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Microstructure and Mechanical Properties of High Purity Copper and Copper Alloys Heavily Deformed by Equal-Channel Angular Pressing

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The equal-channel angular pressing (ECAP) is one of the methods that refine the grain size of metallic materials from a coarse grain size to an ultrafine grain size. This study investigates the effect of ECAP on the formation of the fine grain size in oxygen free Cu and phosphorus de-oxidized Cu alloys. The average grain size has been refined from 150 μm before ECAP to about 300 nm. Microstructure was analyzed by transmission electron microscopy (TEM). The selected area electron diffraction pattern confirmed the formation of nanocrystalline structures with high angle grain boundaries. Mechanical properties such as microhardness and tensile properties of the ultrafine-grained copper specimen were measured.

Key words: ECAP, Cu, Ultrafine-grain, Microhardness, Tensile properties

1. INTRODUCTION

Extensive research on severe plastic deformation processes are under development to obtain ultrafine-grained materials and consequently to obtain high strength in metals and alloys [1,2]. In these processes, high strain is introduced without significantly changing the dimensions of the samples. ECAP is one of the most frequently used processes to obtain ultra-fine grained or even nano-grained structure materials [3,4,5]. The ECAP method involves pressing a sample through a die having two channels that are equal in cross-section and that intersect at an angle. Fig. 1 shows the schematic illustration of ECAP die. During the pressing, the sample undergoes severe shear deformation that refines the grain size and improves strength.

According to the rapid development of electronic industry, high strength high electrical conductivity copper alloys, as a conducting materials are required. Conventionally, high strength in copper alloys was achieved by the addition of alloying elements and subsequent heat treatment. But, these treatments cause inevitably decrease in electrical conductivity of pure copper. The way to increase strength of copper without sacrifice of electrical conductivity is grain refinement by severe plastic deformation. The objective of this research was therefore to refine the grain size of copper by ECAP method. Another object of the present study is improvement of hardness and strength without significant sacrifice of electrical conductivity.

2. EXPERIMENTAL PROCEDURE

The experiments were conducted using 99.99 % pure oxygen-free copper and phosphorus-deoxidized copper (0.02wt.% P contained). Before the ECAP process, the samples were heat treated at 500°C for 1 hour and subsequently air-cooled. The initial grain is about 200 μm. In ECAP process, the inner and outer angle of channel intersection were 90°, 45°, respectively. Repetitive ECAP was accomplished by Bc route, where the rotation of sample between successive pressings passes is always 90° in the same sense. ECAP process was carried out at room temperature up to 12 passes. MoS_2 as lubricant was used at each pass and pressing speed was 5mm/sec. After ECAP, microstructure and mechanical properties were studied. Microhardness values were measured more than 10 times for each specimen, then the average values were used. Cross plane (X-plane) of the ECAPed samples were cut to prepare specimens for transmission electron microscopic observation. Specimens were mechanically polished to a thickness of 100 μm, then subject to twin-jet electropolishing. The solution was 200ml CH_3OH + 100ml HNO_3. The jet thinning was conducted at -30°C.

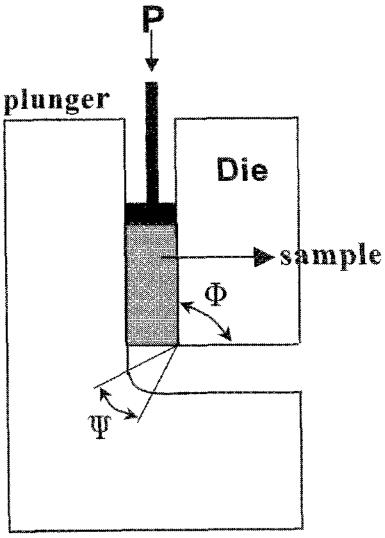


Fig.1 Schematic illustration of ECAP

3. RESULTS AND DISCCCUSSION

The average Vickers microhardness, Hv, was calculated by taking the average of all measurements on each separate sample and the results were then plotted as a function of ECAP pass, as shown in Fig. 2. By the first pass, the microhardness increased drastically due to the shear deformation introduced within the specimen. Then, microhardness increases gradually up to 3 passes of ECAP and tends to saturate with further number of pass.

