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Corrosion and stress corrosion cracking behavior of equal channel angular pressed oxygen-free copper in 3.5% NaCl solution

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In the present study, the corrosion and stress corrosion cracking (SCC) behavior of equal channel angular pressed (ECAPed) oxygen-free copper was examined in 3.5% NaCl solution. The specimen with two ECAP process cycles was found to have the greatest resistance to corrosion and SCC in 3.5% NaCl solution among the specimens studied, while the resistance varied in a complex manner with different number of ECAP process cycles. Micrographic observation and differential scanning calorimeter study suggested that both corrosion and SCC behavior of ECAPed copper was strongly dependent on the microstructural evolution, including the change in grain size and dislocation density, during ECAP process.

1. Introduction

Understanding the corrosion behavior of nanocrystalline materials in aqueous solution is of great importance for the wide range of potential future applications [1]. The formation of nanostructure has been reported to have both beneficial and detrimental effects on the corrosion performance of metallic materials [1]. The detrimental effect in nanocrystalline materials on the corrosion resistance has often been attributed to the higher content of grain boundary and triple junction, which serve as electrochemically active sites. The passive film formed on the nanocrystalline material is also known to be more defective than that on the polycrystalline counterpart [1]. This higher defective film on the nanocrystalline material allows more uniform breakdown of passive film, which in turn leads to a more uniform corrosion. Despite the practical significance, our understanding on the corrosion behavior of nanocrystalline materials is extremely limited. At present, the ECAP (equal channel angular pressing) process is one of the most popular methods for producing nanocrystalline bulk material [2–5]. ECAP is a processing procedure in which a material is subjected to intense plastic straining without introducing any change in the cross-sectional dimensions. In this study, the corrosion and stress corrosion cracking (SCC) behaviors of nano grain-sized, pure copper produced by the ECAP process were examined in 3.5% NaCl solution. The mechanism associated with the corrosion and stress corrosion cracking behavior of ECAPed copper was discussed based on the microstructural examination and differential scanning calorimeter (DSC) measurement.

2. Experimental procedure

In the present study, 99.99% pure, oxygen-free copper was used as a starting material. Before the ECAP process, the alloy was heat treated at 500°C for 1 h and subsequently air-cooled. For the homogeneity of the final product, a Bc route was utilized with a 90° rotation after each ECAP cycle. Fig. 1 shows (a) the optical micrograph of as-annealed copper and (b) the TEM micrograph of ECAPed copper processed by 8 cycles. The grain size of as-annealed copper used in this study was varied from 100–200 μm. After the eighth ECAP processing cycle, equiaxed grains tended to form with an average size of

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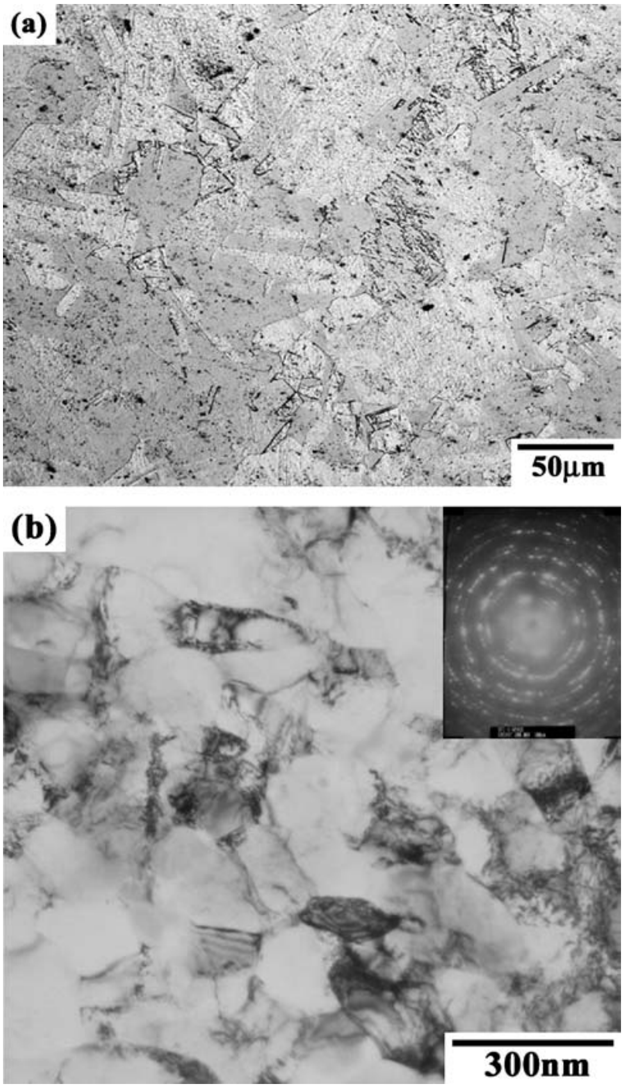

