A Portrait of Copper Processed by Equal Channel Angular Pressing

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Copper is one of the most important materials used for electrical connectors with a high thermal and electrical conductivity, and there is an ongoing demand to improve its mechanical properties without sacrificing other beneficial properties. A possible approach to achieving this aim is to use the method of severe plastic deformation to obtain an ultrafine grained microstructure. Significant grain refinement obtained by equal channel angular pressing (ECAP) leads to an improvement of mechanical, microstructural and physical properties. This paper gives an overview of a range of the properties that can be achieved by ECAP processing of pure copper including microstructural features, thermal stability, thermal conductivity and corrosion resistance. [doi:10.2320/matertrans.ME200717]

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1. Introduction

In recent years, research activity in the area of severe plastic deformation (SPD) has increased due to some interesting properties which can be achieved by SPD in bulk materials.¹⁾ Of specific interest for industrial applications are improved mechanical properties, especially a high strength, in conjunction with reasonable ductility, and the possibility to obtain high strain rate superplastic behaviour.²⁾ In addition, changes in physical properties owing to the small grain size are observed. As the diffusivity is significantly enhanced by severe plastic deformation, the SPD methods can be used to increase the speed of various kinetic processes, *e.g.* precipitation³⁾ or such technologically important processes as nitriding of steels.⁴⁾

The present work was motivated by industry's demand for improving the mechanical properties of copper, particularly for use in connectors, without a detrimental effect on its overall properties profile. Alloying of copper leads to a significant increase in strength, but often the price is an appreciable loss of electrical and thermal conductivity. To investigate the viability of grain refinement by severe plastic deformation in achieving a balance between the required properties, investigations on the mechanical properties, the thermal stability, the corrosion properties and the thermal resistivity were carried out. This paper summarises the results of these studies and demonstrates that it is possible to produce ultrafine-grained copper with the potential to be used for high strength connectors still allowing a good conductivity.

2. Experimental

ECAP of technical purity copper (99.95%) was carried out

using a split design die manufactured from tool steel X38CrMoV 5 1. The angle between the entrance and the exit channels was 90°; a sharp die corner was used to maximize strain per ECAP pass. A typical specimen size was 10 mm × 10 mm × 100 mm. An INSTRON 8502 universal testing machine (maximum load of 200 kN) was used in room temperature ECAP at typical speeds of eight millimetres per minute. To reduce frictional effects, molybdenum disulphide was used for lubrication.

For transmission electron microscopy (TEM) investigations on specimens prepared by mechanical and electrolytic polishing from middle sections of the ECAP processed billets, a Philips CM200 electron microscope operating at 200 kV was used. Electrolytic polishing was carried out at 10°C using 50% H₃PO₄ in a Tenupol 5 (Struers) jet polishing unit.

EBSD (electron backscatter diffraction) measurement on heat treated ECAP specimens were carried out using a LEO 1530 FEG Scanning Electron Microscope.

Mechanical properties were determined by testing tensile specimens in a conventional universal testing machine (INSTRON 5582) fitted with an extensometer. The applied strain rate was 10⁻³ s⁻¹.

Thermal conductivity measurements were performed using a stationary method,⁵⁾ where a copper specimen and a reference specimen (Macor) of known thermal conductivity were subjected to the same unidirectional heat flux, which was generated by placing the specimens between a heated and a cooled platens. To minimize the thermal resistance between the two specimens and between the specimens and the platens, the specimens were mechanically polished. A thermally conducting graphite lubrication paste was also used at the contacts. (For more detail of the thermal conductivity measurement setup, see Ref. 6).)

Fig. 1 Dislocation cell size distributions in technical purity copper after ECAP processing.

To investigate the corrosion behaviour, a Voltalab 10-PGZ 100 (Radiometer Analysis SYS, France) unit consisting of a conventional three electrode cell was used. A saturated calomel electrode (SCE) connected via a Haber-Luggin capillary was chosen as a reference electrode. Using teflon tape, a defined copper electrode surface area of approximately 20 mm² was delineated. The solutions used as corrosive media were 1 kmol/m³ H₂SO₄ and 3% NaCl. Prior to corrosion testing, the specimen surfaces were mechanically polished on a fine emery paper followed by an electropolishing procedure. After cathodic charging employed to remove oxide films which may have had formed, potentiodynamic scans with a speed of 1 mV s⁻¹ were performed. After reaching the transpassive potential, the scans were terminated. More details on the corrosion measurements and the setup used are given in Ref. 7).

To investigate the influence of the corrosion pattern, particularly the degree of localization of corrosion attack, a Tesla BS343 scanning electron microscope operating at 15 kV was used.

