Passive film growth mechanism of nanocrystalline 304 stainless steel prepared by magnetron sputtering and deep rolling techniques

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**ABSTRACT**

The passive film growth mechanisms of deep rolled bulk nanocrystalline (BN) 304ss and magnetron sputtered nanocrystalline (NC) 304ss thin film as well as that of the conventional rolled coarse crystalline (CC) 304ss has been studied by electrochemical measurements and in situ AFM observation in 0.05 M H\textsubscript{2}SO\textsubscript{4} + 0.2 M NaCl solution. The growth of the passive film on all three materials was three-dimensional and the growth rates were, in decreasing order: NC thin film > BN 304ss > CC 304ss. Also, nanocrystallization caused the nucleation mechanism of the passive film to change from progressive to instantaneous. The passive films on the CC 304ss and BN 304ss displayed a monolayer structure while that on the NC thin film had a multi-layered structure.

1. Introduction

It is well known that nanocrystallization can significantly enhance the corrosion resistance of stainless steels [1–3]. It has been shown that nanocrystallization remarkably influences the properties of the passive films on stainless steels, such as the semiconducting properties and compactness, and as well improves corrosion resistance [4]. Although the performance of passive films depends directly on the formation process, only few studies have focused on the growth mechanism of passive films, and on how nanocrystallization influences the growth mechanisms. Therefore, it is necessary to study the passive film growth process of nanocrystalline stainless steels, to enable better understanding of the influence of crystalline structure on the performance of the passive film.

Among several nanocrystallization methods, the magnetron sputtering technique has attracted considerable attention. This is because it results in the formation of a homogenous thin film, with uniform composition and grain size. Also, the sputtered thin film has the same chemical composition as that of the bulk target and good adhesion [5]. In addition, sputtered nanocrystalline thin films have been found to exhibit superior anticorrosive ability compared with that of conventional cast alloys [6–9], and have been used successfully in high-temperature alloys [10–12]. Another method of nanocrystallization is by deep rolling treatment, which directly changes the whole material into a bulk-nano material. Apart from the decrease in the grain size, the physical properties of the nano material obtained by deep rolling treatment remain largely unchanged, but the chemical/electrochemical properties vary. For instance, the electrochemical behavior of deep rolled nanocrystalline 304ss has been studied and it was found that the corrosion resistance was enhanced [13].

In-situ AFM observation, which provides direct information on corrosion process, has recently been used to study pitting corrosion mechanism of stainless steel, such as the location of pit initiation [14], the shape of pit [15] and the role of sulphide inclusions on pit initiation [16]. However, several such investigations have been focused on destruction process of passive film, only little is available on the growth process, especially the sequential in situ AFM observation of growth mechanism during polarization scans. In this work, the passive film formation process of rolled coarse crystalline (CC) 304ss, deep rolled bulk nanocrystalline (BN) 304ss and magnetron sputtered nanocrystalline (NC) 304ss thin film in acidic sodium chloride solution has been investigated by electrochemical measurements and in situ AFM observation to monitor the influence of nanocrystallization on the passive film growth mechanism of CC 304ss in details.

2. Experimental

2.1. Materials preparation

The composition (in wt.%) of CC 304ss was as follows: 8.054\% Ni, 17.10\% Cr, 0.091\% Mo, 1.280\% Mn, 0.277\% Cu, 0.003\% As, 0.006\%
Sn, 0.387% Si, 0.045% C, 0.026% P, 0.002% S and remainder Fe. The NC thin film was deposited on one side of a glass substrate using the SBH-5115D DC magnetron sputtering system with CC 304ss as target. The magnetron sputtering chamber was evacuated to \(5 \times 10^{-3}\) Pa, then filled with Ar, maintained at 0.2 Pa. The temperature of the substrate glass was approximately 200 °C. The DC power was 1800 W and the sputtering duration was 2 h.

The BN 304ss samples were directly fabricated by deep rolling treatment the CC 304ss as described previously [13]. The CC 304ss samples (10 mm × 10 mm × 10 mm) and the BN 304ss samples (10 mm × 10 mm × 2 mm) were ground to 1000 grit SiC paper and degreased in acetone. All 304ss samples were either embedded in epoxy resin or paraffin-resin, leaving an exposed working area of 1 cm².

2.2. Materials characterization

The microstructure of the CC 304ss was characterized by optical metallography. The grain size of the NC thin film was characterized by transmission electron microscopy (TEM) (JEM-2000EXII). The cross-section of the NC thin film was observed by scanning electron microscopy (SEM) (XL30FEG). The phases of the three materials were analyzed by X-ray diffraction (XRD) analysis.