Figure 1 (a) Optical micrograph of as-annealed copper and (b) TEM micrograph of ECAPed copper processed by 8 cycles.

300 nm. For the indirect measurement of dislocation density variation during ECAP process, the heat flow values of the selected ECAPed specimens were measured using a Perkin Elmer Instruments (Oak Ridge, TN) model DSC7 differential scanning calorimeter (DSC) in nitrogen environment with a ramping rate of 1.67°C/min up to 500°C. For the study of general corrosion behavior, polarization tests were conducted in 3.5% NaCl aqueous solution using a PAR model Versastat II potentiostat at a scan rate of 3 mV/sec. The in-situ slow strain rate (SSR) tests were also conducted in air and 3.5% NaCl aqueous solution at a nominal strain rate of 1×10^{-6}/s on an R&B (Daejeon, Korea) model S2 constant extension rate tester (CERT). The SSR test specimens were prepared from the central portion of each rod with a gauge length of 20 mm and a diameter of 4 mm. The side surfaces of the tested specimens were examined by using a scanning electron microscope (SEM).

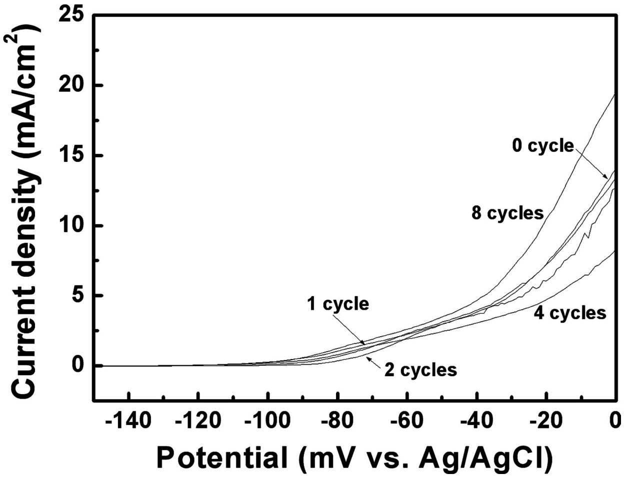

Figure 2 Representative polarization curves for the ECAPed copper with different process cycles in 3.5% NaCl solution.

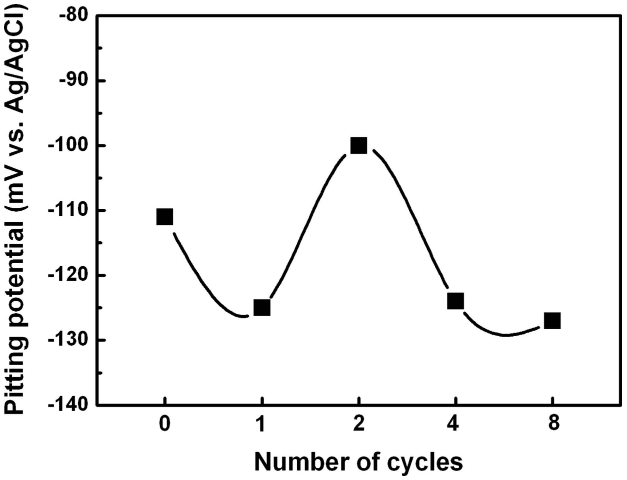

Figure 3 The pitting potential values in oxygen-free copper with different number of ECAP process cycles in 3.5% NaCl solution.

