



The effect of nanotwins on the corrosion behavior of copper

Y. Zhao, I.C. Cheng, M.E. Kassner, A.M. Hodge*

University of Southern California, Department of Aerospace and Mechanical Engineering, Los Angeles, CA 90089-1453, USA

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Abstract

Ultrafine grain sized ($\sim 0.4 \mu\text{m}$) Cu samples having different fractions of nanotwinned grains ($\sim 5\%$, $\sim 60\%$ and $>90\%$) were synthesized in order to evaluate the effect of the nanotwins on the overall microstructure. It was observed that nanotwins have a fundamental effect on altering the grain boundary network and texture of sputtered Cu samples. Increasing the fraction of nanotwinned grains increases both the fraction of special ($\Sigma 3$) grain boundaries and the intensity of the $\{111\}$ texture. Polarization and immersion corrosion tests using a 3.5% NaCl solution were performed on the nanotwinned Cu samples and compared to microcrystalline Cu (grain size $\sim 9 \mu\text{m}$). It was found that highly nanotwinned Cu (nanotwinned grains $> 90\%$) had the highest corrosion resistance among all samples, which is attributed to its unique grain boundary network and $\{111\}$ texture. In addition, the passive layer formed on highly nanotwinned Cu during corrosion achieved the highest pitting resistance when compared with the other samples.

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1. Introduction

Nanotwinned (nt) metals have a special type of microstructure, where their grains contain nanotwins which are bundles of twin ($\Sigma 3$) boundaries with nanoscale spacings typically less than 100 nm. Most of these nt boundaries are coherent twin boundaries (CTBs), and some of them have incoherent segments such as steps along the grain boundary plane [1–3]. Based on grain boundary engineering principles [4–6], increasing the fraction of special grain boundaries such as CTBs [7,8] will lead to improved material properties. In the case of nt metals, the presence of these CTBs has been shown to improve the strength, ductility [2,3] and thermal stability [9–11] as compared to ultrafine-grained or nanocrystalline metals of similar grain sizes. Furthermore, since grain boundary engineered metals (but without nanotwins) typically have high resistance to intergranular corrosion [12–14], nt metals could also present improved corrosion behavior.

To date, most studies of highly nt metals have been focused on metals with low stacking fault energy (SFE, γ_{SFE}) such as nt Ag ($\gamma_{\text{SFE}} = 16\text{--}22 \text{ mJ m}^{-2}$) and nt Cu ($\gamma_{\text{SFE}} = 35\text{--}78 \text{ mJ m}^{-2}$) [15,16], and to the authors' knowledge there have been no published studies of the corrosion behavior in these materials. However, there are a number of studies [17–20] on the corrosion behavior of sputtered Al and electrodeposited Ni samples containing nanotwins, even though these types of material tend not to twin due to the high SFE of Al ($\gamma_{\text{SFE}} = 135\text{--}200 \text{ mJ m}^{-2}$) and Ni ($\gamma_{\text{SFE}} = 125\text{--}300 \text{ mJ m}^{-2}$) [15,16]. It is thus difficult to assess whether the samples in the Ni and Al studies were highly nanotwinned, especially since the manuscripts are mainly focused on the electrochemical aspect of corrosion rather than the microstructural characterization. However, these studies provide an initial assessment about the possible effects of nanotwins on corrosion. For example, Meng et al. [17–19] studied the electrochemical behavior of Ni with nanotwins in borate buffer solution with and without the addition of NaCl, and found that its passive layer was thinner and less defective, and had a higher pitting corrosion resistance compared with both cast Ni and

* Corresponding author. Tel.: +1 213 740 4225; fax: +1 213 740 8071.

E-mail address: ahodge@usc.edu (A.M. Hodge).

industrial electrodeposited (presumably without nanotwins) Ni. It was also reported [20] that Al with nanotwins had a lower corrosion current density and a higher pitting resistance than cast Al in acidic NaCl solution. Additionally, a study [21] of 316L stainless steel in an $\text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$ solution showed that the nt microstructure had a higher corrosion resistance than microstructures without nanotwins.

In this paper, the corrosion behavior of nt Cu samples was studied by both polarization and immersion corrosion tests in artificial seawater (3.5% NaCl, pH \sim 8.0). Since the GB character [13], grain size [22] and grain orientation [23] could strongly affect the corrosion properties of a metal, it is crucial to characterize the microstructures with and without nanotwins sufficiently in order to explore the effect of nanotwins on the corrosion properties. Therefore, three types of Cu foil having different fractions of nt columnar grains (or columnar grains with nanotwins) were studied and compared to microcrystalline (mc) Cu. The microstructure was characterized before and after corrosion. The chemical compositions of the passive layers were also identified in order to relate the passive layer composition and structure to the observed passivation behavior.

