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Corrosion of ultra-fine grained copper fabricated by equal-channel angular pressing

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Abstract

Corrosion of ultra-fine grain (UFG) copper fabricated by equal-channel angular pressing (ECAP) has been investigated in comparison with that in recrystallized coarse grain (CG) copper. Corrosion current was estimated by a Tafel extrapolation method to examine the kinetics of corrosion in a modified Livingstone etchant, which is sensitive to dislocations and grain boundaries. UFG copper exhibited a lower corrosion current in comparison with that in its recrystallized coarse grain (CG) counterpart despite the fact that the dislocation density and total fraction of grain boundaries are much greater in UFG copper than in CG copper. Corrosion damage on the surface of UFG copper is macroscopically rather uniform whereas obvious attack at grain boundaries and selective corrosion of some grain interiors were observed in CG copper.
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1. Introduction

Equal-channel angular pressing (ECAP) is one of the modern techniques utilizing severe plastic deformation (SPD) for significant materials hardening due to increasing dislocation density and considerable grain size reduction down to sub-microcrystalline scale of 0.1–0.2 μm [1]. The grain size reduction in combination with higher dislocation density causes many unique physical and mechanical properties of SPD-manufactured materials. For example, while the strength increases spectacularly after ECAP, the ductility remains relatively high or even increases in some cases [1,2]. The influence of corrosive environment on service characteristics such as resistance to corrosion and stress corrosion cracking (SCC) of ultra-fine grain (UFG) materials fabricated by SPD is a practically important issue which has received attention for the last 10 years [3–9].

The beneficial effect of grain size reduction down to the nano-scale was first demonstrated for intergranular corrosion in electrodeposited nanocrystalline nickel by the pioneering work of Rofagha et al. [10], and followed by Kim et al. [11,12]. They observed a rather smooth surface with a smaller penetration rate at grain boundaries and thus considerable improvement in intergranular corrosion. Vinogradov et al. [3] have first reported the anodic polarization behaviour of UFG copper fabricated by SPD in modified Livingstone etchant, and concluded that the anodic current in UFG copper is higher in both active and passive regions than that in coarse grained (CG) counterparts. However, the corroded surface appeared rather smooth with shallow corrosion grooves at the grain boundaries whereas deeper grooves were formed at the grain boundaries in CG copper. In other words, the susceptibility to the most dangerous form of environmental degradation – localized corrosion – was found to be lower in the UFG state of Cu. The corrosion behaviour of UFG titanium produced by ECAP was compared with that in CG samples by Balyanov et al. [4],

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and the higher resistance to corrosion in the UFG state was attributed to a higher passivation rate and lower amount of impurities segregated at grain boundaries. In these studies, the corrosion behaviour was examined where the entire specimens were polarized from equilibrium state to the anodic direction.

According to the mixed potential theory, any electrochemical reaction can be divided into oxidation and reduction reactions, which occur at separate sites, with no net accumulation of electrical charge. In equilibrium conditions while an externally applied potential is absent, the metal oxidation and the reduction of some species in solution occur simultaneously at the metal/electrolyte interface. Hence, the corrosion rate at equilibrium is determined by local cells between anodic and cathodic sites on the surface. The grain (cell) boundaries as well as individual dislocations and their arrays having latent elastic energy are expected to be preferentially anodic sites. Indeed, the degree of microstructural heterogeneity, which is characterized for instance by the fraction of grain boundaries and dislocation density, affects both the corrosion rate and the heterogeneity of corroded regions on the surface. Thus, in this study, we shall pay a special attention to the corrosion kinetics in a UFG structure produced by SPD. In corrosion practice, the so-called Tafel extrapolation method was employed in order to examine the corrosion kinetics in a natural state of immersion, i.e. at thermodynamic and electrochemical equilibrium between the surface and electrolyte. Pure copper was selected for the present work since it is among most studied materials readily available in the UFG state after ECAP. Besides, the corrosion behaviour of pure copper is well documented and understood [13,14], providing a solid ground for comparison. The use of equilibrium conditions for evaluation of corrosion resistance and corrosion kinetics differs the present work from previous studies, e.g. [3]. Hence, the aim of the present communication is to clarify the role of SPD-processing in environmentally affected degradation of materials and its potential for improvement of corrosion resistance.

