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Research paper

Transition of oxide film configuration and the critical stress inferred by scanning probe microscopy at nanoscale

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ABSTRACT

Scanning probe microscopy (SPM) equipped in high temperature nanoindentation instrument is adopted to in situ characterize the oxide film growth on Ni-base single crystal at nanoscale. SPM images reveal a transition of oxide film configuration that the originally flat surface roughens during oxidation. Based on the stress-diffusion coupling effect during oxidation, the stress evolution in the oxide film and the evolution of surface configuration are analyzed. A new method to infer the critical stress in the oxide film at the transition point is proposed by measuring the undulated surface wavelength based on the surface morphology obtained by SPM.

1. Introduction

Understanding the mechanism of the evolution of surface morphology has been scientifically appealing as well as technologically important as in order to develop new materials and structures with enhanced novel functions [1,2]. For instance, Li et al. [1,3] studied the self-organizing nanomesa and nanowell patterns in Langmuir–Blodgett films to guide the design and optimization of nanostructures in thin films. The surface roughening of an originally flat surface is also commonly observed in film deposition in semiconductor engineering [2], where the surface evolution plays a vital role in fabricating thin films with desired properties. In addition, the surface roughening has also been an increasingly attractive topic related to oxide film growth on substrate subjected to relatively high temperature [4,5]. It has been theoretically predicted that a flat thin film is configurationally unstable during its growth (or thickening) [2,6]. In the theoretical analysis, it is assumed that the original surface is nominally flat but in reality slightly undulated at small scale. The reason for such a surface roughening phenomenon has been attributed to the stress-induced surface instability [7]. It is well recognized that stress plays an important role for the behavior of thin films [1,2,8–10]. A critical wavelength is proposed to estimate and characterize the evolution of surface configuration [2]:

$$\lambda_{cr} = \frac{\pi U_s E}{\sigma_m^2} \tag{1}$$

In Eq. (1), λ_{cr} is the critical wavelength, U_s is surface energy of the thin film and can be treated as a material constant, E is the modulus, and σ_m is the stress in the film. For a given surface which is nominally flat but slightly undulated, assume the surface has an intrinsic wavelength λ_{in}. This intrinsic wavelength is related to the surface property and can be determined by the surface configuration and morphology for a given surface, for example, a pre-polished surface for experiment. When $\lambda_{in} < \lambda_{cr}$, the surface is stable during the growth of the thin film and does not become rougher; when $\lambda_{in} > \lambda_{cr}$, the surface is unstable and roughens during the film growth [2]. In this Letter, such a transition of surface morphology evolution from flat to rough is observed for oxide film growth by using scanning probe microscopy (SPM) method. Moreover, the stress evolution is analyzed based on the stress-diffusion coupling effect during oxide film growth and the critical stress in the oxide film at the transition point is calculated by determining the critical wavelength λ_{cr} in Eq. (1).

2. Experiments

The experiment is conducted on single crystal nickel-based superalloy (René N4, with 9.0 Cr, 8.0 Co, 2.0 Mo, 6.0 W, 4.0 Ta,

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3.7 Al, 4.2 Ti, weight percentage) oriented in $\langle 001 \rangle$ direction and a state-of-the-art system with the function of SPM integrated in a high temperature stage in nanoindentation equipment (Hysitron® TI950) is adopted to in situ and real time characterize the oxide film evolution at elevated temperatures [4,5]. The surface of the specimen is first mechanically polished with 200–1200-grit silicon carbide papers and then with diamond paste with particle size of 0.5 μm to ensure the finish quality of the surface. The specimen is then placed in the high temperature stage in the nanoindentation equipment and an indentation is first conducted on the surface at room temperature to create a 'marker'. Then the specimen is heated from room temperature to elevated temperatures, with an integral of 100 °C. For instance, when the temperature stabilizes at T = 100 °C, the SPM operation is conducted to scan and record the surface morphology. It is noted that the high temperature stage in the equipment is an open system in atmospheric environment. As the temperature increases, the oxidation process begins. Then the temperature is increased and analogously, the SPM operations are conducted at T = 200 °C, 300 °C and 400 °C, until the surface roughening effect during oxidation is observed.

3. Results and analysis

The SPM results in Fig. 1 intuitively show the transition of the surface morphology from smooth to rough at micro/nanoscale.

For a more quantitative examination of the roughness change during surface evolution, a sub-image (indicated by the red[2] rectangles in Fig. 2) with an area of approximately $1.8 \times 1.8\ \mu m^2$ located in the same region related to the indented 'marker' is chosen for the calculation of the average roughness and the results are presented in Fig. 2. The results show clearly that the average roughness increased steeply at T = 400 °C, corresponding to the morphology change in Fig. 1.

Here it should be noted that the SPM images in both Figs. 1 and 2 display some lateral drift indicated by the indent marker. Here, similar to the method proposed Broekmaat et al. [11], we used the indent marker as indication to calculate the drift, which gives a lateral drift of ~18 nm/min from 100 °C to 200 °C, and ~40 nm/min from 200 °C to 300 °C. Within the tested period of time, we neglect the effect of the lateral drift on the morphology measurement to establish the theoretical model.

