



Duplex stainless steel passive film electrical properties studied by *in situ* current sensing atomic force microscopy



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ABSTRACT

The duplex stainless steel passive film electrical properties before and after passivation were investigated by current sensing atomic force microscopy and X-ray photoelectron spectroscopy (XPS). The current maps and band gap energies extracted from I–V curves show that the conductivity of passive film covering austenite and ferrite is different and decreases with increasing film formation potential due to the changes in the passive film thickness and composition, confirmed by XPS analysis. I–V curves reveal that the passive films exhibit *p*-type or *n*-type semiconducting properties depending on the film formation potential, attributed to different film chemical composition, supported by XPS results.

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1. Introduction

The corrosion resistance of stainless steel to various corrosive environments is primarily due to the protective passive layers formed on the surface. The changes in passive film and breakdown of passive film directly affect the localized corrosion resistance, leading to pitting, crevice, and intergranular corrosion, along with stress corrosion cracking [1,2]. The passive film properties can vary in terms of the alloy composition, environment, film thickness, structure, stoichiometry, etc. [3,4]. Therefore, investigating passive films local properties is important for understanding the mechanisms of passivity breakdown. Moreover, it is assumed that the breakdown of the passive films on stainless steels is mainly controlled by ionic and electronic transport processes [5–7]. Both of these processes are in part controlled by the electronic properties of the passive film [8–10]. Consequently, the electrical properties are expected to be crucial for understanding the film corrosion resistance characteristics. Recent research of the electronic properties of passive films formed on stainless steels has provided an important contribution for understanding the passive film breakdown mechanisms [11–13]. Several studies at the macroscopic scale indicated that passive oxide films formed on stainless steel are generally composed of two distinct regions of different chemical composition and the semiconductor type [14–16]. However, both chemical and electronic properties of passive films are un-

likely to be uniform along the stainless steel surfaces, especially for duplex stainless steels. This is because of a combination of austenite and ferrite phases with a complex microstructure, leading to the differences in corrosion resistance between the two phases [17–19]. Therefore, it is necessary to examine the local characteristics of passive films formed on duplex stainless steel surfaces at the microscopic scale by precise measurements.

Atomic force microscopy (AFM) with a conductive probe can simultaneously characterize both surface topography and the current distribution of passive films with high spatial resolution. By using the current sensing atomic force microscopy (CSAFM), Souier et al. characterized the local electronic properties of the passive film on duplex stainless steel, and demonstrated that the passive film covering austenite and ferrite phases exhibits different properties [20]. They also investigated the effect of surface preparation of 304L stainless steel on electrical conductivity of passive film by CSAFM [21]. However, there is no information available about the semiconducting properties of passive films, including the semiconductor type, which is vital for understanding of mechanisms behind passivity and localized corrosion. Mott–Schottky analysis is widely employed to determine the semiconductor type of the passive film, but it is carried out in the solution at the macroscopic scale, and the results depend on the electrolytic media and the applied potential [22–24]. In order to characterize the semiconductor type and properties of the passive film in air environment at the microscopic scale, a novel measurement approach must be used, which is independent of the measurement conditions, such as the electrolyte and the applied potential.

The present study aims to investigate the semiconducting type and properties of passive films formed in air and at different

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potentials on duplex stainless steel by using CSAFM in air environment. X-ray photoelectron spectroscopy (XPS) was used to characterize the changes in the chemical composition of the passive film.

2. Experimental

2.1. Material and samples preparation

The material used for experiments is conventional 2507 duplex stainless steel, with the chemical composition shown in Table 1, as described in our previous reports [25–27]. The specimens were machined into square sheets with 6 mm × 6 mm × 0.7 mm dimensions. The surface of each specimen was wet ground with SiC paper up to the 2000 grit, and polished using diamond paste to 0.5 μm. Once the mechanical polishing was finished, a final electrochemical etching was performed in a mixed solution of HNO₃:H₂O = 1:1 for 20 s at an applied voltage of 1.2 V, so that the ferrite and austenite phases could be distinguished. Then the specimens were ultrasonically cleaned in ethanol and dried in N₂ gas flow. To identify the scanning region, indentations were made on the surface of each specimen using the digital microhardness tester (HVS-1000) prior to CSAFM measurements.

After surface preparation, specimens were kept for 24 h in air, allowing the formation of a native passive layer. For the formation of passive films, the specimens of 2507 duplex stainless steel were pretreated cathodically at $-0.8 V_{SCE}$ (voltage per saturated calomel electrode), applied for 0.5 h to remove the native oxide film and then polarized in the 0.1 M Na₂B₄O₇ solution (pH = 9.2) with a scanning rate of 2 mV/s for 2 h at different film formation potentials. The experiments were carried out at room temperature with the electrochemical cell consisted of specimen as the working electrode, and a saturated calomel and platinum as reference and counter electrodes. Since the passive potential ranges from about -0.2 to $1.1 V_{SCE}$, the passive films studied were formed at 0, 0.3 and 0.9 V_{SCE} , representing different potential passive regions.