2. Experimental

Commercial purity (99.96%) copper deoxidized by phosphorus was employed. Copper rods of 20 mm diameter and 100 mm length were pressed through the 90° ECAP die up to eight passes by the so-called route Bc. In route Bc, the sample was rotated by 90° about the working axis in the same sense between each pass. After ECAP, some billets were left in the as-processed state while some were annealed as described later in order to reduce the dislocation density without changing the grain size. Annealing was also aimed at possibly transforming the grain boundaries from their non-equilibrium structure inherited form SPD to more equilibrium structures having lower stress fields [1]. Completely recrystallized CG copper with an average grain size of 10 μm, annealed at 673 K, was also tested for comparison. The microstructure of the specimens was examined by a Hitachi H8100 transmission electron microscope (TEM). The Tafel extrapolation method was implemented in the modified Livingstone etchant ($HCl:CH_3COOH:H_2O = 1:3:80$, pH 0.5) at ambient temperature in a flat polarization cell, using a platinum counter electrode and Ag/AgCl reference electrode to measure the corrosion current and corrosion potential. In this electrolyte, such defects as dislocations and grain boundaries are preferentially subjected to a local corrosive attack [15]. Prior to the tests, the electrolyte was deaerated for 30 min by flowing argon. The range of potential variations was controlled by Hokuto HABF5001 to be within 100 mV(Ag/AgCl) from the corrosion potential so that the possible disturbance of the local cells was hindered. In addition to the Tafel tests, natural immersion tests were also carried out so that corroded surface without the influence of disturbance by applied potential can be observed. Corroded surfaces were observed by a scanning electron microscopy (SEM, JEOL JSM-6400).

3. Results

3.1. Influence of post-ECAP annealing temperature and time on hardness

It is commonly accepted that UFG structures formed by SPD are less thermally stable than conventional CG structures. The non-equilibrium grain boundaries readily transform to their equilibrium states with lower density of extrinsic and intrinsic dislocations at relatively low temperatures [1]. To obtain the recovered UFG microstructures with reduced dislocation densities, the influence of annealing temperature after ECAP on hardness was investigated as shown in Fig. 1. Similarly to many other investigations, the Vickers hardness remained nearly constant until 473 K, and then decreased noticeably at higher temperatures. There was no visible grain growth with average initial grain size of 300 nm until 473 K while partial abnormal grain growth was observed at higher temperature as shown in Fig. 2 illustrating a bimodal structure formed by coarse grains embedded into a UFG matrix. Thus, the appropriate temperature for post-ECAP annealing is determined as 473 K where

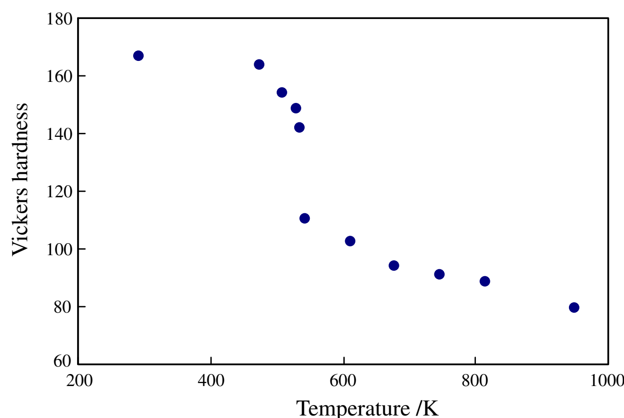

Fig. 1. Influence of annealing temperature for 40 s on Vickers hardness of UFG copper after ECAP.