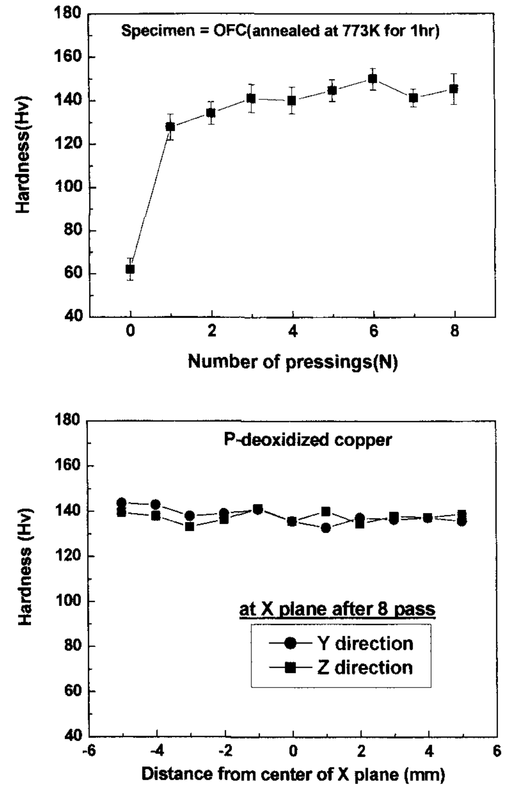


Fig. 2 Hardness change of oxygen-free copper with ECAP pass, and hardness distribution after 8 passes of ECAP in P-deoxidized copper.

Figure 3 shows the tensile properties of oxygen-fee copper and phosphorus-deoxidized copper as a function of number of ECAP pass. Both yield and tensile strength values of OFC increased drastically in the initial stage (1 and 2 passes) of ECAP process. After 3 passes, the yield and tensile strength values tended to saturate with further ECAP passes. Accompanied with the increase in the strength level, the tensile elongation value greatly decreased by 1 pass of ECAP. With further ECAP process, the tensile elongation value also began to saturate. The tensile elongation values of over 20 % for the present alloy were, however, still extremely high considering the tensile elongation value of approximately 4 % for the conventionally cold-worked, pure copper with a similar tensile strength value. Interestingly, the tensile elongation of oxygen-free copper began to increase after 4 pass of ECAP, suggesting that the strain hardening mechanism alone could not explain the present behavior. This unusual tensile behavior is caused by the ultrafine-grained structures generated by ECAP process. This behavior is also reported in some Al and Ti alloys [6,7].

At the same time, in phosphorus-deoxidized copper, we observed an extraordinary combination of high strength and high ductility at specimen deformed more than 4 passes of ECAP.

