–austenite interface, and thus an increase in the metal atom activity. Moreover, it is well known that the Cr content in δ-ferrite is 3–5% higher than that in austenite [10,14,37]. Therefore, the oxidation sensitivity of δ-ferrite is much lower than that of the adjacent austenite matrix, such that an electrochemical micro-corrosion couple is formed between the δ-ferrite and austenite, in which the δ-ferrite acts as a cathode with high corrosion resistance while the austenite matrix acts as the anode. Therefore, stress corrosion cracks grow along
the ferrite-austenite boundary and SCC retardation is clearly observed, given that the presence of the δ-ferrite increases the lengths of the SCC propagation pathways.

4. Conclusion

In the present study, we investigated the effect of δ-ferrite on the SCC of CF8A SS in a simulated PWR environment by performing CERT tests. The main conclusions are as follows:

1. δ-ferrite on the specimen surfaces was oxidised preferentially and formed many micro-cracks because the potential energy of the δ-ferrite increased during plastic deformation.
2. An oxide spike morphology was formed at the δ-ferrite-austenite grain boundary due to the higher interfacial energy and dislocation accumulation.
3. The preferential oxidation zone forms inner nonstoichiometric (Ni,Fe)(Fe,Cr)2O4 spinel-structure oxides and denser outer Fe3O4 granular oxides.
4. SCC retardation is clearly observed because the presence of δ-ferrite changes the direction of the SCC propagation and increases the lengths of the SCC propagation pathways.

Conflicts of interest

The authors declare no conflicts of interest.

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