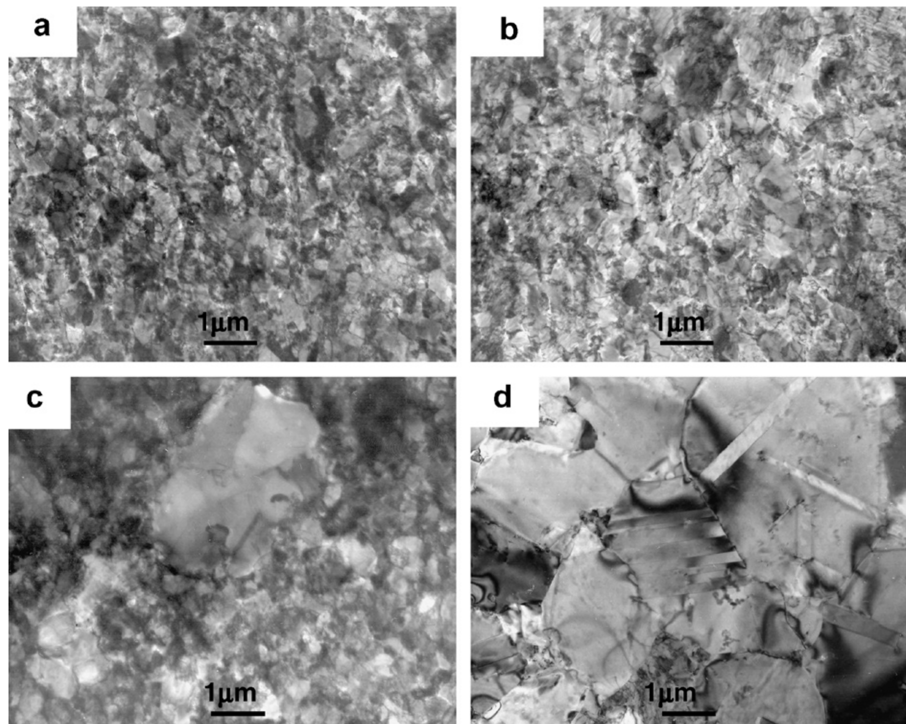

Fig. 2. TEM microstructures observed after annealing for 40 s, (a) as-ECAPed, (b) 473 K, (c) 533 K and (d) 553 K, respectively.

dislocations density should decrease without complete recrystallization and grain growth. Since recovery is a time-dependent process, we investigated the softening behavior as a function of annealing time at 473 K as shown in Fig. 3. A slow decrease of hardness is recognized during annealing up to 80 s followed by remarkable softening due to grain growth. Thus, it is plausible to evaluate the effect of degree of recovery on corrosion while utilizing the specified range of annealing time at 473 K.

3.2. Corrosion test

The anodic and cathodic currents near the corrosion potential for as-fabricated, post-ECAP annealed and completely recrystallized CG copper are shown in Fig. 4. All these curves showed some extent of concentration polarization where the cathodic currents were virtually constant and independent of the decreasing potential whereas the anodic currents increased proportionally with increasing potential. During concentration polarization, diffusion of oxidizers such as H^+ and O_2 to the metal surface dominates the kinetics of overall electrochemical reaction. Importantly, the anodic currents of all specimens were nearly identical, i.e. insensitive to the grain size and dislocation densities. The corrosion currents and corrosion potentials estimated by the Tafel extrapolation method were plotted as a function of post-ECAP annealing time (Fig. 5). In accord with common practice, these quantities are estimated at the crossing

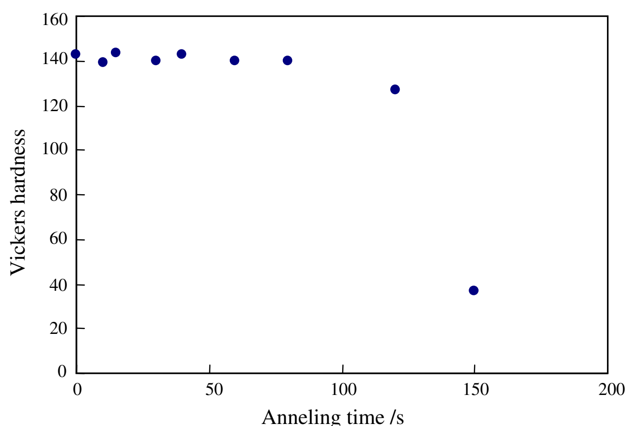

Fig. 3. Influence of annealing time at 473 K on Vickers hardness after ECAP.