2.2. Passive film in situ CSAFM measurements

The CSAFM measurements of passive film were performed using Agilent 5500 AFM (Agilent Technologies, USA) operated in the current sensing mode, which measures the surface topography in contact mode along with a voltage applied between the tip and the sample, allowing to obtain topography and current data simultaneously. In addition to topography and current maps, current–voltage (I–V) curves were acquired by setting the probe tip in contact with the passive film at different locations in ferrite and austenite phases of the current maps, which were done at least 10 times at different locations of the specimen, or at different sites of the same locations, to understand the reproducibility. Both current and I–V measurements were carried out in air environment and relative humidity of about 25%. The surface region (80 μm × 80 μm) was scanned at a frequency of 0.1 Hz. The probes used were DPE14/AIBS conductive Pt-coated silicon tips with a force constant of 5.7 N/m and a tip radius of 50 nm.

Table 1
The chemical composition of the 2507 duplex stainless steel.

Phase	Composition in (wt.%)							
	C	Cr	Mn	Fe	Ni	Mo	N	S
α	0.011 ± 0.001	28.59 ± 0.17	0.66 ± 0.09	61.59 ± 0.31	5.06 ± 0.12	5.04 ± 0.07	0.06 ± 0.01	0.002 ± 0.001
γ	0.012 ± 0.001	25.72 ± 0.16	0.81 ± 0.09	62.40 ± 0.31	7.15 ± 0.12	3.75 ± 0.06	0.59 ± 0.01	0.001 ± 0.001

2.3. Surface analysis

The chemical compositions of the passive films formed in air and at different formation potentials were investigated with XPS using an AXIS ULTRA^{DL}D instrument with a monochromatic Al Kα radiation source with the energy of 1486.6 eV and a pass energy of 40 eV. As for the total energy resolution, the full width half maximum (FWHM) of Ag 3d_{5/2} is less than 0.48. The curve fitting was performed using the commercial software XPS Peak, version 4.1, which contains the Shirley background subtraction and Gaussian–Lorentzian tail functions, to achieve better spectra fitting.

3. Results

3.1. CSAFM of the native passive film formed in air

After etching of duplex stainless steel specimen, the ferrite (dark color) and austenite (light color) can be distinguished clearly in optical micrograph, shown in Fig. 1a, which is in good agreement with our previous work [25]. The assignment of phases in the image is further demonstrated by magnetic force microscopy (MFM) image (Fig. 1b) from the area shown in the box in Fig. 1a, where striped magnetic domains can be observed in the region of ferromagnetic ferrite, but not in the paramagnetic austenite. The AFM image (Fig. 1c) on the same area as the MFM image (Fig. 1b), also exhibits the brighter austenite grains and the darker ferrite matrix, and the average height difference between the ferrite and austenite grains is about 50 nm, which is obvious in AFM topography profile, shown in Fig. 1c1.

Fig. 1d shows CSAFM map obtained by applying +0.8 V bias to the probe tip after formation of a native passive layer in air in the same area as MFM and AFM images (Fig. 1b and c). With the aid of AFM and MFM images, the ferrite and austenite phases can be easily distinguished in the current images. Current map indicates that the austenite has a higher current than the ferrite, as shown in Fig. 1d. A line profile in the current map (Fig. 1d1) shows that the current measured on austenite is about 0.23 nA, while on the ferrite it is about 30 pA. The current in austenite obtained at +1.5 V bias has strongly increased compared with the current map obtained at +0.8 V, shown in Fig. 1e and e1. Moreover, the electrical current measured by CSAFM depends on the applied voltage sign, which agrees with the previous reports [28,29]. Compared with the current map obtained with the positive bias (+1.5 V), the current measurements with the negative bias (−1.5 V) display drastic changes of contrast in the current image (Fig. 1f and f1).

3.2. CSAFM of the passive films formed at various potentials

Fig. 2 shows the topography image and the current maps, along with the corresponding current profiles of the passive films formed at 0 V_{SCE} potential in the same scanning region. Compared with the freshly prepared specimen (Fig. 1c), the topography in Fig. 2a remained unchanged, however, the current maps in Fig. 2b–d exhibit significant differences for the same applied tip bias. Although the passive layer on austenite still has higher current than on ferrite, the current drops rapidly on both phases at the same tip bias, i.e.

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