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Short communication

Direct observation of thin membrane passive film over the growing pit on sputtered nanocrystalline austenitic stainless steel film

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ABSTRACT

Potentiostatic polarization with a temperature scan was applied to initiate formation of a single pit on a sputtered nanocrystalline austenitic stainless steel film and the thin membrane passive film over the growing pit was directly observed for the first time in this study. The results showed that the passive film consisted of two different layers, both of which exhibited an amorphous structure. The outer layer comprised of a Fe-enriched oxide, whereas the inner layer was a Cr-enriched oxide. Compared with conventional coarse-grained stainless steel, the passive film of sputtered nanocrystalline austenitic stainless steel possessed higher elastic modulus and hardness.

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1. Introduction

In previous studies [1,2], sputtered nanocrystalline austenitic stainless steel (SNAss) was shown to possess considerably superior corrosion resistance in corrosive solutions, compared with conventional coarse-grained stainless steel (CCGss). One of the main reasons is the formation of a more protective passive film on the surface [3,4].

Although various ex-situ and in-situ techniques have been used to characterize the passive films [5–9], the composition and structural details have yet to be well understood [7,10]. Recently, cross-sectional investigation using FIB/TEM has been applied to characterize the native passive film on CCGss [11–13]. The results revealed the cross-sectional image as well as the amorphous structure of the passive film, with an enrichment of Cr. However, the detailed structure of the passive film, such as the duplex-layer structure, which has been previously confirmed [10], was not directly observed in these cases, possibly because of the extremely thin and non-uniform nature of the passive film on CCGss, which makes it extremely difficult to distinguish the possible sub-layers and the film/substrate interface. According to our previous study [3], the passive film formed on SNAss is significantly more compact and uniform than that on CCGss. Consequently, techniques (other than cross-sectional investigation), which can enable direct observation and investigation of the native passive film and its detailed structure on SNAss, need to be employed, for more effective characterization.

The presence of covers over the pits growing on stainless steel in chloride solution has been observed earlier [14–18]. According to Burstein [19], such covers are formed during the pit growth and act as a barrier when metastable–stable transition occurs. Further investigations by Newman and co-workers [20–22] revealed that the covers on most stainless steels present lacey-morphology. According to these studies, the pit cover should consist of a vestige of unreacted metal, and probably also contains the passive film which had originally covered the metal surface before the occurrence of pitting corrosion. Unfortunately, except for the lacelike residual metal, the coexisting passive film has never been directly observed in previous studies, and most discussions have been essentially theoretical.

In the present work, a single stable pit has been initiated by potentiostatic polarization with a temperature scan on a SNAss film. The thin membrane passive film over the growing pit was directly observed, for the first time, by both scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The structure, composition and mechanical properties of the passive film have been further characterized.

2. Experimental

The SNAss film studied in this work was prepared by magnetron sputtering, using the target of a coarse-grained austenite stainless steel (wt.% composition: 20.4% Ni, 14.45% Cr, 2.66% Mo, 2.72% Al, 1.58% Mn, 0.98% Nb, 0.21% Si, 0.075% C, 0.010% B, 0.0031% P, 0.004% S and remainder Fe). The SNAss film was deposited on a glass substrate. The obtained film was about 20 μm thick and displayed a columnar crystal structure with an average grain size of about 50 nm. In the previous studies [1–3], the SNAss film have been shown to possess strong

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passive ability and excellent corrosion resistance with a high pitting potential.

Potentiostatic polarization with a temperature scan was applied to initiate formation of the single pit. The test was performed in a standard three-electrode cell, using an Autolab PGSTAT302. The counter electrode (CE) was a high-purity Pt electrode and the reference electrode (RE) was a saturated calomel reference electrode (SCE). The SNAss film served as the working electrode (WE) with an exposed working area of 0.3 cm^2. The test solution was 3.5% NaCl solution.

Before the test, the sample was exposed entirely to the test solution, initially at 0 °C. After an initial temperature stabilization period, the water bath was heated at a rate of 1 °C/min. Because of the thermal losses, the actual average heating rate of temperature in the test solution was about 0.85 °C/min. About 60 s before the temperature scan commenced, the sample was anodically polarized to a constant potential above the pitting potential range, 700 mV (SCE) in the present work. The test was terminated when the pitting current reached about 3 mA.

The microstructure of the passive film was visualized by both SEM (ZEISS SUPRA 55) and TEM (JEOL 2100F operating at 200 kV). The composition of passive film was analyzed by X-ray photoelectron spectroscopy (XPS) (ESCALAB250).

The mechanical properties of the passive film were characterized by nanoindentation. The tests were carried out at room temperature by an Agilent G200 Nano Indenter using a diamond Berkovich tip with a maximum penetration depth of 350 nm. Four different samples (the blank samples without passivation treatment: blank-SNAss and blank-CCGss; the samples with passivation treatment: passive-SNAss and passive-CCGss) were tested and sixteen indentations were performed for each sample. The Poisson's ratio of the investigated material was chosen to be $\nu = 0.3$. The elastic modulus (E) and hardness (H) were calculated from load-displacement curves using the Oliver–Pharr method.

