



The bi-layer structure and the higher compactness of a passive film on nanocrystalline 304 stainless steel



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ABSTRACT

The structure and compactness of the passive films on nanocrystalline (NC) and coarse crystalline (CC) 304 stainless steels (SSs) are investigated. A bi-layer passive film composed of an inner Cr₂O₃-rich layer and an outer Fe₂O₃-rich layer is obtained on both NC and CC 304SSs. The lower oxide formation potential $U_{ox(Cr)}$ of chromium causes the Cr₂O₃-rich inner layer to form initially, and when the surface potential of the passive film increases due to Cr₂O₃ formation, Fe₂O₃ with a higher formation potential $U_{ox(Fe)}$ forms and predominates in the outer layer as a result of the higher diffusion rate of Fe than that of Cr across the inner layer. Compared with the CC-304SS, the inner layer of the passive film on the NC-304SS possesses a higher Cr₂O₃ content, which is attributed to the greater nucleation sites and faster growth rate of Cr₂O₃ in NC-304SS and is believed to be responsible for the higher compactness of the passive film on NC-304SS.

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1. Introduction

The high electrochemical stability and corrosion resistance of austenitic stainless steel (SS) are dependent on the passive film properties, including its chemical composition and structure (thickness, compactness and layered model), which are influenced by the chemical composition and microstructure of the substrate [1–3]. Under the same substrate composition, the structure of the passive film on SS is greatly affected by the microstructure of the substrate, including its grain size and dislocation density. On the nanometer scale, the passive film of austenitic SS exhibits a higher compactness and consequently better electrochemical stability and corrosion resistance [4–6]. However, there are opposite results for different nanocrystallization processes [7–9]. Different nanocrystallization processes may produce nano-structures with different grain refinement, dislocation density and stress distribution in the SS and may therefore influence the structure and electrochemical stability of the passive film.

The passive film on the SS has been described as a distinct bi-layer structure, where the inner layer is enriched in chromium oxide Cr₂O₃ and the outer layer is enriched in iron oxide Fe₂O₃ [10,11]. Numerous research results suggest that nanocrystallization does not change the bi-layer structure of the passive film on SS but improves its compactness and electrochemical stability [12,13]. However, the mechanisms for

how the bi-layer structure forms and why nanocrystallization makes the passive film more compact are still not clearly understood.

The point defect model (PDM) proposed by Macdonald [14,15] provides a microscopic description of the growth and dissolution of passive films. PDM-III [16] is undergoing rapid development, particularly with respect to the growth of the bi-layer structure of the passive film on SS under controlled electrochemical conditions. However, PDM is limited to only the equilibrium state of the passive film and cannot be used to analyze the initial period of passive film formation in a non-equilibrium process. Therefore, PDM cannot explain why the outer layer is Fe₂O₃-enriched and the inner layer is Cr₂O₃-enriched of the passive film. In some research [17–19], solution theory is used to explain the Cr₂O₃ enrichment phenomenon of passive films, where Fe₂O₃ is selectively dissolved due to the much lower bond dissociation energy of Fe–O than that of Cr–O [18]. Solution theory can successfully explain the Cr-enriched oxide in the inner layer but is invalid for the Fe-rich oxide in the outer layer.

The passive film on nanocrystalline (NC) SS is more compact than that on coarse crystalline (CC) SS. Many works have been conducted to interpret the mechanism, but different results were obtained. Wang [20] attributed the more compact oxide film on NC-304SS created by severe rolling to the larger percentage of both Cr³⁺ and Cr in the oxide film. The literature [21–23] reported that the higher ratio of Cr oxide to Fe oxide was responsible for the greater compactness of the passive film on NC-304SS prepared by magnetron sputtering. According to Li [24], the enhanced compactness of the passive film on the NC-304SS by dynamic plastic deformation was attributed to a Cr⁰-rich layer at the passive film/metal interface, whereas the total Cr content did not

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increase. The present authors found no total Cr (including the metallic and oxide states) enrichment in the passive film on NC-304SS produced by equal channel angular pressing (ECAP), but whether there was enrichment of the metallic state (Cr^0) or oxide state (Cr^{3+}) was not studied [4]. The mechanism for the compactness improvement of the passive film induced by NC structure is still not well understood or established for SS.

Thus, the present work focuses on two aspects: first, a reasonable interpretation of the bi-layer structure of the passive films on both the NC and CC 304SSs; second, a detailed explanation for the higher compactness of the passive film on the NC-304SS, with the aim of better understanding the whole process of passive film formation on both the NC and CC 304SSs.

2. Experimental materials and procedures

The as-received material was AISI 304SS, with a chemical composition (wt.%) of Cr 18.60, Ni 7.88, Mn 0.94, Si 0.40, C 0.08, S 0.002, and balance Fe. The NC-304SS was prepared by equal channel angular pressing, and more details about the ECAP set-up and procedures are described in Ref. [4]. The solution-treated CC specimen and the NC specimen subjected to ECAP for eight passes were used for the investigation.

The microstructures on the transversal plane of the CC and NC specimens were observed by an optical microscope (OM) and a transmission electron microscope (TEM). For TEM observation, slices with a thickness of 0.5 mm were cut from the transversal plane of the ECAPed rods, manually thinned to 80 μm and then cut into discs with a diameter of 3 mm. Thin foils were made from these discs with a twin-jet polisher at a current of 90 mA in an electrolyte of 10% perchloric acid and ethanol at room temperature. A JEM-2100 operating at 200 kV was used for microstructure observation. The grain size was calculated and estimated by a combination of linear intercept method and TEM observation.