2. Experimental

High-purity Cu (99.999%) foils (\sim 25 μm thickness) having different fractions of nt columnar grains were synthesized by magnetron sputtering following procedures described elsewhere [9,24]. In addition, mc Cu samples were prepared by heat-treating the as-sputtered Cu (without nanotwins) at 600 $^\circ\text{C}$ for 3 h in an MTI-GSL1100X furnace under a vacuum (\sim 3 \times 10⁻⁵ torr). The samples were mounted in epoxy so that only the top surface of each foil could be exposed to the corrosion solution. The exposed areas for polarization and immersion corrosion tests were \sim 0.36 and \sim 0.64 cm², respectively. All samples were ultrasonically cleaned in acetone and ultrapure water before the corrosion tests, and rinsed gently with water after corrosion. The corrosion solution is artificial seawater, which is a naturally aerated 3.5% (35 g l⁻¹) NaCl solution prepared by mixing ultrapure water with NaCl. NaOH was also added to the solution to adjust its pH value to 8.0 \pm 0.1. The temperature of the corrosion solution was maintained at 21.5 \pm 1 $^\circ\text{C}$.

Polarization tests were performed in a three-electrode cell filled with 200 ml of 3.5% NaCl solution. The (1) working electrode was the Cu sample. The (2) reference electrode was silver/silver chloride (Ag/AgCl), which was placed close to the working electrode. The potential that was measured by Ag/AgCl can be converted to the potential measured by a standard hydrogen electrode (SHE) through E (vs. SHE) = E (vs. Ag/AgCl) + 0.198 V. The (3) counter electrode was a platinum wire. These three electrodes were connected to a potentiostat (Gamry Reference 3000), which performed two types of polarization test: linear polarization and potentiodynamic polarization.

In linear polarization tests, the corrosion potential (U_{corr}) of each Cu sample was stabilized in the solution for 15 min before polarization in order to achieve a linear relationship around U_{corr} . The potential was then swept from -10 to $+10$ mV (vs. U_{corr}) at a rate of 0.1 mV s⁻¹. For potentiodynamic polarization tests, the potential was polarized from -450 to $+450$ mV (vs. Ag/AgCl) at a scan rate of 0.5 mV s⁻¹ immediately after the sample was placed in the solution. Immediate polarization of the potential minimizes the reaction between the Cu sample and the corrosion solution, so that the cathodic peak [25–27] which perturbed the Tafel linear region could be minimized.

The curves of linear and potentiodynamic polarization tests were analyzed by Gamry Echem Analyst software. At least two samples from each type (columnar highly nt, columnar partially nt, columnar non-nt and non-columnar mc) of Cu foil were tested in either linear polarization or potentiodynamic polarization. The polarization resistances (R_p), Tafel slopes (β_c , β_a) and passivation current densities (I_{pass}) were measured. The corrosion current densities (I_{corr}) of each type of Cu were calculated through the Stern–Geary equation by inputting the measured β_c , β_a and each R_p . The standard deviations of R_p , I_{corr} and I_{pass} were calculated.

Furthermore, Cu samples after linear polarization were subsequently polarized from -450 mV to the passivation point at a scan rate of 0.5 mV s⁻¹ in order to observe the passive layers of the samples. For immersion corrosion tests, two samples from each type of Cu foil were placed in 100 ml 3.5% NaCl solution containers with the lid closed for a total of 10 days. The NaCl solution was replenished every 2 days. The samples were cleaned ultrasonically and their passive layers were evaluated after immersion corrosion. Since the passive layers of the two samples from each type of Cu foil were similar, only one of them is presented.

The cross-sectional and top-surface (corrosion surface) microstructures of the as-prepared Cu samples were characterized by focused ion beam (FIB) and electron backscatter diffraction (EBSD), respectively. The EBSD analysis procedure in this study is consistent with that in the previous studies [9]. An $\{hkl\}$ grain orientation means that its crystal direction $\langle hkl \rangle$ is normal to the top surface, and crystal orientations within 7 $^\circ$ of a specific $\{hkl\}$ are considered to belong to that $\{hkl\}$ grain orientation. After corrosion, the top-surface morphology and cross-sectional views of passivated samples during polarization tests were characterized by scanning electron microscopy (SEM) and FIB, respectively. The passive layers formed during immersion corrosion were also characterized by SEM. Energy-dispersive spectroscopy (EDS) was used to obtain the compositions at the microscopic (10–100 μm) level, while X-ray diffraction (XRD) was used to detect the chemical compounds and crystal orientations of corrosion products at the macroscopic (\sim 10 mm) level.

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