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Electrochemical corrosion behavior of nanocrystalline copper bulk

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Abstract

The corrosion behavior of nanocrystalline (nc) copper bulk prepared by IGCWC (inert gas condensation and in situ warm compress) was studied in 0.1 mol/L $CuSO_4$ + 0.05 mol/L H_2SO_4 solution. It was found that nc copper exhibited a corrosion behavior quite different from conventional coarse-grain copper. Nanocrystalline copper exhibited uniform dissolution of the surface and discrete localized corrosion typically, but conventional coarse-grain copper exhibited considerable preferential attack along the grain boundaries with signs of pitting corrosion dispersed throughout the surface uniformly. Compared with coarse-grain copper, nc copper decreased in resistance to corrosion. This decrease in corrosion resistance was mainly attributed to the high activity of surface atoms and intergranular atoms. The high activity of surface atoms and intergranular atoms, resulting from the reduction of grain size, leaded to an enhancement of passivation ability and to an increase of dissolution of passive film. In addition to the defects such as micro-gap produced in the fabrication of nc sample had great effect on the overall corrosion performance of nc sample, which were weakness to corrosion.

Keywords: Nanocrystalline copper; Corrosion behavior; Grain size; Defect

1. Introduction

In recent years, there has been an interest in understanding the corrosion performance of nc metals [1,2]. For the most part, the research has focused on the surface nanocrystallization and nano-scaled alloys [3–6]. Zeiger et al. [7] reported an enhanced corrosion resistance of nc Fe–8 wt.% Al in Na_2SO_4 solution. They attributed this enhanced corrosion resistance to the fast diffusion of Al in the grain boundaries which form a protective oxide film on the surface. Wang and Li [8] investigated electrochemical property of nc surface of brass produced by sand and blasting in a dilute NaCl solution. They found that the polarization behavior of nc surface was superior to that of a regularly grained surface. Youssef et al. [9] studied the corrosion behavior of nc zinc produced by pulse electrodepositing in de-aerated 0.5N NaOH solution. The nc zinc deposits exhibited a lower corrosion rate than that of conventional electrogalvanized steel and the oxide film on nc zinc was more protective than that on conventional electrogalvanized steel. Li et al. [10] studied the corrosion performance of nanocrystallized Fe–20Cr surface fabricated by using an ultrasonic shot peening technique in 0.5 mol/L NaCl + 0.05 mol/L H_2SO_4 solution. The results showed that the capability of corrosion resistance of nanocrystallized surface was lower than that of the cast alloy.

However, corrosion studies on pure nc metals in general have been rather limited. To date there have been little knowledge could be available. Actually, different synthesis method gives rise to differences in microstructure and property of nc metal with the same composition [11]. Therefore, corrosion behavior study on nc metal should be further carried out by taking account of many factors.

Copper is widely used in industrial application. Nanocrystalline copper has even more potential use because of the nano-size effect. IGCWC is one of the most useful techniques to synthesize nc bulk metals. The main objective of the present work was to study the corrosion behavior of nc copper bulk prepared by IGCWC in 0.1 mol/L $CuSO_4$ + 0.05 mol/L H_2SO_4 solution, by comparing the corrosion behavior with the corrosion response of conventional coarse grained copper in the same solution. The results showed that nc cooper exhibited a quite different corrosion behavior from its coarse grained counterpart.

2. Experimental details

Nanocrystalline copper bulk sample with a diameter of 60 mm and a thickness of 5 mm was prepared by IGCWC (inert

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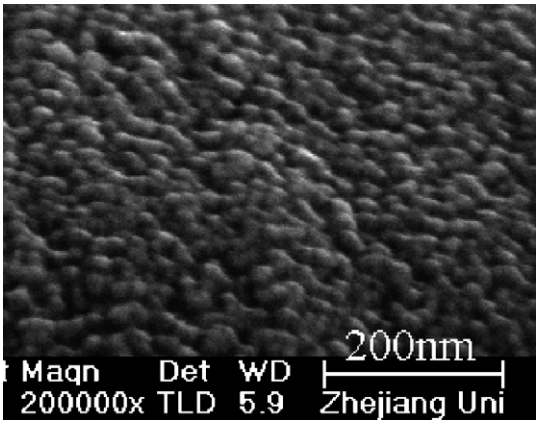

Fig. 1. Microstructure of the nanocrystalline copper bulk sample prepared by IGCWC.

