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Interaction between austein-ferrite phases on passive performance of 2205 duplex stainless steel

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ABSTRACT

The passive behavior of 2205 duplex stainless steel (DSS) and its individual phases (α-phase, γ-phase) in neutral 3.5% NaCl solution was investigated by various electrochemical methods. The results indicated that galvanic effect between α and γ phases cannot deteriorate local corrosion, but favors the enhancement of the passive film. Under the galvanic effect, the diffusion of the dissolved passive cations would be promoted in a short distance between α and γ zones, leading to modifications of the chemical composition and semiconductive property of the passive film and therefore the enhancement of the corrosion resistance of DSS 2205.

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1. Introduction

Duplex stainless steels (DSSs), known as a two-phase structure comprising island-like austenite (γ-phase, fcc) and continuous ferrite matrix (α-phase, bcc) [1–4], possess excellent mechanical properties and high corrosion resistance, and thus are widely employed in various industrial fields, such as oil, chemical, petroleum (offshore), and electric power industries. The passive film on stainless steels, which is a key to the high corrosion resistance, is strongly influenced by alloy elements. Therefore, a heterogeneous passive film is formed on DSS, due to the different chemical compositions of two constituent phases. Especially, Cr and Mo are more enriched in α-phase, while Ni and Mn are more partitioned in γ-phase [5–7]. Thus, the passive behavior of each phase of DSS is important, because the weaker phase shows the dominant effect on the overall corrosion behavior. Additionally, the interaction effect of these two phases of DSS on the whole passive performance is also worth of discussing, since DSS exhibits greater corrosion resistance than conventional single-phase stainless steels, such as ferrite and austenitic stainless steels, in chloride-rich media [8,9].

With the widespread use of DSSs in more aggressive environments, more detailed information about the passive film on single-phase and dual-phase is definitely needed. However, there are still several important aspects about the essential reason for the higher corrosion resistance of DSSs than single-phase stainless steels, which are not fully understood. Olsson [10] studied the passivity of single phase of DSS by using alloys with compositions similar to austenite and ferrite phases, indicating that the anti-corrosion ability could be partially owed to the interaction between the austenite and the ferrite. But the exact element contents of the composed phases of DSS were not ascertained in this work, and thus the passive properties of single-phase cannot be precisely presented.

Fortunately, selective dissolution technique, as a novel preparation of single-phase samples, was proposed by Tsai et al. [11,12]. According to those reports, for 2205 DSS as reported in mixed H_2SO_4/HCl solution, two anodic peaks existed in the active-to-passive transition region of the potentiodynamic polarization curves: one for selective dissolution of γ-phase (-255 mV vs saturated calomel electrode, SCE) and the other for α-phase (-320 mV vs SCE). After etching DSS samples at the two characteristic potentials for 10 h, exclusive γ-phase and α-phase could be exposed, respectively. Thus, the single-phase electrodes could show exact chemical compositions as the counterparts of DSS. Using this etching technique, it has been revealed that the coupling effect of the constituent phases in DSS enhanced the stability of Cr^{3+} species in

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the passive layer and thus benefited the overall passive behavior [13].

Moreover, localized electrochemical measurements, including localized electrochemical impedance spectroscopy (LEIS) and scanning vibrating electrode technique (SVET), are massively employed in corrosion science in the past decade [14,15]. Compared to traditional electrochemical techniques, these new methods could be employed for in situ tests and mechanism research more conveniently, due to the capability of obtaining local electrochemical signals at the micrometer scale. The local electrochemical reactions that occurred in an iron-zinc galvanic couple immersed in aqueous sodium chloride solution has been revealed by SVET and scanning electrochemical microscope (SECM) techniques [16]. Cheng et al. [17] also studied the local galvanic corrosion between coupled TA2 and 316L stainless steel by these techniques. For DSS, the constituent phases are always at micrometer magnitude, and thus these techniques are well suited to characterize the passivity and coupling effect.

In the present work, single α and γ phase would be fabricated from 2205 DSS samples by selective dissolution. Their passive behavior and interaction were investigated by comparing with the dual-phase electrode (2205 DSS) in 3.5 wt% NaCl solution. Various electrochemical methods, such as OCP (open circuit potential), potentiodynamic curves, EIS (electrochemical impedance spectroscopy) and Mott-Schottky plots, were employed in the study. XPS (X-ray photoelectron spectrometer) and SEM (scanning electron microscopy) together with EDS (energy dispersive spectroscopy) were also used for compositional analysis. LEIS and SVET were applied to characterize the coupling effect between the constituent phases. It is anticipated that the result provides an essential insight to the passive behavior of single phase of 2205 DSS and the interaction between both phases on the electrochemical behavior of the material.