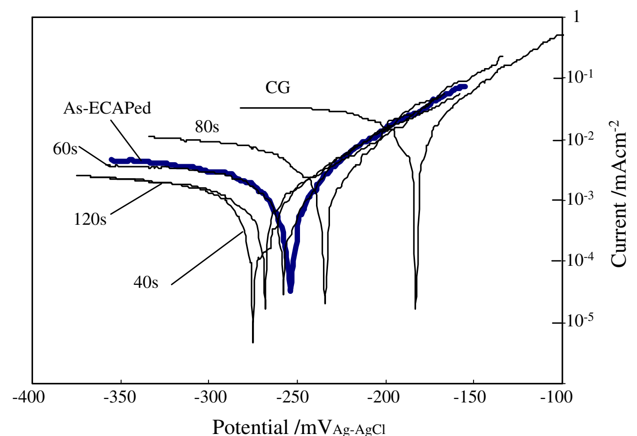

Fig. 4. Tafel plots for as-ECAPed and annealed, recrystallized CG copper in modified Livingston etchant.

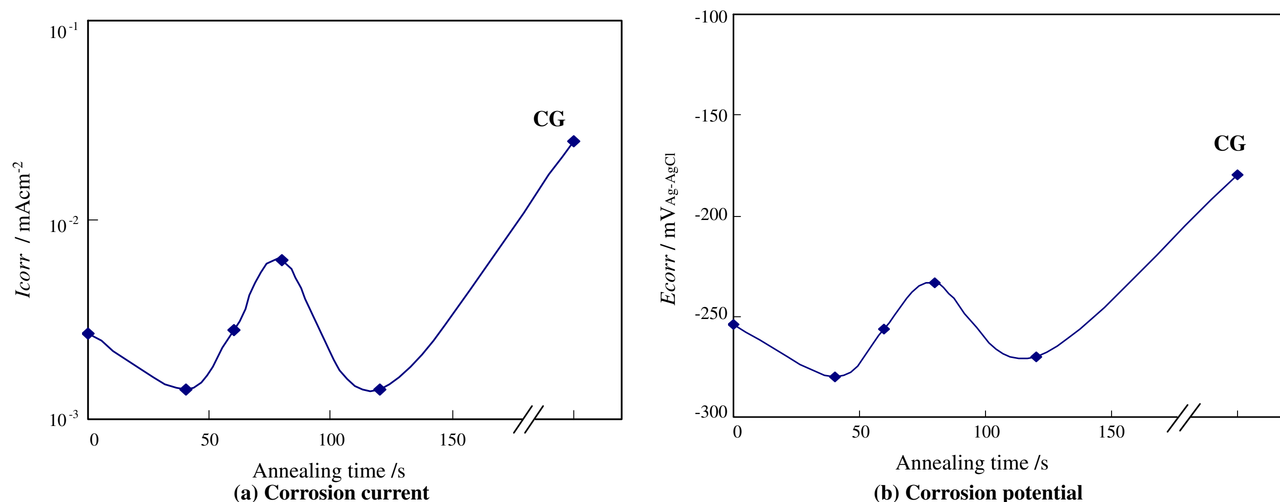

Fig. 5. Corrosion current and potential estimated by Tafel plots as functions of annealing time.

point of extrapolated anodic and cathodic curves. The corrosion currents, which indicate the total loss of metal per unit time, are apparently lower in as-ECAPed copper than in the CG counterparts. It is worth noticing that UFG structures showed lower corrosion rate in the electrolyte which is primarily sensitive to dislocations and grain boundaries despite higher density of these defects. The influence of post-ECAP annealing time on the corrosion current appears to be small. In view of experimental scatter it is not yet clear whether short-term annealing at relatively low temperatures is beneficial or not for corrosion resistance. The view of corroded surfaces after natural immersion tests are shown in Fig. 6. In UFG copper, surfaces were rather smooth and uniform so that the degree of local environmental attack at grain boundaries is small. In CG copper, however, grain boundary grooves are clearly visible: some grains have been selectively attacked while others remain intact by environment. This selective corrosion of grains is attributed to the difference of surfaces crystallographic orientation. The present results indicating that the degree of heterogeneity of corrosion is higher in CG than in UFG structure agree with those reported by Vinogradov et al. [3].