3. Results and discussion

Fig. 2 shows the representative polarization curves for the ECAPed copper with different process cycles in 3.5% NaCl solution. The pitting corrosion potential tended to decrease from −111 to −125 mV vs. Ag/AgCl after the first ECAP cycle. After the second process cycle, the pitting corrosion potential increased to −100 mV vs. Ag/AgCl. After the fourth process cycle, the pitting corrosion potential decreased to −124 mV vs. Ag/AgCl. With further ECAP process, the decrease was not significant. The pitting corrosion potential values for ECAPed copper with different number of process cycle are shown in Fig. 3.

In the present study, the in-situ slow strain rate tests were conducted in air and 3.5% NaCl aqueous solution on the ECAPed copper with different number of process cycles at a nominal strain rate of 1×10^{-6}/s. Table I represents the SSR test results of ECAPed copper in air and the corrosive environment. Each data represents the average of at least three test results. The resistance to SCC

TABLE I. The slow strain rate test results for ECAPed copper with different process cycles in air and 3.5% NaCl solution

Number of cycles	Environment	YS[a] (MPa)	UTS[b] (MPa)	Tensile elongation (%)	%change in tensile elongation[c] (%)
0	Air	89	217	51.3	
	3.5% NaCl	40	178	44.9	−12.5
1	Air	330	338	12.1	
	3.5% NaCl	305	312	10.5	−13.2
2	Air	350	354	11.1	
	3.5% NaCl	337	351	10.4	−6.3
4	Air	373	397	13.9	
	3.5% NaCl	349	375	12.1	−12.9
8	Air	303	345	24.4	
	3.5% NaCl	272	311	15.6	−36.1

[a] YS = Yield strength.

[b] UTS = Ultimate tensile strength.

[c] %change in tensile elongation = $(e_{3.5\%NaCl} - e_{air})/e_{air} \times 100$.

is often correlated to either the percent change in tensile elongation or the percent change in total time to failure with exposure to the SCC-causing environments with respect to the reference environment (i.e., air in the present study) [6]. Table I demonstrated that the SCC resistance of copper at an anodically applied potential (pitting corrosion potential + 50 mV vs. Ag/AgCl) varied significantly with increasing ECAP process cycle. The SCC resistance was, for example, slightly impaired with one ECAP cycle. Like the polarization test results observed in Fig. 2, the specimen with two ECAP cycles showed the greatest resistance to SCC among the specimens studied. With further ECAP process, the SCC resistance tended to decrease substantially. The variation in the % change in tensile elongation is graphically illustrated as a function of the number of ECAP process cycles in Fig. 4.

Fig. 5 shows the SEM micrographs of surface areas of ECAPed copper with different processing cycles of (a) 1, (b) 2, (c) 4 and (d) 8, respectively, close to the fractured surfaces documented after slow strain rate test in 3.5% NaCl solution. This figure clearly demonstrates that the crack morphologies of the tested specimens in 3.5% NaCl solution were quite different with each other depending on the number of ECAP processing cycle. The specimen with one ECAP cycle showed a pitting type of corrosion on the surface. Any sharply developed stress corrosion cracks were, however, not observed. In the specimen with two ECAP processes, almost no notable stress corrosion cracks were observed on the surface. Unlike these two specimens, those with 4 and more ECAP processing cycles showed considerable number of stress corrosion cracks along the axial direction.

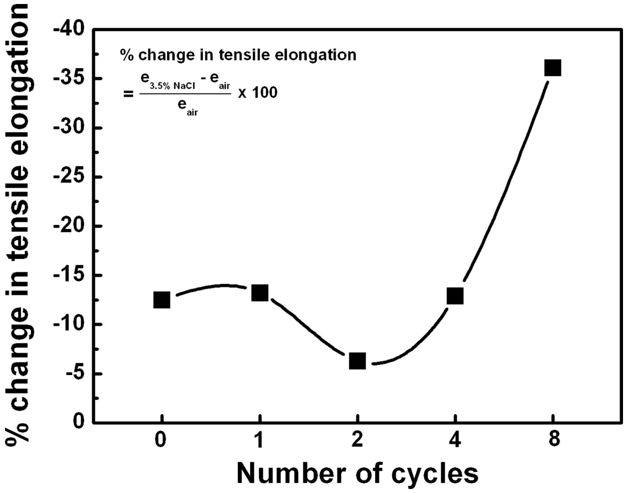

Figure 4 The percent change in tensile elongation of SSRTed, oxygen-free copper in air and 3.5% NaCl solution as a function of ECAP process cycles.

