The beneficial galvanic effect of the constituent phases in 2205 duplex stainless steel on the passive films formed in a 3.5% NaCl solution

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ABSTRACT

The galvanic effect of the composed phases in 2205 duplex stainless steel on the passive films formation of the two phases in a 3.5% NaCl solution was investigated by electrochemical measurements and composition analyses. The results show that the galvanic effect benefits the stability of the passive films of both phases. However, the inner part of the α-phase passive layer benefits the most because of the increase in the concentrations of Cr, Ni and Mo in the passive film, the decrease in the formation rate and transfer velocity of the oxygen vacancies, and the reduction in the defect density.

1. Introduction

The high resistance of stainless steels to corrosion is attributed to the dynamic properties of their passive films [1], which are influenced by many factors, such as the metal type, alloy composition, electrode potential, pH and electrolyte composition [2]. However, for duplex stainless steels (DSSs), their two-phase microstructure (γ-phase and α-phase) is an additional variable that has to be taken into account [3].

In fact, the corrosion resistance of DSS is higher against stress corrosion cracking and crevice corrosion than that of austenitic stainless steels with the same pitting resistance equivalent (PRE) values [4]. Although it is less clear for pitting, the distinctly high corrosion resistance of some DSSs in certain chloride solutions suggests the existence of a beneficial interaction between the constituent phases in DSS that influences the overall passive behaviour [4]. Perren [5] investigated the passive performances of some super DSSs and their constituent phases by an electrochemical microcell, and the results showed that the overall passive performance of a super DSS was better than that of each single phase. Two kinds of interactions between the two phase were found: a superposition or separation of the two polarization curves of the single phases. Femenia [6] employed scanning Auger electron spectroscopy (SAES) to characterize the phase boundary region between ferrite and austenite in three DSSs and found a few micrometer-scale composition gradient across the phase boundary. Olsson [4] reported that the interaction of the two phases of 2205 DSS can be described as the synergism of N (in the passive film of austenite) and Mo (in the passive film of ferrite), and their high mobility helped formed a comparatively homogeneous passive film on the DSS. The film was virtually independent of the underlying phase structure and enhanced the overall passive ability. Previous investigations concerning the interaction between the two phases in DSS have mainly focused on the diffusion, mobility and synergic effect of the species in the passive films.

The galvanic effect of the composed phases in DSS is another kind of interaction, and its effect on selective dissolution has been studied [7,8]. However, the exclusive galvanic effect on the formation of passive films has not been reported. A reasonable assumption is that the exclusive galvanic effect has a great influence on passive films since its potential is one of the dominant factors affecting the composition and property of passive films during formation. The passive film of the austenite phase or ferrite phase is assumed to have different properties when it is formed under galvanic coupling and without galvanic contact.

The prerequisite for studying the exclusive galvanic effect of DSS is separating the two phases in DSS and independently studying them. This requires the fabrication of single-phase samples that have compositions nearly identical to that of the phases in DSS. The conventional method for preparing single-phase samples is to design single-phase stainless steels that have the same elemental compositions as the two phases in DSS [4]. However, when designing an austenite steel, one has to increase the 2%+ Ni content to stabilize the austenite phase. Therefore, single-austenite samples made by this kind of preparation
deviate from the real behaviour of the austenite phase in 2205 because Ni strongly influences the passivity of stainless steels. Fortunately, Tsai [7] developed a novel single-phase sample preparation method using selective dissolution, and this method can ensure the compositions of single-phase samples are nearly identical to those of the two phases in DSS. Our previous work [9] prepared single-phase samples of 2205 DSS by this preparation method and proved the reliability of this sample preparation method and the existence of the beneficial effect of the interaction between the two 2205 DSS phases.

Therefore, in the present work, with the help of single-phase samples fabricated by Tsai’s method [7], the exclusive galvanic effect of the constituent phases in 2205 DSS on the formation of the passive film of each phase was investigated. Zero resistance ammeter (ZRA) measurements were employed to monitor the galvanic current between the γ-phase and α-phase to reflect the duration and degree of the galvanic effect. Electrochemical impedance spectroscopy (EIS) and Mott-Schottky analyses were applied to characterize the galvanic effect on the passive reactions and electronic properties of the passive films. Approach curves obtained by scanning electrochemical microscopy (SECM) were utilized to quantify the galvanic influence on the electrochemical reactivity of the passive films. Finally, X-ray photoelectron spectroscopy (XPS) depth profiles were used to illustrate the compositional changes in the passive films.

2. Material and methods

2.1. Sample preparation by selective dissolution

The used 2205 DSS steel sheet supplied by Avesta Inc. with a thickness of 5 cm was solution heat treated at 1200 °C for 4 h, followed by water quenching. The specimens had a size of 10 mm × 5 mm with a copper wire connected to the rear surface and were mounted in resin with a 0.5 cm² area exposed to solution. The composition (wt.%) of the sample was 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. Before selective dissolution, the samples were smeared with 400# SiC paper to leave the exclusive phases exposed on the surface. Fig. 1(b)–(f) show the preparation process of a single-phase sample. After selective dissolution, the samples were smeared with epoxy resin and placed into a vacuum chamber to completely expel the air in the cavities. After 24 h, the epoxy resin was carefully removed by grinding with 2000# SiC paper to leave the exclusive phases exposed on the surface. These prepared single-phase electrodes were used for the subsequent electrochemical tests. The real surface areas of the single-phase samples were obtained by the image analysis.

The morphology and characteristics of the single-phase sample were explored by scanning electron microscopy (SEM) together with energy dispersive spectroscopy (EDS) (FEI Quanta 250) and magnetic force microscopy (MFM) (Bruker Nano Scope V).

2.2. Electrochemical tests

ZRA, EIS and Mott-Schottky analyses were performed to characterize the passive behaviours and properties of the two phases using an AUTOLAB PGSTAT 302N instrument. After removing the air-formed oxide films by reduction at −1.0 V_<SCE> for 20 min, the electrochemical experiments were carried out at room temperature in a neutral 3.5% NaCl solution. For ZRA, the γ-phase sample served as the working electrode, and the coupling duration was 12 h. After that, EIS tests were applied with frequencies from 100 kHz to 1 mHz, and 10 mV was chosen as the peak to peak amplitude. In addition, the Mott-Schottky measurements were carried out from −1.0 V_<SCE> to 0.8 V_<SCE> at a frequency of 1 kHz using a 10 mV ac signal and a step rate of 25 mV in the anodic direction. The reference electrode was a saturated calomel electrode (SCE), and the counter electrode was a platinum foil.

The approach curves were obtained on a PAR Model 370 Scanning Electrochemical Workstation with a 25 μm Pt probe at a relative humidity of approximately 25% and room temperature. The electrolyte solution was a neutral 3.5% NaCl solution with 10 M K₃Fe(CN)₆ prepared in permuted water. The Fe(CN)₆⁴⁻ ion was used as a redox mediator for the feedback mode. Before the test, the two samples were immersed in a neutral 3.5% NaCl solution for 12 h.

2.3. XPS surface analysis

The chemical compositions of passive films on the coupled and uncoupled α-phase and γ-phase samples were investigated by XPS (Thermo Escalab 250). The XPS experiments were excited by a monochromatic Al Kα radiation source operated at 150 W. Before the XPS tests, the samples were cleaned by distilled water and transferred to the