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An electrochemical impedance spectroscopy and polarization study of the role of crystallographic orientation on electrochemical behavior of niobium

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ABSTRACT

In this work, the influence of grain orientation on electrochemical behavior and semiconductor properties, such as donor density, flat-band potential, and diffusivity of point defects (D_0), of the passive films were studied on Nb single crystals with orientations of (100), (110), and (111) in phosphate buffered saline (PBS) and 1 M NaOH solution by cyclic voltammetry, electrochemical impedance spectroscopy, Mott-Schottky analysis, and point defect model. The results shown that the (100) crystal face of Nb exhibits the lowest corrosion rate in both PBS and 1 M NaOH solutions. The Mott-Schottky analysis revealed that the passive film formed on the (100) face has the lowest donor density and the flat-band potential was almost independent of the grain orientations, but decreased with an increase of pH. A different relationship between steady-state current density (j_{ss}) and film formation potential was observed in these two solutions and the possible causes were discussed. The diffusivity was calculated based on the point defect model. D_0, of the passive films in PBS solution is in the range of 10–21 to 10–19 cm^2/s, depends on the grain orientation and film formation potential. In 1 M NaOH solution, D_0 is close to 10–18 cm^2/s independent of the film formation potential.

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1. Introduction

Niobium (Nb) exhibits good corrosion resistance in most acidic and near neutral environments [1–5]. Nb has been considered to be a promising bio-implant due to its excellent biocompatibility [6]. Nb was also widely used as an alloying element in various metals, such as a Ti-based alloy [7,8], to improve the corrosion resistance of these alloys. These applications are based on the fact that Nb can form a corrosion resistance passive film. The passive film formed on metals, such as on Fe [9], Ti [10], W [11], Ni [12], and stainless steel [13], is reported to be a semiconductor. The passive film formed on the Nb surface is reported to be an n-type semiconductor [14–16]. The semiconductor properties, such as carrier density, flatband potential, and carrier diffusivity, are of great importance to further understand the growth or the breakdown of the passive film.

Macdonald and co-workers developed the point-defect model (PDM), which aims to descript the growth and breakdown of passive films that form on the surfaces of reactive metals in contact with corrosive, condensed phase environments [17–20]. The PDM assume that the passive film on a metals surface contains high concentration of point defects and the growth or breakdown of the passive film involves the transport of the point defects under the electrostatic field in the film. PDM was successfully used to study transport properties of the passive films on various metals, such as Ti [10], Cr [21], Fe [9], W [11], Ni [12,22], and stainless steel [13,23,24]. Recently, Li *et al.* used PDM to study the effect of potentiostatic aging, temperature, and pH on the diffusivity of Nb passive films formed in HCl solution based on PDM [14]. However, only little work was available concerning the use of PDM to study the transport property of Nb passive films.

Grain orientation has been reported to have great influence on the electrochemical behavior of metals. Schreiber *et al.* studied the grain dependence of the corrosion behavior of iron in an acetate buffer solution pH 6.0, and their results showed that grains with (100) orientation dissolved much slower [25]. Whereas, Fushimi *et al.* reported that that the (100) plane showed the highest corrosion activity and the surface tomography of iron grains with different grain orientation is different after the dynamic polarization test [26,27]. The difference of these results about iron anisotropic corrosion might be caused by the pH of the solutions. Fushimi *et al.* suggested that in pH 1 sulfuric acid, the corrosion reaction is governed by the cathodic hydrogen evolution reaction on iron grain and the coverage of H on Fe as well as the covalent bonding of Fe and H influence the hydrogen evolution reactions on iron single grains [26]. However, in acetate buffer pH6.0 solution, because the H$^+$ concentration is much lower than that in pH 1

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sulfuric acid, different corrosion-rate control steps might exist. Song and co-workers studied the corrosion behavior of Mg and their results showed that the basal plane is much more corrosion resistant than the prismatic and other crystal planes in neutral chloride-containing solutions or alkaline saturated solutions [28,29]. Konig and Davepon [30] studied the microelectrochemical properties of Ti and their result suggested that the high atomic surface density of the (0001) plane in Ti leads to an oxide layer with a high donor concentration, which accelerated the corrosion rate of the (0001) plane. Their results also showed that the oxygen evolution starts around 4 V on the passive film formed on the near (0001) orientation, however, no oxygen evolution was observed on the other planes up to 10 V, which suggested that the grain orientation of Ti can even greatly affect the semiconductor properties of the passive film (TiO_2) formed on it. These results indicated that the grain crystal orientation can greatly affect the electrochemical behavior as well as the passive film properties of metals, however, this influence is dependent on the crystal structure of the metal as well as the corrosion environment.

In this work, we aim to study the effect of grain orientations on electrochemical behavior, semi-conductor properties, and the point defects transfer property of the passive film formed on Nb single crystals at various potentials in phosphate buffered saline (PBS) (pH 7.4) and NaOH (pH 13.8) solutions. The electrochemical formation of the passive films on Nb was also discussed by the cyclic voltammetry method. The semiconductor properties, such as carrier density (N_d) and flatband potential (E_{FB}), of the passive film were studied by the Mott-Schottky method. The diffusivity of the point defects was analyzed based on the PDM.