All specimens for electrochemical tests were embedded in epoxy resin leaving an exposed working area. The specimens were mechanically ground using emery paper up to 1500 grade and then polished and rinsed in distilled water. The back sides of the specimens were welded with copper wire using tin solder and then sealed with wax.

Electrochemical tests were performed in 0.5 M H_2SO_4 solution using an Autolab PGSTAT30 Potentiostat at room temperature (25 $^\circ\text{C}$). A three-electrode cell was used with the specimen as working electrode, a piece of graphite as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The solution (0.5 M H_2SO_4) was prepared from analytical grade 97% H_2SO_4 and distilled water. The pH value of the solution was directly measured with a glass electrode pH meter (Sartorius PB-10, Germany) throughout the experimental process. Prior to each experiment, the working electrode was cathodically polarized at $-1.2 V_{\text{SCE}}$ for 600 s to remove the air-formed oxide. The scan rate was 0.5 mV/s for the potentiodynamic polarization measurement. In the galvanostatic polarization experiment, the variation of the potential over time was measured at the passive current density of 1.0×10^{-5} and $5.0 \times 10^{-5} \text{ A cm}^{-2}$ for NC and CC samples respectively to obtain the information about passive film growth. In the potentiostatic polarization measurement, the variation of the current density over time was measured at 0.5 V_{SCE} in the passive region to characterize the compactness of the passive film as a whole. In the capacitance measurement (Mott–Schottky plot) and the XPS depth profile analysis of the passive film, the specimens after cathodic reduction were passivated for 1200 s at 0.5 V_{SCE} in the passive range in 0.5 M H_2SO_4 solution. Capacitance measurements were conducted at a frequency of 1 kHz using a 5 mV AC signal (peak to zero) and a step rate of 40 mV in a potential range from -0.5 to 1 V_{SCE} .

XPS analysis was performed at room temperature using an ESCALAB250 instrument with monochromatic Al-K α X-ray radiation and a hemispherical electron analyzer operating at constant

transmission-pass energy of 20 eV. The thickness of the passive layer was determined using a raster 1 keV Ar^+ ion beam at a rate of 2.04 nm/min, which was calibrated by measuring the sputtering depth per minute in a standard specimen (SiO_2). After background subtraction and processing with XPSPEAK software, the XPS signals were separated into the contributions of different species. The evaluation of the spectra was performed using the parameters of standard peaks.

3. Experimental results

3.1. Microstructure

The microstructure of the solution-treated stainless steel (CC-304SS) is shown in Fig. 1a. It is seen that the grains of CC-304SS are approximately equiaxed with grain size of about 50 μm and there exists a large number of annealed twins. The grains of NC-304SS become so refined that could not be seen by OM in Fig. 1b. TEM observation was therefore performed to study the more detailed microstructure of NC-304 SS. Fig. 1c shows the bright field images and selected area electron diffractions (SAED) of NC-304SS. Fig. 1d is the dark field image corresponding to Fig. 1c. The TEM observation indicates an equiaxed grain size of about 80–120 nm for the NC-304SS. It can be concluded that 8-pass ECAP has effectively refined the CC-304SS into NC-304SS.

3.2. Potentiodynamic polarization

The anodic potentiodynamic polarization curves of the CC and NC 304SS samples in 0.5 M H_2SO_4 solution are shown in Fig. 2. The shape of the polarization curves is not influenced by the nanocrystallization process, which implies that the electrode reaction process of the two samples is essentially the same. Both CC and NC 304SSs display a self-passive behavior in the solution, with a similar passive region from 0 to 0.9 V_{SCE} and a similar breakdown potential. Compared with the CC sample, the NC sample shows a more positive corrosion potential (E_{corr}) and a lower steady-state passive current density, which indicates that the general corrosion resistance and electrochemical stability of the passive film on NC-304SS are improved. Accordingly, the passive films formed at 0.5 V_{SCE} in the passive region are chosen as the experimental objects in the following tests.

3.3. Potentiostatic polarization

The variation of current density (I) with time (t) during passive film formation in potentiostatic polarization reflects the compactness of the passive film. If the contribution of the double layer charge is neglected, the initial decrease in the current density is related to the growth of a protective film on the electrode surface. For prolonged polarization, the current density will decay continuously, and the time dependency of the potentiostatic current density can be expressed by the formula [25],

$$I = 10^{-(A+k \log t)} \quad (1)$$

where I represents the current density, t is the time, A is a constant and k represents the slope of the double-log plot for potentiostatic polarization. According to the literature [26], $k = -1$ indicates the formation of a compact, highly protective passive film, whereas $k = -0.5$ indicates the presence of a porous film, growing as a result of a dissolution and precipitation process.

Fig. 3 shows the double-log plots for the potentiostatic polarization of CC and NC 304SS samples at 0.5 V_{SCE} in 0.5 M H_2SO_4 solution. Initially (approximately 60 s), the values of k of the passive films on both samples are similar (-0.18 to -0.20), which indicates the inability to form good quality passive films for both samples. However, transitions

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