2.3. Electrochemical experiments

All electrochemical measurements were carried out using a PAR2273 Electrochemical Measurement System (EG&G) in a conventional three-electrode cell with a large platinum plate as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All potential values reported in this paper are with reference to SCE in saturated KCl solution whose potential value versus SHE is 0.2438 V. The aggressive medium used in all experiments was 0.05 M H₂SO₄ + 0.2 M NaCl solution prepared from reagent grade chemicals and distilled water, pH of which was 1.26 measured by laboratory pH meter. The test solution was degassed with nitrogen for 1.5 h before experiment. A water bath was used to maintain the solutions at 30 ± 1 °C during testing. Prior to all electrochemical measurements, the specimens were initially reduced potentiostatically at −1 V SCE for 2 min to remove air-formed oxides on the surface and then kept in solution until a stable corrosion potential was attained.

The scanning rate of the potentiodynamic polarization measurements was 20 mV/min. In the potentiostatic–galvanostatic (P–G) transient technique, the electrode was first held at a constant potential of −0.05 V SCE for 15 min with a passive current \(I_p\), and then was switched instantly to a constant assigned current value \(I = 1/2 I_p\) (ΔI = I – I_p = −1/2 I_p, ΔI < 0). The response potential was recorded as a function of time. In the procedure of galvanostatic anodic polarization, the potential \(E\) followed as a function of time at constant current densities 2.3 × 10⁻⁶ A cm⁻², 9.4 × 10⁻⁷ A cm⁻² and 5.5 × 10⁻⁸ A cm⁻² for the CC 304ss, BN 304ss and NC thin film respectively, and the \(E/I\) curves were recorded. All the electrochemical measurements have been repeated at least three times until good reproducibility of the data was obtained.

2.4. In-situ AFM measurements

For AFM measurements, the samples were cut into coupons of dimensions 20 mm × 20 mm × 2 mm and fixed in a Teflon electrochemical cell with an O-ring to prevent the liquid from leaking out. The measurements were carried out with a three-electrode setup: the working electrode was the sample on the bottom of the cell, the counter electrode was a Pt ring line with 0.25 mm diameter around the cell, and an Ag line with 0.51 mm diameter was used as the reference electrode. All the AFM experiments were carried out in contact mode. The scanning area in the images was 2 μm × 2 μm. In-situ AFM scanning was performed under anodic potential at −0.05 V SCE for the three materials. To calibrate the potential of the Ag reference electrode with respect to the SCE used for polarization experiments, the OCP differential using both reference electrodes was determined and a corresponding potential (anodic) was imposed on the samples during AFM measurements.

3. Results and discussion

3.1. Microstructure

Optical photomicrography of the CC 304ss is shown in Fig. 1, and reveals the grain size to be about 100 μm. Previous TEM investigation indicated that the grain size of the BN 304ss was about 100 nm [13]. The dark-field TEM result shown in Fig. 2 indicates an average grain size of the NC thin film is less than 50 nm. Moreover, the fine grain size is further demonstrated by the continuous ring character of the electron diffraction pattern. Fig. 3 depicts cross section morphology of the NC thin film, which reveals a typical column-
narrow structure along the deposition direction and thickness of about 12 μm. XRD patterns of the three materials, presented in Fig. 4, shows that the CC 304ss and BN 304ss exhibit single austenitic structure, while the NC thin film exhibits a single ferritic structure. However, for single phase structured sputtered thin films, the transition from austenitic to ferritic does not influence its corrosion resistance remarkably [17,18].

3.2. Potentiodynamic polarization measurement

Fig. 5 displays the potentiodynamic polarization curves for the three samples in the test solution and reveals significant differences in the corrosion behavior of the three materials. The existence of three corrosion potentials for the CC 304ss reveals that it was an unstable passive system, while the BN 304ss and NC thin film, directly entered the passive region under the applied potential and exhibited excellent passivation ability. The breakdown potentials of the BN 304ss and NC thin film are more positive than that of the CC 304ss and the passive regions are wider which indicate that nanocrystallization increases the passivation ability of the CC 304ss. However, the minimum passive current density of the passive film on the NC thin film significantly increases, compared with that on the other two materials. The potential at which the three samples were studied was chosen to be -0.05 V SCE, under which the steady passive films on all samples could be obtained.