3. Results and discussion

3.1. Observation of thin membrane passive film over the growing pit

Fig. 1 shows the plot of potentiostatic polarization with a temperature scan. The pit initiation process can be divided into two stages, the passive stage and the pitting stage. The passive stage lasted for about 3400 s with the passive current maintained at about ~10^{-8} A. During this stage, the passive film was formed and then developed over the SNAss surface. However, increasing the temperature appeared to enhance the tendency of pitting on the surface, and the metastable pitting obviously occurred at the end of the passive stage, as shown in the arrowed plot in Fig. 1. Immediately after this metastable pitting region, the current rose sharply, indicating the occurrence of stable pitting. After the test, the substrate under the cover was entirely dissolved, whereas the pit cover remained in perfect condition.

Fig. 2(a) displays the corrosion morphology observed from underneath the pit cover. Fig. 2(b) and (c) shows that the pit cover contained a mesh of residual metal with the "holes" covered with thin membrane passive film, which is consistent with Burstein's theory [19]. The residual metal displayed a lacey morphology, which is in agreement with Newman's observations on stainless steel [21,22], whereas the passive film was presented as a thin membrane state. An observation at a higher magnification by TEM in Fig. 2(d) suggests the curly state of the passive film at the edge of pit cover, which is a novel observation. According to previous work [3], the passive film of the SNAss possesses an excellent stability. It is believed that there is no obvious difference between the passive films originally covering the metal surface and that remaining after pitting.

3.2. The structure and composition of the passive film on SNAss

The high magnification SEM image in Fig. 2(c) shows that the passive film was clearly made up of two different layers. The bright-field TEM image with selected area electron diffraction (SAED) pattern inset, as displayed in Fig. 2(e), shows the distinctly duplex-layer-structured passive film. The light color region corresponded to the first layer while the darker region referred to the overlap of the first and the second layers. The SAED patterns of the two regions appeared as an amorphous diffraction ring, indicating that both layers had amorphous structures. The bilayer was observed to be incomplete in some places, which may due to the mechanical rupturing during pitting or sample preparation.

XPS was carried out near the corrosion pit to analyze the composition of the passive film. Fig. 3(a) and (b) displays the Fe and Cr spectra of the outer layer (ion sputtered for 0 s), respectively. The main constituents of the outer layer were: 50.49 at.% Fe_2O_3, 16.43 at.% Cr_2O_3, 29.73 at.% Al_2O_3 and 3.35 at.% MoO_3. Fig. 3(c) and (d) displays the Fe and Cr spectra of the inner layer (ion sputtered for 15 s), respectively. The main constituents of the inner layer were: 27.35 at.% (Fe_2O_3 + FeO), 41.55 at.% Cr_2O_3, 30.11 at.% Al_2O_3 and 0.99 at.% MoO_3.

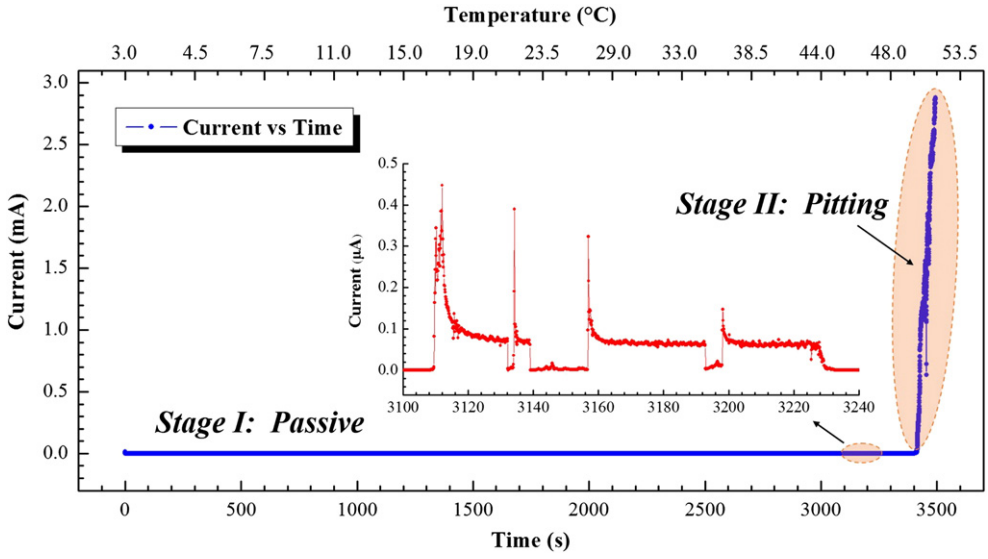

Fig. 1. Potentiostatic polarization with a temperature scan plot.

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