2. Experimental

2.1. Materials

The high purity (99.99%) Nb single crystals with (100), (110), and (111) surface orientation were obtained from Goodfellow Cambridge Limited and used as-received. The surface crystal orientation was confirmed by the electron backscatter diffraction (EBSD) method, as shown in Fig. 1. The samples were embedded into a cold-cure epoxy resin and only one face made contact with the electrolyte for the electrochemical tests.

2.2. Electrochemical measurement

The electrochemical tests were carried out in two different solutions, PBS and NaOH solution, in naturally aerated environments. The PBS solution is composed of 8.0 g/L NaCl, 0.2 g/L KCl, 1.15 g/L Na_2HPO_4, and 0.2 g/L KH_2PO_4 at pH 7.4 (maintained constant due to the buffer). The NaOH solution is composed of 40 g/L (1 M) NaOH, pH 13.8.

The experimental setup used was a conventional water-jacketed, three-electrode cell with a graphite rod counter electrode and an Ag/AgCl ([KCl] = 4 M) reference electrode. All potentials in

this work are reported vs. Ag/AgCl reference electrode (0.197 V vs. SHE). A water bath was used to maintain a solution temperature of $37 \pm 0.5\,°C$.
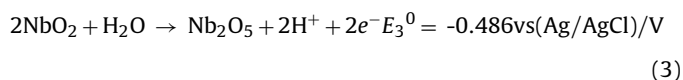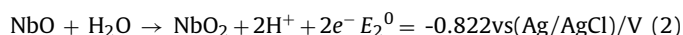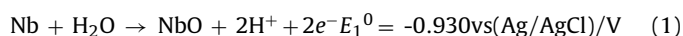
The electrochemical measurements were carried out using a Princeton Applied Research Versastat4 potentiostat/galvanostat. Before the electrochemical tests, the working electrode was ground with SiC paper up to 1200 grit, washed with double-distilled water, and then the tests were started immediately. The cyclic voltammetry measurements were carried out from -1.2 V to 9 V with a scan rate of 200 mV/s. In order to study the properties of the passive films, stable-state passive films were formed by potentiostatically polarizing the samples at different film formation potentials (0.25 V, 0.35 V, 0.45 V, 0.55 V, 0.65 V, 0.75 V, 0.85 V, 1 V, 2 V, 3 V, 4 V) for 6 h. The electrochemical impedance spectroscopy (EIS) tests were carried out at the film formation potential with an *ac* amplitude of 10 mV (rms) at the film formation potential in the frequency range of 5×10^4 to 10^{-2} Hz and a sampling rate of 10 points per decade. The Mott-Schottky tests were performed by stepping the potential in the negative direction from 0.35 V to -1.0 V in 50 mV decrement. To avoid the frequency dispersion in Mott-Schottky tests, at each applied potential, the impedance was recorded from the frequency of 5×10^4 to 1 Hz and capacity under each applied potential was calculated from the impedance results [31–33].

3. Results and discussion

3.1. Cyclic voltammetry measurements

Cyclic voltammetry measurements were carried out on Nb single crystals in the potential range of -1.2 V to 9 V in a sweep rate of 200 mV/s in PBS and NaOH solutions, respectively. As shown in Fig. 2, the shapes, such as the number of peaks and potential corresponding to the peaks, of the cyclic voltammograms of different orientations are almost identical in the same solution, which could be concluded that the thermodynamic process is independent of the grain orientations. In the first sweep cycle, the (100) oriented sample exhibited the lowest current density in both PBS and NaOH solutions, however, this difference seems to decrease in the second cycle. This result is consistent with the previous report of pure iron in acetate buffer solution [25].

As suggested by the previous studies [34–37], during the anodic potential sweep process, the following reactions might occur:

$$Nb + H_2O \rightarrow NbO + 2H^+ + 2e^-\; E_1^0 = \text{-0.930 vs(Ag/AgCl)/V} \quad (1)$$

$$NbO + H_2O \rightarrow NbO_2 + 2H^+ + 2e^-\; E_2^0 = \text{-0.822 vs(Ag/AgCl)/V} \quad (2)$$

$$2NbO_2 + H_2O \rightarrow Nb_2O_5 + 2H^+ + 2e^-\; E_3^0 = \text{-0.486 vs(Ag/AgCl)/V} \quad (3)$$

As no reduction peaks were observed on the backward scan, the electrochemical reactions on the Nb electrode surface could be treated as irreversible reactions. For the irreversible reactions, the
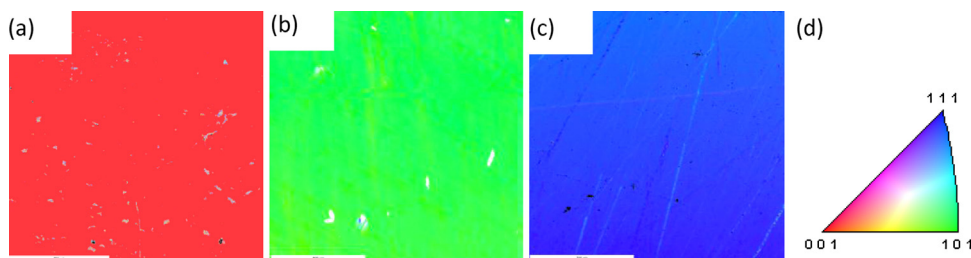

Fig. 1. Electron backscatter diffraction (EBSD) results of the surface crystal orientation of (a) (100), (b) (110), and (c) (111) single crystals; (d) stereographic triangle.