2. Experimental

2.1. Sample preparation

The composition (wt%) of the sample is as follows: Si 0.59, Mn 1.2, P 0.029, Mo 2.62, Cr 22.57, Ni 4.63, C 0.029, S 0.0043, N 0.13, and Fe balance. The 2205 DSS steel sheet with thickness of 5 cm was solution heat treated at 1100 °C for 30 min, and then water quenched. The samples were prepared with size of 10 mm × 10 mm, welded to wires, embedded in epoxy resin leaving a working area of 1 cm². The sample surface was ground with 400–2000# SiC papers and then rinsed in distilled water, ethanol and acetone.

2.2. Selective dissolution

The solution for selective dissolution was a mixed 2 M H_2SO_4 + 0.5 M HCl. A VMP3 advanced electrochemical system from Princeton Applied Research was used to perform the electrochemical experiment.

A saturated calomel electrode (SCE) was served as the reference electrode and a platinum foil was employed as the counter electrode. The characteristic peak potentials, −255 mV vs SCE and −320 mV vs SCE, were selected for potentiostatic etching of 10 h to ensure the selective dissolution in the specified phase, leaving almost exclusive α-phase or γ-phase exposed on the surface, respectively. After potentiostatic etching, specimens were observed by SEM and EDS.

The preparation process of single-phase electrode is as follows: firstly, the etched sample surface was filled with epoxy resin and put into a vacuum chamber. With the increase of vacuum degree, jammed air in the cavities caused by selective dissolution

expelled and epoxy resin filled in. Lasting for 24 h, the epoxy resin was then carefully removed with 2000# SiC papers and then polished, leaving almost exclusive phase exposed on the surface. After the sequences for single-phase electrode preparation, specimens exposed exclusive phase on the surface, were composed of α-phase when 2205 DSS etched at −255 mV vs SCE and γ-phase when etched at −320 mV vs SCE according to the document [11]. These prepared single-phase electrodes and dual-phase sample with an exposed area 1 cm² were used for subsequent electrochemical tests. The real surface areas of single-phase samples were obtained by the image analysis.

2.3. Electrochemical tests

The electrochemical behavior of α-phase and γ-phase and dual-phase electrodes were investigated in 3.5 wt% NaCl solution at ambient temperature (25 °C) with electrochemical testing device as mentioned above. The working electrodes were initially reduced potentiostatically at −1.0 V vs SCE for 20 min to remove air-formed oxides, and then OCP curves were recorded for 30 min. EIS tests were obtained with the frequency from 100 kHz to 10 mHz. 10 mV was chosen as the peak to peak amplitude. To interpret the EIS data on the basis of equivalent electric circuits, ZSimpWin software was used. Moreover, the potentiodynamic polarization tests were carried out at a potential scan rate of 0.1667 mV/s from −0.6 V vs SCE until anodic current density reached 1 mA/cm². Measurements of capacitance were performed on films of specimens with the frequency of 1 kHz from −0.6 V vs SCE to 1.0 V vs SCE. Similarly, the peak to peak amplitude single was 10 mV, and the scan rate was 45 mV/s. Sufficient short testing time ensured the stability of passive films during the test while the capacitance was measured as a function of potential.

The localized electrochemical measurements were performed through a PAR Model 370 scanning electrochemical workstation, which was composed of a 370 scanning control unit, a M236A potentiostat, a M5210 lock-in amplifier, and a video camera system. The 3.5 wt% NaCl solution was used as test solution. A single-phase α sample and a single-phase γ sample were prepared by the selective dissolution technique. They were electrical connected and fixed by epoxy resin. Then the cured resin on the selective dissolved surface was carefully removed with 2000# SiC papers and polished, exposing α single-phase on one side and γ single-phase on the other side. The two-phase-coupled specimen working electrode is represented in Fig. 1. An SCE was employed as reference electrode and a platinum plate as counter electrode. Area-scan mode was used in LEIS measurements. The platinum microprobe with a 10 μm tip was set above the working surface. The measurement frequency was fixed at 10 Hz with applied AC amplitude of 10 mV at open circuit potential.

$$i = -\frac{k\nabla\phi}{d} = -\frac{\nabla\phi}{\rho d}$$

where i is the localized current density of specimen, ∇F is the potential gradient over the test area in the solution, κ is the conductivity of the solution, ρ is the resistivity of the solution and d is the amplitude of the platinum tip microprobe.

In 3.5 wt% NaCl solution, anodic process is characterized by the dissolution of iron:

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{1}$$

Cathodic process is characterized by the reduction of dissolved oxygen:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{2}$$

Reaction (1), which leads to an upward flow of metal cations above the test region, is detected as negative currents. Conversely,