Previously, it was demonstrated that the microstructure of pure copper, including the dislocation density and the size of grain, varied greatly with ECAP process. As reported in the reference [7], a large number of dislocations began to be observed in pure copper after the first ECAP process. Simultaneously, the equiaxed grains in the as-received copper changed to largely elongated grains with a width of 500 nm and a length of several tens of μm. After the second ECAP process, the length of grain greatly reduced to several μm, while the decrease in the width was not significant. After the fourth ECAP cycle, equiaxed grains tended to form with an average size of 400 nm. The size of these equiaxed grains decreased to 300 nm with further ECAP process up to 8 cycles. Once the equiaxed grains formed, the dislocation density inside the grains tended to decrease with further ECAP process. Similar results have been reported for the other severe plastic deformed (SPDed) copper alloys [8]. To confirm this notion of the dislocation density reduction with the ECAP process, the heat flow values of the specimens with different ECAP process cycles were measured by using DSC. The rationale for this measurement method was that the heat flow of pure copper would be solely controlled by the generation and/or annihilation of dislocation and grain boundary during the ECAP process, unlike the other alloys with either precipitation hardening or solid solution hardening mechanism [7, 8]. The use of DSC technique has previously been reported to be successfully for quantifying the change in dislocation density during severe

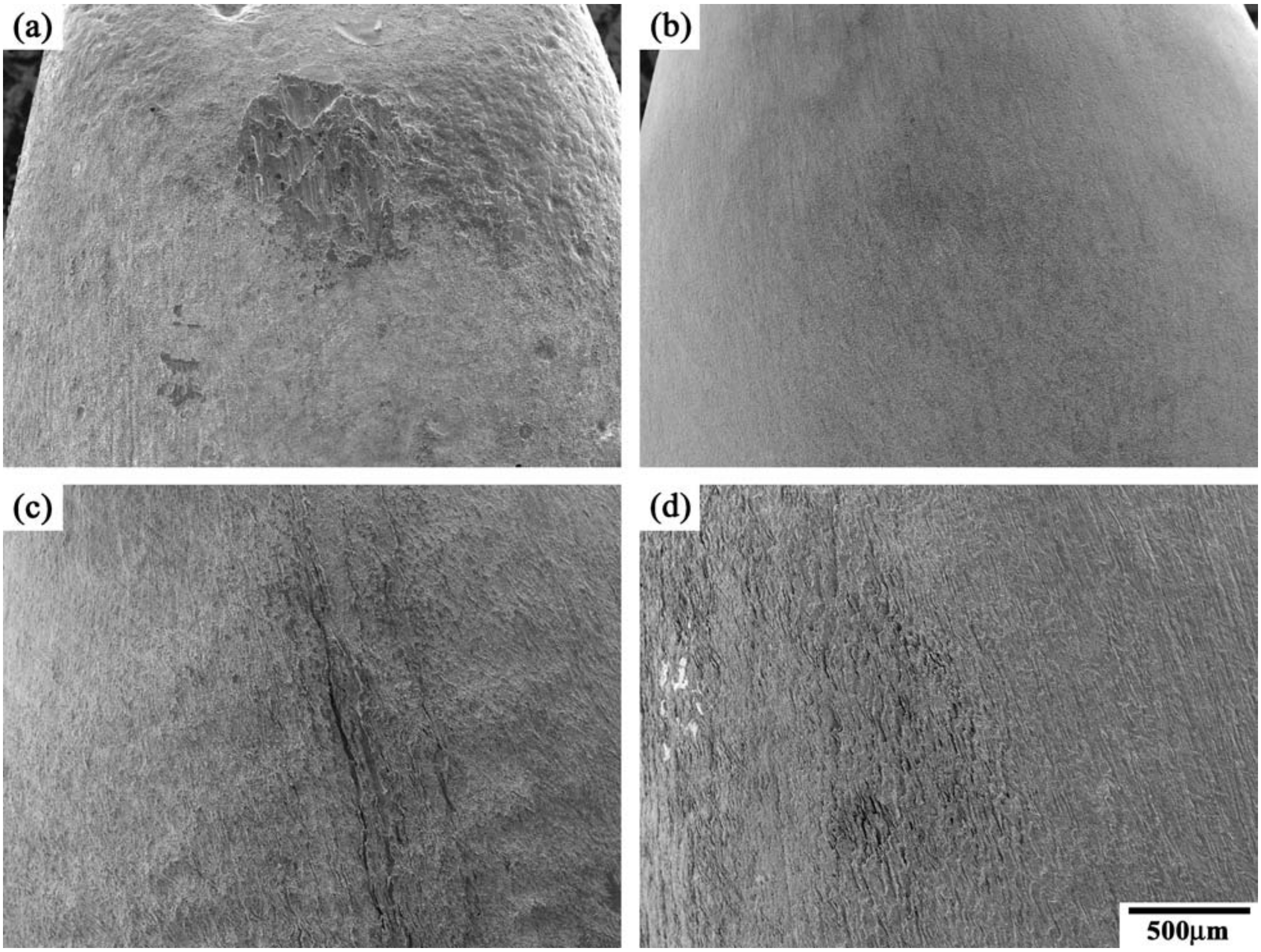

Figure 5 SEM micrographs of surface areas of ECAPed copper with different processing cycles of (a) 1, (b) 2, (c) 4 and (d) 8, respectively, close to the fractured surfaces documented after slow strain rate test in 3.5% NaCl solution.

TABLE II. The change in the heat flow values of oxygen-free copper with ECAP process

Number of cycles	0	1	2	4	8
Heat flow (J/g)	∼0	101.9	95.0	93.5	52.4