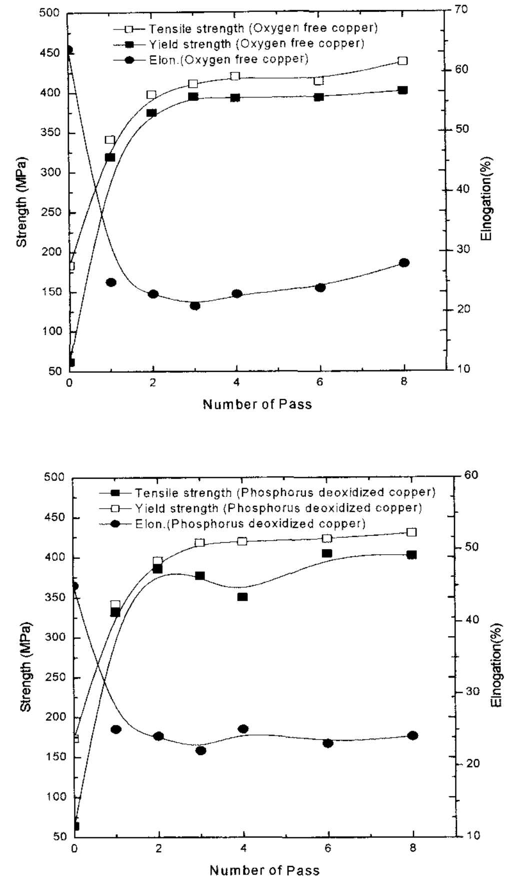
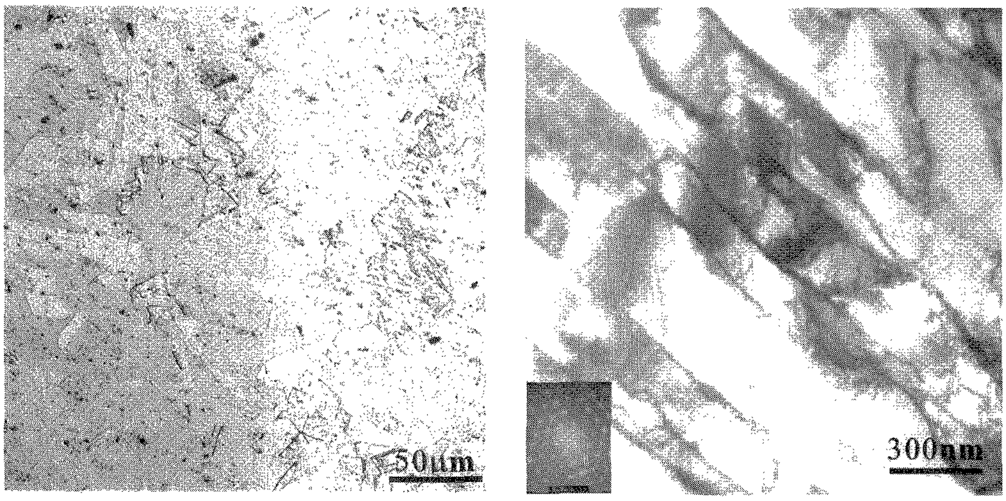
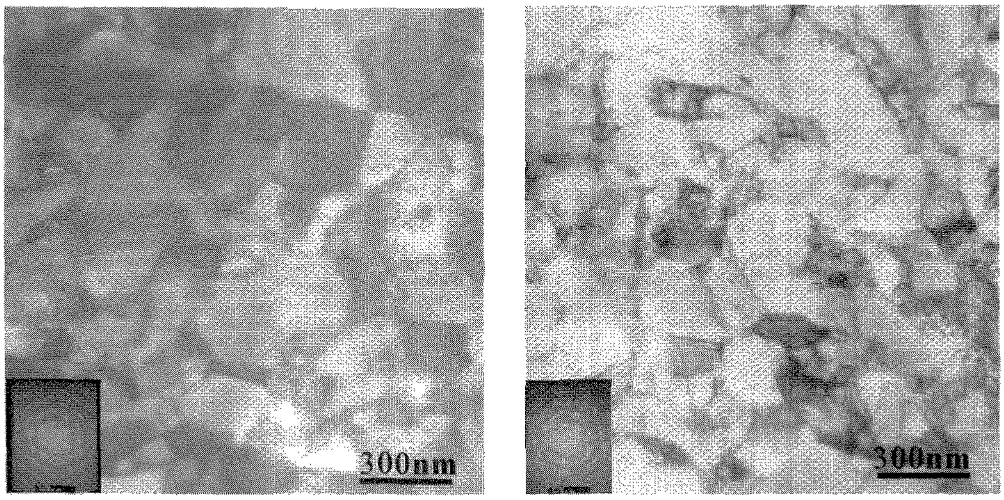


Fig. 3. Tensile properties of copper alloys with respect to the number of ECAP pass.