3.3. Nucleation mechanism of the passive film

Nowadays current-time transients have been widely utilized to study the kinetics of anodic film formation [19–21]. In this work, the widely used theoretical model for electrochemical nucleation developed by Scharifker and Hills [22] was chosen to analyze our experimental current–time transients. This model enables simple and rapid classification of experimental transients into the two limiting nucleation mechanisms—progressive or instantaneous. The equations of the theoretical models for progressive and instantaneous nucleation can be expressed as follows:

Progressive nucleation: \[ \frac{j^2}{j_m^2} = \frac{1.2254}{t/t_m} \left[ 1 - \exp \left( -2.3367 \left( \frac{t}{t_m} \right)^{3/2} \right) \right] \]

Instantaneous nucleation: \[ \frac{j^2}{j_m^2} = \frac{1.9542}{t/t_m} \left[ 1 - \exp \left( -1.2564 \left( \frac{t}{t_m} \right)^{3/2} \right) \right] \]

where \( j_m \) and \( t_m \) are the current density and the time, as respective peak coordinates. Fig. 6 displays the experimental current transient plots of the three materials which are characterized by an initial current increase as a response to the applied potential and a subsequently decreasing portion due to the nucleation process. The plots of the experimental current transients in \( j^2/j_m^2 \) vs \( t/t_m \) coordinates can follow either of the two limiting cases: instantaneous and progressive. Fig. 7 shows the experimental current transients plotted in reduced current-time coordinates for three materials, along with the lines for instantaneous and progressive nucleation described by Eqs. (1) and (2) in each plot for clearer illustration of the experimental nucleation types.

It is obvious that in the case of the passive film on the CC 304ss (Fig. 7a), the decreasing portion of the experimental plot follows closely the theoretical progressive nucleation curve. That is to say that the passive film on the CC 304ss followed the progressive nucleation mechanism. For the passive films on the BN 304ss and NC thin film (Fig. 7b and c), the decreasing portion of the experimental plots seem to follow the theoretical instantaneous nucleation curve more closely, suggesting that the passivation process for the two nanocrystalline materials was by instantaneous nucleation mechanism. In a word, nanocrystallization changed the nucleation mechanism of the passive film on the CC 304ss from progressive to instantaneous nucleation. Instantaneous nucleation
corresponds to active sites which are all activated at the same time, while progressive nucleation corresponds to active sites which are activated gradually during polarization. That is to say that, all the active sites on the surfaces of BN 304ss and NC thin film were activated rapidly and almost simultaneously, which was more beneficial to formation of passive films in the early stages compared with that of CC 304ss.

3.4. Growth mechanism of passive film

So far, it has been established that nanocrystallization modified the nucleation mechanism of CC 304ss. The next objective is to study the passive film growth mechanisms of the three samples and hence determine any influence of nanocrystallization on the process. This was achieved by recording in situ AFM images of three samples during the entire passive film formation process. The in situ AFM images had been obtained for the CC 304ss, BN 304ss and NC thin film respectively after 3 min, 9 min, 15 min and 27 min of potentiostatic polarization in the test solution, which could record any differences of the surface in detail as time changed.

The roughness of the sample surface indicating changes of the passive film can be represented by fractal dimensions ($D_f$) which are computed by the well-known box-counting methods [23,24]. In order to perform this operation, the in situ AFM images were firstly changed into grey-scale images with cubic box of $256 \times 256 \times 256$, and then the number of boxes covering the surface ($N$) was counted by MATLAB software. The fractal dimensions were calculated by [25]:

$$D_f = \frac{\log(N)}{\log(255)}$$  \hspace{1cm} (3)

The fractal dimensions of passive films on three samples with different anodic polarization time were calculated by the corresponding in situ images. The results of the calculations are listed in Table 1. The value of $D_f$ for CC 304ss increased initially and then

<table>
<thead>
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<th>Time (min)</th>
<th>CC 304ss</th>
<th>BN 304ss</th>
<th>NC thin film</th>
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<tr>
<td>3</td>
<td>2.9242</td>
<td>2.9179</td>
<td>2.8861</td>
</tr>
<tr>
<td>9</td>
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<td>2.9010</td>
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<td>27</td>
<td>2.9269</td>
<td>2.9175</td>
<td>2.8935</td>
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</table>

Fig. 6. $i\cdot t$ transients for passive film formation of CC 304ss, BN 304ss and the NC thin film in 0.05 mol dm$^{-3}$ H$_2$SO$_4$ + 0.2 mol dm$^{-3}$ NaCl solution.