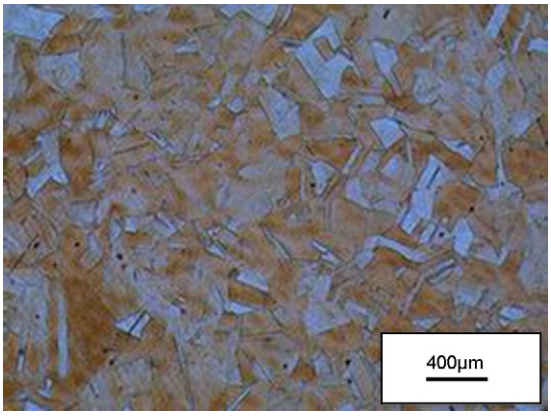

Fig. 2. Microstructure of the coarse-grain copper sample.

gas condensation and in situ warm compress), the microstructure of which is shown in Fig. 1. IGCWC process was described in detail in Ref. [12]. The density of the nc bulk copper sample was 99.51% of theoretical value measured by Archimedes method with an error of 1%. The coarse-grain copper used for the experiment was commercial rolled pure copper, the microstructure of which is shown in Fig. 2. Chemical compositions of nc and coarse-grain copper, determined by spectroscopy analysis method, are listed in Table 1.

The corrosion behavior of samples was determined by potentiodynamic anodic polarization tests. The electrolyte was 0.1 mol/L $CuSO_4$ + 0.05 mol/L H_2SO_4 solution prepared by using reagent grade chemicals dissolved in distilled water. Square coupons with 8 mm × 8 mm were spark-cut from the nc copper bulk. Two groups of coupons were annealed in vacuum for 30 min at 250 and 350 °C, respectively, in order to produce different grain size. Grain sizes of coupons were determined using a X-ray diffractometer (model Rigaku D/max2550pc)

Table 1
Chemical compositions of nc and coarse-grain copper samples (wt.%)

	Cu	Sn	Fe	Si	P	S	Others
nc copper	99.907	0.055	0.018	0.014	–	–	Balance
Coarse-grain copper	99.838	0.057	0.022	0.027	–	–	Balance

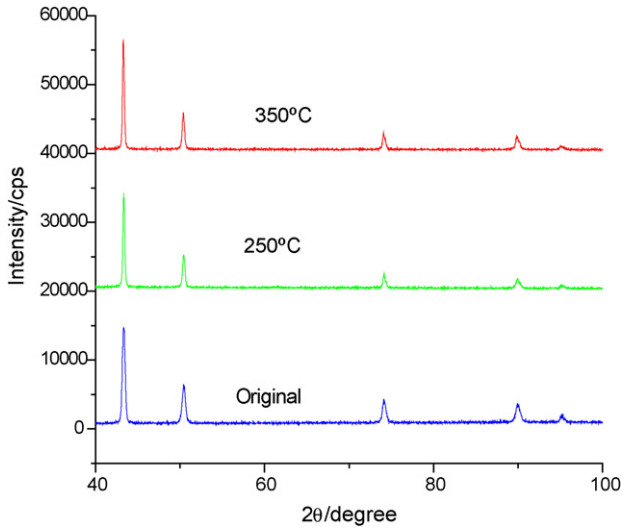

Fig. 3. XRD patterns of original and annealed nanocrystalline copper samples.

Table 2
Average grain sizes of nanocrystalline copper bulk samples

Sample	Grain size (nm)
As-prepared	21
Annealing at 250 °C	42
Annealing at 350 °C	58

with Cu Kαradiation. The diffraction patterns of samples are shown in Fig. 3 and the analysis results are listed in Table 2. Only one surface of each sample exposed to the electrolyte, which was ground, polished and cleaned with acetone, and the other surfaces were simply covered with epoxy resin. The boundary between the sample and the epoxy resin was sealed with paraffin wax to avoid crevice corrosion. Room temperature polarization tests were performed using a 1287 electrochemical interface manufactured by Solartron Instruments, which controls the potential at a sweep rate of 10 mV/min, and a glass polarization cell with saturated calomel reference and platinum counter electrodes. Before polarization the sample was immersed in the solution for 10 min to stabilize the open circuit potential. For comparison, the same corrosion test was carried out under the same experimental conditions on the conventional rolled coarse-grain copper.

Field emission gun scanning electron microscopy (FEGSEM), X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDS) were used to characterize the surface microstructure and to analyze the surface composition after the polarization test of the samples.

3. Results and discussion

Figs. 4 and 5 show typical anodic polarization curves obtained from coarse-grain, nc and annealed nc copper samples, respectively. The electrochemical data measured in the tests are listed in Table 3. These curves have qualitatively similar behavior but with different values of their electrochemical data. In