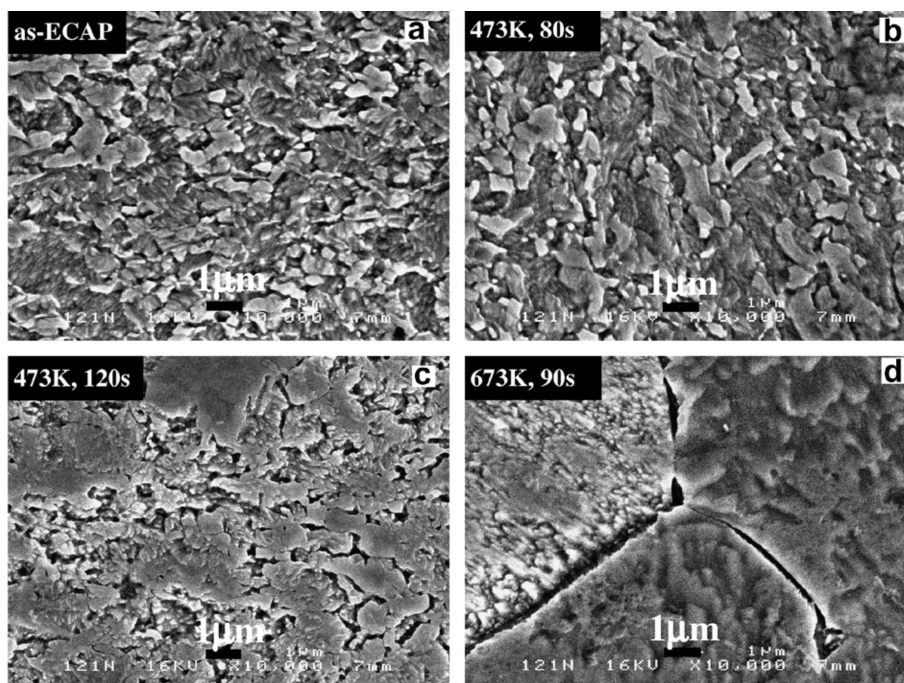

Fig. 6. SEM micrographs showing corroded surfaces after natural immersion tests, of (a) as-ECAPed, (b) annealed at 473 K for 80 s, (c) annealed at 473 K for 120 s, (d) recrystallized CG copper.

4. Discussion

Intergranular corrosion is often induced by impurity segregation and precipitation at grain boundaries. Defects such as dislocations and grain boundaries have also intrinsic susceptibility to local attack, and reactivity of these defects increases with increasing extra free energy associated with intrinsic structural disorder [13,14].

In thermodynamic consideration, the extra free energy lowers half-cell electrode potential, resulting in greater tendency for electrochemical dissolution in certain corrosive environments. Thus, UFG structures with larger number of larger grain boundaries should be active compared with CG structures. This, however, appears to be inconsistent with the present results.

When we consider a corrosion process, two steps must be taken into account [16],

(1) Initiation stage which is controlled to a large extent by metallurgical factors and inhomogeneity of structures.
(2) Growth and propagation stages which may be structure sensitive but also influenced by kinetic factors such as diffusion reactions and polarization.

Since the degree of degradation in the present experiment is largely determined by the second step, the discussion hereafter is concentrated on the second step. According to the electrochemical theory, corrosion proceeds by forming local cells between anode and cathode reactions, where oxidation reaction of metal and reduction reaction of oxidizer such as dissolved O_2 and H^+ ion occurs, respectively. The rate of corrosion, i.e., the mass loss per unit time, which is related directly to the corrosion current, is determined by the difference between the half-cell electrode potentials of the anodic and cathodic reactions, kinetics of reactions, diffusion of oxidizer such as O_2 and H^+, and the relative area of anodic and cathodic sites. Beaunier et al. [16,17] proposed an atomic-scale model which describes the penetration rate at grain boundaries, using kinetic parameters such as activation energy for the formation of active site and that for dissolution. According to the model, the dissolution rate of the surface intersecting with the grain boundaries is higher than that in the grain interiors, and the ratio of both the dissolution rates is related to the difference in the activation energy of the formation of active sites. Thus, larger area of grain boundaries due to grain refinement should simply lead to higher dissolution, and this is also inconsistent with the present results.