Fig. 7. Non-dimensional $j^2/j_{0a}^2$ vs $t/t_{lm}$ plots for passive film on the CC 304ss (a), BN 304ss (b) and NC thin film (c).
decreased with increasing polarization time. The trend of $D_f$ for the other two nanocrystalline materials was the same as that of the CC 304ss but more pronounced. The passive film grew with increasing polarization time, which led to changes of their surface roughness. In addition, the values of $D_f$ representing the changes of the surface roughness were calculated by the in situ AFM images. That is to say, the values of $D_f$ could reflect surface changes of the passive films in the same area as time changed. Therefore, the initial increase of $D_f$ for three materials can be attributed to changes of the surface roughness due to passive film growth. In other words, the growth mechanism of the passive films on the three samples was three-dimensional. The following decrease of $D_f$ will be discussed in next.

In order to analyze the passive film formation process in detail, a linear scan plot of the in situ AFM images was adopted, which could demonstrate clearly the changes of passive film though the in situ AFM images look alike in the morphology. Figs. 8–10 depict the in situ AFM images of the surface morphology and their corresponding linear scan plots after 3 min and 27 min, respectively. It is clear that with increasing polarization time, the passive film on the CC 304ss grew at hollows (from 33.2 nm to 35 nm) while dissolution occurred at bulges (from 53 nm to 51.5 nm). Similar results were also observed on the two nanocrystalline materials. The combined effect of these growth and dissolution processes led to some sort of smoothening of the passive film surface, thereby decreasing the surface roughness. This also accounts for the observed decrease in the values of $D_f$. In addition, it is important to note that growth and dissolution rates in three-dimensional scale of the passive film on CC 304ss and BN 304ss were comparable, while those of the NC thin film were much faster. This is easily verifiable by carrying out simple subtractions on the values displayed in the linear scan plots. The small grain size on the NC thin film promoted the diffusion of element to increase the growth rate in three-dimensional scale of the passive film, while the high population of grain boundaries serves as fast diffusion conduits for the corrosive medium, leading to higher dissolution rates.

The in situ AFM images (Figs. 11–13) present the 2-D changes in the dimensions $(x, y)$ of a single particle in the passive films on three materials with an increase in polarization time. Such 2-D changes can be clearly visualized from the corresponding linear scan plots of the in situ AFM images and could represent the passive film growth rate in a 2-D scale. The change in the dimensions of particle on the CC 304ss was 6 nm $(x$-direction) and 4 nm $(y$-direction); however, those of BN 304ss and NC thin film were 17 nm $(x$-direction), 20 nm $(y$-direction) and 12 nm $(x$-direction), 7 nm $(y$-direction) respectively, within the same time interval. This means that nanocrystallization favored the formation of a continuous, compact and protective film by promoting the 2-D growth rate of the passive films, which increased in the order: CC 304ss < NC thin film < BN 304ss.

3.5. Growth rate of passive film

The passive film formation rate on the three materials could be obtained from galvanostatic anodic polarization curves, in which the potential is followed as a function of time at constant current density [26]. At the initial stages of polarization, there is a potential drop due to the beginning of the anodic dissolution process (before film formation). When the film formation eventually overcomes anodic dissolution, the potential starts to rise in the anodic direction and the $E$/$t$ relationship gives fairly linear segments whose slopes $(dE/dt)_s$ represent the passive film formation rates. Higher values of the slope correspond to more rapid passive film formation [26,27].

Fig. 14 displays the galvanostatic plot of the three materials in this study. The slopes of the corresponding linear segments were calculated and listed in Table 2. Based on the results, the potential in the linear part of the curve for CC 304ss increased steadily with time, which suggests that the film grew continu-

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**Fig. 8.** In-situ AFM images and corresponding linear scan plot of CC 304ss in growth stage of passive film under anodic polarization after passivation 3 min and 27 min in 0.05 mol dm$^{-3}$ H$_2$SO$_4$ + 0.2 mol dm$^{-3}$ NaCl solution.
Fig. 9. In-situ AFM images corresponding linear scan plot of BN 304ss in growth stage of passive film under anodic polarization after passivation 3 min and 27 min in 0.05 mol dm$^{-3}$ H$_2$SO$_4$ + 0.2 mol dm$^{-3}$ NaCl solution.