plastic deformation of pure copper [7, 8]. Table II shows the change in the heat flow value during the ECAP process of the present alloy. As expected, the heat flow value of fully annealed, pure copper was almost zero. With the ECAP process by one cycle, the heat flow increased drastically accompanied with the increase in the dislocation density. After the second ECAP process, the stored energy, as represented by the heat flow value, began to gradually decrease. Eventually, the specimen with 8 ECAP process cycles showed the lowest heat flow value, suggesting that the dislocation density was greatly decreased due to dynamic recovery [8].

The present study showed that the resistance to corrosion and stress corrosion cracking of copper was strongly related to the microstructural evolution during ECAP process. As indirectly demonstrated in Table II, the dislocation density was the highest for the specimen with just a single ECAP process. Dislocation serves as an electrochemically active site, and eventually, a single ECAPed copper showed lower resistance to general corrosion and stress corrosion cracking in 3.5% NaCl aqueous solution compared to the as-received counterpart. The dislocation density began to decrease after the second ECAP process due to dynamic recovery as suggested in the reference [7]. In that sense, the resistance to corrosion and stress corrosion cracking should increase with increasing number of ECAP process. However, the resistance to both corrosion and stress corrosion cracking began to decrease significantly after the fourth ECAP process. The present observation strongly suggested that nano grain size in copper could be detrimental to corrosion and, more significantly, stress corrosion cracking in 3.5% NaCl aqueous solution due to the higher grain boundary area.

4. Summary

In the present study, the corrosion and stress corrosion cracking (SCC) behavior of equal channel angular pressed (ECAPed) oxygen-free copper was examined in 3.5% NaCl solution, and the resistance was found to be varied in a complex manner with different number of

ECAP process cycles. The corrosion and stress corrosion cracking behavior of ECAPed copper in 3.5% NaCl solution appeared to be determined by two competing mechanisms of the decrease in dislocation density due to dynamic recovery and the increase in grain boundary area with increasing ECAP process cycle. Eventually, the double ECAP processed copper, which had intermediate dislocation density and sub-micron grain size, showed the best corrosion properties among the specimens studied.

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