The inconsistency between Beaunier's model and the present result may arise because this model is based on the assumption that the entire specimen is under anodic polarization. In heterogeneous structures, however, the defects, such as dislocations and grain boundaries, have higher free energy, and have therefore, lower half-cell electrode potential whereas the grain interiors having relatively low energy have higher half-cell electrode potential. Thus, there is a spatial distribution of the potentials in the surface. The degree of local attack leading to the heterogeneous corrosion is well associated with these two half-cell potentials and oxidizing power of the solution, i.e., equilibrium potential of reduction reaction. When the oxidizing power is between the half-cell electrode potentials of grain boundaries and grain interior, anodic sites are restricted on the grain boundaries, resulting in the local attack at the grain boundaries. Typical case is seen in well-known sensitized austenitic stainless steels in hydrochloric acid. In this case, relative surface area of anodic to cathodic sites influences the degree of penetration as a result of local anodic reaction. The large cathode area facilitates the reduction reaction so that the anodic dissolution current must increase to comply with local electric neutrality. In other words, when the area of grain interior is larger by orders of magnitude than that of grain boundaries, the penetration rate at grain boundaries is enhanced. In particular, under concentration polarization where overpotential of cathodic reaction is higher, decreasing cathode area by grain size reduction may result in a decrease of apparent cathodic current. Moreover, the equivalent anodic current should be distributed over increasing grain boundary area exposed to the solution. It means that the penetration rate at the grain boundaries should decrease with decreasing grain size. Palumbo et al. estimated the volume fraction of intercrystalline region such as grain boundaries and triple junctions [18,19]. According to their analysis, if grain size is reduced from 10 to 0.3 μm, the volume fraction of intercrystalline region increase from 0.03% to about 1%. It seems that such small increase of intercrystalline region is not associated with the drastic change of polarization behavior in UFG copper.

Dilution of segregated impurities at grain boundaries is well-known beneficial effect of grain size reduction for corrosion resistance [20]. Based on the analysis of volume fraction of intercrystalline region mentioned above, Palumbo et al. estimated content of segregated impurities at grain boundaries assuming the complete segregation. When grain size is decreased from 10 to 0.3 μm, segregated impurities is estimated to be diluted by about 1/30. For example, bulk impurity content in copper of commercial purity is assumed to be about 0.04 at%, therefore the segregated impurity at grain boundaries in CG copper can be multiplied to almost 100 at% because bulk impurity content is over the volume fraction of intercrystalline region. On the other hand, segregated impurity in UFG copper is estimated to be about 4 at%. Such drastic diminishing of impurities from 100 to 4 at% could reduce the corrosion at grain boundaries.

The diffusion of oxidizer such as O_2 and H^+ can be considered as another possible cause of suppressed cathodic reaction. As shown in Fig. 4, while anodic current was minimally affected, cathodic current was drastically reduced. When grain size is reduced in ultra-fine grain size, Cu^{2+} ion dissolved at grain boundaries can easily flow in the close vicinity of surface of grain interiors. These Cu^{2+} ions near the surface interrupt the supply and reduction reaction of O_2, resulting in diminishing of cathodic current.

The dissolution rate at non-equilibrium grain boundaries with extrinsic dislocations should be higher than that at equilibrium grain boundaries, because excess extrinsic dislocations in and near the grain boundaries provide more active sites with lower activation energy for dissolution. Erb et al. [21] reported that boundary corrosivity and boundary energy scale differently with deviation from the ideal low energy structures. They assumed that boundary corrosion occurs primarily at secondary dislocations superimposed with an ideal low energy structure. As shown in Fig. 6, the variation of corrosion currents with increasing post-processing annealing time was anomalous, and the effect of grain boundary state is not clear in this study.

5. Conclusions

Tafel tests revealed that UFG copper exhibits remarkably lower corrosion current under natural corrosion conditions in comparison with that in its recrystallized coarse grain counterpart despite the higher dislocation density and total fraction of grain boundaries in the UFG state. The corrosion damage of UFG copper is macroscopically rather uniform whereas an obviously preferential grain boundary degradation and selective corrosion of some grain interiors was observed in CG copper. The dilution of impurity content of grain boundaries can responsible for lower corrosion rate and penetration rate at grain boundaries. Effect of low temperature annealing intended to diminish grain boundary dislocations is small compared with the grain size effect, and is not clear in present experiments.

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