Based on the aforementioned analysis, this transition of surface roughness shown in Figs. 1 and 2 indicates a change from $\lambda_{in} < \lambda_{cr}$ to $\lambda_{in} > \lambda_{cr}$ from temperature T = 300 °C to T = 400 °C. It is envisaged that for a given pre-polished specimen, the value of λ_{in} is a constant determined by the surface morphology. Thus, this change from $\lambda_{in} < \lambda_{cr}$ to $\lambda_{in} > \lambda_{cr}$ suggests that λ_{cr} is changing during the growth of the oxide film. Furthermore, according to Eq. (1), such a change of λ_{cr} is indeed attributed to the stress evolution in the oxide film during oxide growth [12–14]. In order to explicitly demonstrate the evolution of λ_{cr}, we first present here the evolution of the stress σ_{ox} (as a replacement of σ_m) in the oxide film.

Generally, the oxide growth is diffusion-controlled [15]. Dong et al. pointed out that stress in the oxide can modify the diffusion process, which is termed as stress-diffusion coupling effect [14,16,17]. The following presents a simple way to calculate the stress evolution within the oxide.

Consider the oxide film/substrate system based on the experimental result in Fig. 1. Here a flat film (before the transition point) is adopted for the analysis of the stress in the oxide film during single side oxidation. Assume that H is the thickness of the oxide film/substrate system, h_{ox} is the thickness of the oxide film and $h_s = H - h_{ox}$ is the thickness of the substrate. Here for simplicity, we consider that the film thickness is very small compared to that of the substrate, thus the expansion effect of the material from metal to oxide is ignored. Such an expansion is usually characterized by using Pilling-Bedworth ratio [15]. The rate form of the force balance of the system gives [14]:

$$\dot{\sigma}_{ox}h_{ox} + \sigma_{ox}\dot{h}_{ox} + \dot{\sigma}_s(H - h_{ox}) - \sigma_s\dot{h}_{ox} = 0 \tag{2}$$

As for the strain in the oxide, there is usually [18,19]:

$$\varepsilon_{ox}(t) = \varepsilon_e(t) + \varepsilon_{creep}(t) + \varepsilon_g(t) + \alpha_{ox}\Delta T \tag{3}$$

where t is time, $\varepsilon_{ox}(t)$ is the strain in the oxide, $\varepsilon_e(t)$ is the elastic strain, $\varepsilon_{creep}(t)$ is the creep strain, $\varepsilon_g(t)$ is the growth strain, α_{ox} is the coefficient of thermal expansion of the oxide and ΔT is the temperature change. Due to the fact that the surface of the oxide film often roughens at the early stage of oxidation and the creep effect in the oxide during this time is not dominating, thus we neglect the creep effect in the present analysis. Meanwhile, notice that the rate form of thermal expansion does not appear in the expression of strain rate, there is:

$$\dot{\varepsilon}_{ox}(t) = \dot{\varepsilon}_e(t) + \dot{\varepsilon}_g(t) = \dot{\sigma}_{ox}/M_{ox} + D_{ox}\dot{h}_{ox} \tag{4}$$

where $\dot{\varepsilon}_e = \dot{\sigma}_{ox}/M_{ox}$ according to Hook's law, and $\dot{\varepsilon}_g(t) = D_{ox}\dot{h}_{ox}(t)$ according to Clarke's model [13]. M_{ox} is the biaxial modulus of the oxide, and D_{ox} is a material constant of the oxide film.

For the substrate, there is no growth strain rate but only elastic strain rate:

$$\dot{\varepsilon}_s = \dot{\sigma}_s/M_s \tag{5}$$

where M_s is the biaxial modulus of the substrate. Notice that $\dot{\varepsilon}_{ox} = \dot{\varepsilon}_s$, there is:

$$\dot{\sigma}_s = \frac{M_s}{M_{ox}}\dot{\sigma}_{ox} + M_s D_{ox}\dot{h}_{ox} \tag{6}$$

Substitute Eq. (6) into Eq. (2), it yields the stress evolution within the oxide film:

$$\left(\frac{M_s}{M_{ox}}h_s + h_{ox}\right)\dot{\sigma}_{ox} + \sigma_{ox}\frac{H}{h_s}\dot{h}_{ox} + M_s D_{ox}\dot{h}_{ox}h_s = 0 \tag{7}$$

Additionally, the oxidation kinetics can be depicted by:

$$\dot{h}_{ox} = \beta\frac{\Delta c}{h_{ox}}D_0\exp\left(\frac{\alpha\Omega\sigma_h}{RT}\right) \tag{8}$$

where $\dot{h}_{ox}$ is the growth rate of the oxide film, β is a material constant, Δc is the concentration difference at the gas/oxide interface and oxide/substrate interface, h_{ox} is the thickness of the oxide film, $D_0\exp\left(\frac{\alpha\Omega\sigma_h}{RT}\right)$ is the diffusion coefficient by considering the stress effect on the diffusion process [14], σ_h is the hydrostatic stress within the oxide film, and for the case depicted in Fig. 1, there is $\sigma_h = \frac{2}{3}\sigma_{ox}$.

Eqs. (7) and (8) are the governing equations for stress-diffusion coupled oxidation model. Based on the dimensionless form of Eqs. (7) and (8), it is simple to demonstrate the evolution of stress in the oxide film, as shown in Fig. 3.

The stress evolution in the oxide film shown in Fig. 3 indicates that the compressive stress increases as the oxide film thickens, which would result in a decrease of the critical length λ_{cr} according to Eq. (1). The change of λ_{cr} as with the evolution of stress is further shown in Fig. 4. Here $U_s = 1$ N/m, [2] $E = 150$ GPa are adopted for the calculation.

Meanwhile, for a given pre-polished specimen, the surface is nominally flat (again here by nominal it means that it is impossible to have perfectly smooth surface at nanoscale prepared under real condition). At the early stage of oxidation, when the stress is small

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[2] For interpretation of color in Fig. 2, the reader is referred to the web version of this article.