Figure 4 represents the OM micrograph before ECAP and typical TEM micrographs and the matching SADPs (selected area diffraction patterns of center area, 1 μm in diameter) for the ECAPed oxygen-free copper processed by (b) 1, (c) 4, and (d) 8 passes, respectively. The initial microstructure of oxygen-free copper consists of inhomogeneous grains with an average grain size of about 200 μm. After 1 pass of ECAP, micro-deformation bands with an average thickness of about 300 nm are clearly revealed. A large number of dislocations are observed with in these bands. With following deformation of ECAP (after 4 passes), the micro-deformation bands with high dislocation density transform to subgrains with low angle grain boundaries due to the dynamic recovery and recrystallization. After 8 passes of ECAP, the equiaxed fine grains with an average size of 300 nm were formed from subgrains. The main process of evolution of the equiaxed grains is the progressive growth of misorientation of low angle boundaries and their gradual transformation into high-angle boundaries.



(a) OM before ECAP (b) After 1 pass of ECAP



(c) After 4 passes of ECAP (d) After 8 passes of ECAP

Fig. 4 OM and TEM micrographs and the matching SADPs for the ECAPed OFC (a) OM before ECAP, (b) 1, (c) 4, and (d) 8 passes of ECAP, respectively.

The SADPs taken from these regions indicate ring-like patterns, showing the grain boundaries with high angle misorientations after 8 pass of ECAP. This change of microstructure with number of pass of ECAP process illustrates the increase in tensile elongation after 4 passes of ECAP, shown in Fig. 2. The increase in strength of oxygen-free copper with increasing number of ECAP pass is attributed to the strain hardening in the initial stage. In this stage, the elongation decreased. At high strains (after 4 passes of ECAP), the strain hardening mechanism was annihilated by the dynamic recovery and recrystallization. Instead, fine-equiaxed grains were formed by dynamic recrystallization, illustrating the increase in the tensile elongation at higher pass of ECAP. To confirm the change microstructure with the ECAP process, the heat flow values of the specimens with different ECAP passes were measured by using DSC (Differential Scanning Calorimeter).

Figure 5 shows the change in the heat flow value of ECAPed of oxygen-free copper. 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. As, expected, the change of heat flow value of fully annealed copper was almost zero. The calculated values of heat flow change after 1, 4, and 8 passes of ECAP were 101.9, 93.5, 52.4 J/g, respectively. With the ECAP process by one pass, the change of heat flow value increased drastically accompanied with the increase in the dislocation density. Furthering the ECAP process, however, the stored strain energy, as represented by the heat flow value, began to gradually decrease reflecting the TEM observation shown in Fig. 4.