Fig. 10. In-situ AFM images corresponding linear scan plot of NC thin film in growth stage of passive film under anodic polarization after passivation 3 min and 27 min in 0.05 mol dm$^{-3}$ H$_2$SO$_4$ + 0.2 mol dm$^{-3}$ NaCl solution.
Fig. 11. In-situ AFM images and corresponding linear scan plots (x-direction and y-direction) of single passive particles on the CC 304ss in growth stage of passive film under anodic polarization after passivation 3 min and 27 min in 0.05 mol dm$^{-3}$ H$_2$SO$_4$ + 0.2 mol dm$^{-3}$ NaCl solution.

The passive film formation rates of the BN 304ss and NC thin film were faster than that of the CC 304ss and both showed similar profiles at the initial stages. After about 1000s, the plot of BN 304ss appears to stabilize and, the growth rate of the passive film becomes very slow. On the other hand, the growth rate of the NC thin film increased almost rapidly (with a larger slope $6.55 \times 10^{-5}$ V s$^{-1}$), which indicates the commencement of a faster growth stage. This implies two dis-

![Fig. 11](image1)

![Fig. 12](image2)

Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>CC 304ss</th>
<th>BN 304ss</th>
<th>NC thin film</th>
</tr>
</thead>
<tbody>
<tr>
<td>The slopes of linear segments of plots (V s$^{-1}$)</td>
<td>$6.12 \times 10^{-6}$</td>
<td>$2.02 \times 10^{-5}$</td>
<td>(1) $2.50 \times 10^{-5}$ (2) $6.55 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
tinctive growth stages for the passive film on the NC thin film, which is very different from that of the other two materials having only one stage. Above results indicates that nanocrystallization increased the growth rate of the passive film on the CC 304ss, and the NC thin film, with small grain sizes displays a rapid stage in the growth kinetics, which was not observed for the other two materials.

In summary, the two nanocrystallization methods both accelerated the growth rate of the passive film on the CC 304ss. The differences were that deep rolling treatment promoted growth rate in two-dimensional scale of passive film, however, magnetron sputtering technique enhanced the growth ability of passive film both in two-dimensional and three-dimensional scale.

3.6. Growth structure of passive film

Based on the galvanostatic anodic polarization results, it is obvious that the growth of passive film on the NC thin film is a multi-phase process, which could lead to some structural differences when compared to that of the other two materials. In other words, different nanocrystallization methods may influence the structure of the passive films, and hence the performance of the passive films in different ways.

The P-G transient technique [28], which is a rapid electrochemical method for studying the structure of passive films, was employed in order to analyze the structure of the passive films on the three materials. If a passive film has a multi-layer structure, the stability at the interface between dissimilar layers is less stable than the interior of each layer. Such an interface can be dissolved under the effect of $-1/2I_d$ current after transition from potentiostatic to galvanostatic mode. The difference current ($I_d$) results from movement of charged particles arising from the dissolution of the interface. The higher the value of $I_d$, the larger will be the dissimilarity between layers. The formula of a P–G transient plot of the passive film can be expressed as follows [28]:

$$
\Delta E(t) = R_p \left[ -1/2I_d + \frac{I_d \exp(-t/T_d)}{1 - R_p C / I_d} - \frac{1}{2I_d + \frac{I_d}{R_p C / I_d}} \exp \left( -\frac{t}{R_p C / I_d} \right) \right]
$$

where $R_p$ is the polarization resistance of passive film, $C$ is the total capacitance (including the passive film and the double layer), $I_d$ is the difference current, $T_d$ is the decay time of $I_d$ and $t$ is the recorded time. P–G response plots of the three materials are shown in Fig. 15. The values of $R_p$, $C$, $I_d$ and $T_d$ (Table 3) were calculated by simulating the experimental data with MATLAB software. The simulated curves basically coincide with the experimental data. $I_d$ values are very important because they represent the dissimilarity between adjoining layers. From the obtained $I_d$ values, it is clear that the dissimilarity between the different layers of passive film on the NC thin film was much more pronounced than that on both BN 304ss and CC 304ss. This implies that the passive film on the NC thin film has a different structure from the other two materials, possibly because of the earlier observed multi-phase growth. If the passive films on the BN 304ss and CC 304ss are considered to be single layer, the
passive film growth occurred at hollows while film dissolution occurred at bulges and was more pronounced on the nanocrystalline materials. Nanocrystallization also accelerated the growth rate of the passive film on CC 304ss. Instantaneous nucleation and fast growth rate of passive film on both nanocrystalline materials increased the passivation ability of materials, which exhibited more positive breakdown potential and wider passive region compared with that of the CC 304ss.

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