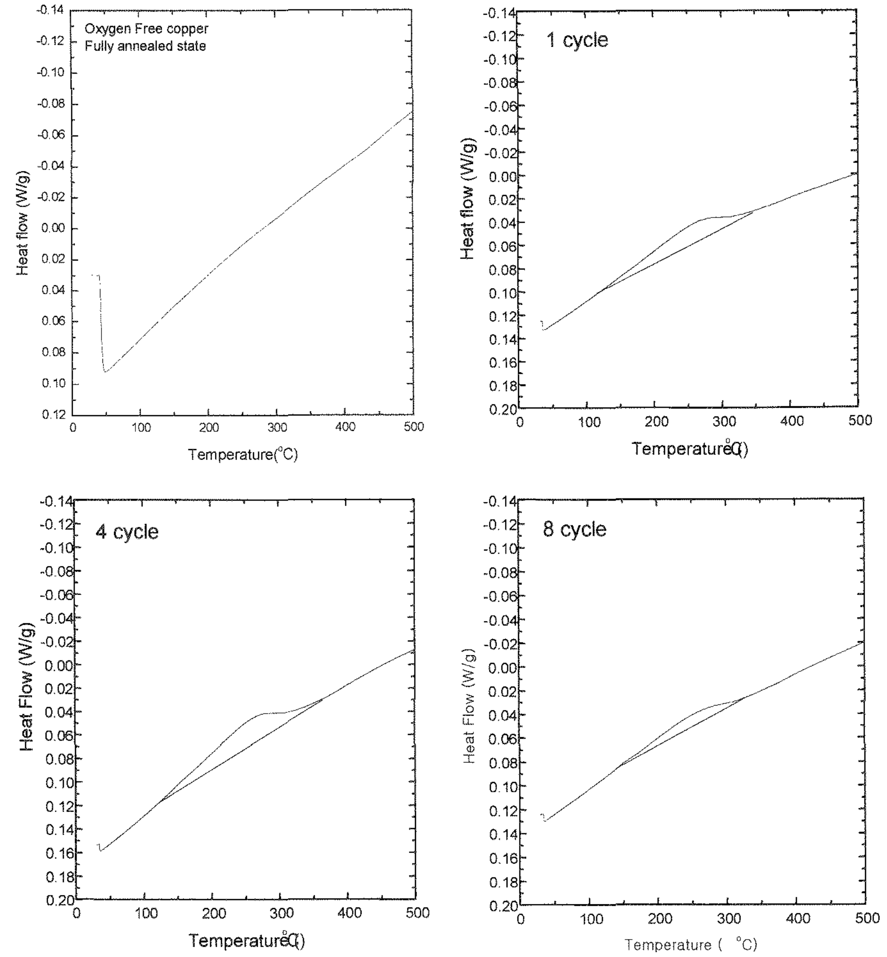


Fig. 5 EDS curves for the ECAPed oxygen-free copper processed by (a) 0, (b) 1, (c) 4 and 9d) 8 passes, respectively.

4. SUMMARY

Samples of oxygen-free copper and phosphorus-deoxidized copper (0.02wt%. P contained) were deformed at room temperature by ECAP process up to 8 passes. The microhardness and tensile strength increased about more than twice in the first pass of ECAP process. Accompanied with the increase in the strength level, the tensile elongation value decreased in this stage. After 3 passes, strength value tends to saturate and elongation goes to minimum, and then began to increase after 4 passes of ECAP. This elongation increase behavior after 4 passes was attributed to the grain refinement.

After first pass of ECAP, the microstructure was composed of deformation bands with high dislocation density. Further pass of ECAP leads to the change of deformation bands to subgrain and the increasing misorientation of subgrain boundaries due to the dynamic recrystallization. After 8 passes of ECAP, equiaxed ultra-fine grains with high angle grain boundaries were formed.

High strain energy was stored by one pass of ECAP process. Increasing the ECAP passes, the stored energy began to gradually decrease due to the dynamic recovery and recrystallization.

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4. REFERENCES

[1] R. Z. Valiev, "Ulrafine Grained Materials II", Ed. By Y. T. Zhu, T. G. Langdon, et al., A Pubrication of The Minerals, Metals & Materials Society, (2002), pp. 313-322.

[2] Y. T. Zhu, T. C. Lowe, *Mater. Sci. Eng.*, **A291**, 46-53, (2000).

[3] Y. Iwahashi, Z. Horita, M. Nemoto and T. G. Landon, *Acta Mater.*, **47**, 4733-4737 (1997).

[4] R. Z. Valiev, A. V. Korznikov, R. R. Mulyukov, *Mater. Sci. Eng.*, **A186**, 141-147 (1993).

[5] R. Z. Valiev, N. A. Krasilnikoe, N. K. Tsenev, *Mater. Sci. Eng.*, **A137**, 35-43, (1991).

[6] Z. Horita, D. J. Smith, M. Furukawa, M. Nemoto, R. Z. Valiev, and T. G. Langdon, *J. Mater. Res.*, **11**, 1880-1885, (1996).

[7] K. Oh-ishi, Z. Horita, D. J. Smith, M. Furukawa, R. Z. Valiev, M. Nemoto, and T. G. Langdon, *J. Mater. Res.*, **14**, 4200-4207, (1999).

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