3. Results

3.1 Effect of ECAP on the grain structure and the mechanical properties

As already known, in case of pure copper ECAP leads to a significant grain refinement resulting in a microstructure with an average grain size of about 200 nm as determined by TEM. This structural refinement occurs already after the first ECAP pass, during which a large number of low angle grain boundaries are introduced in the microstructure. With an increase in the number of ECAP passes, an equiaxed grain structure is formed combined with an increase of the amount of newly formed high angle grain boundaries. Still, a significant number of low angle grain boundaries remain present in this kind of microstructure.⁸⁾ The evolution of the dislocation cell size can be seen in Fig. 1, which shows that almost no change in the typical structural scale produced in the first ECAP step occurs with subsequent ECAP passes. The cell size distribution was obtained by measuring the apparent cell diameter, which is given by the diameter of a circle of the same area as the cell investigated. A log-normal distribution appears to fit the cell size distribution data

Fig. 2 0.2% proof stress of technical purity copper before and after ECAP processing.

Fig. 3 Microhardness variation of ECAP processed copper (8 passes) with the temperature of isochronal annealing (10 min).

obtained from TEM analysis pretty well. However, a detailed analysis⁶⁾ showed that a different function accounts for the cell size distribution more adequately than a log-normal one.

Investigations of the strength of copper after ECAP revealed a similar tendency, as can be seen from Fig. 2. Already after a single ECAP pass, the 0.2% proof stress increases significantly, to more than 300 MPa, and it hardly grows with further ECAP processing.

3.2 Studies of thermal stability

Generally, the increase of strength reported in the previous section is accompanied with a drop of ductility. To improve ductility, a thermomechanical route that combines ECAP with a suitable heat treatment can be followed. One of the ideas discussed in literature is to produce a bimodal microstructure and increase strength and ductility at the same time.⁹⁾ This was also shown to be beneficial with regard to the fatigue behaviour.¹⁰⁾

To accomplish this goal, the thermal stability of copper after ECAP needs to be known. In order to obtain these data, isochronal annealing (10 minutes) was performed on specimens after 8 ECAP passes in a temperature range of 100°C to 200°C. Hardness tests were carried out to characterize thermal stability. The results of this investigation can be seen in Fig. 3. At about 150°C a strong decrease of the microhardness is observed. Figure 3 suggests that a bimodal

Fig. 4 TEM micrographs of ECAP processed copper (8 passes) after isochronal annealing (10 min), left: at 110°C, right: at 150°C.

microstructure may be obtained through using such isochronal heat treatment in the temperature range between 150°C and 170°C due to recrystallisation effects.

The influence of the mentioned heat treatment on the microstructure is presented in Fig. 4. The TEM micrograph on the left-hand side shows the structure after annealing at 110°C. (The original microstructure exhibiting a grain size of about 200 nm can still be recognised in the micrograph.) The micrograph on the right-hand side shows parts of the microstructure after annealing at 150°C, grain growth being obvious. Very sharp grain boundaries can also be seen. Numerous small grains of about 200 nm in size are still present after the 150°C heat treatment.

To get an overview picture of the structural changes after heat treatments, EBSD investigations were carried out. Figure 5 shows the orientation images after isochronal annealing at 110°C (a), 150°C (b) and 170°C (c). After the 110°C annealing no significant change of the microstructure was observed. An ultrafine grain size and homogeneous grain distribution were still found. The fraction of high angle grain boundaries (HAGBs) as determined by EBSD was at about 48%.

In Fig. 5(b), first changes in the microstructure are visible. Obviously, the annealing process at 150°C leads to the occurrence of first macroscopic recrystallised grains. This result is consistent with the TEM observations described before. Numerous ultrafine grains are present in the microstructure after the annealing. Again, the measured proportion of HAGBs was about 48%.

Annealing at 170°C (Fig. 5(c)) led to a completely changed microstructure. It was still relatively fine-grained having an average grain size of 740 nm, but large parts of this microstructure were recrystallised, and the fraction of HAGBs increased to about 93%. Between large recrystallised grains there was still a sizeable amount of ultrafine grains

leading to a bimodal grain size distribution.

The expected positive effect of the heat treatment on the mechanical properties is illustrated by Fig. 6. A significant increase in ductility is seen to be possible without compromising the strength too much. After heat treatment at 110°C, hardly any changes in the tensile properties could be observed. An increase of the annealing temperature to 160°C or 170°C is seen to lead to an increase in ductility owing to the aforementioned bimodal microstructure. These results demonstrate that the use of an appropriate thermo-mechanical route makes it possible to establish a favourable combination of strength and ductility of technical purity copper simply by controlling its recrystallisation behaviour.

3.3 Effect of ECAP on thermal conductivity

Another property which is very important for the application of copper as a connector is its thermal and electrical conductivity (which are correlated through the Wiedemann-Franz law). As it is crucial to retain the high conductivity when producing a material with enhanced mechanical strength, we have studied the thermal conductivity of ECAP processed copper. Figure 7 shows clearly that there is no significant loss of thermal conductivity after ECAP. The variations of conductivity with the number of ECAP passes may correspond to slight variations in the grain size distribution, cf. Figure 1, which can be explained in terms of the concomitant variation of the electron reflectivity.⁶⁾ The simple model used can be described as follows:

A simple one-dimensional chain of N grains of equal size l , total length $L = Nl$ and cross-sectional area S can be assumed. The overall thermal resistance of this chain can be expressed as:

$$R = \frac{L}{S\kappa_{bulk}} + NR_{dist} = \frac{L}{S\kappa_{bulk}} + \frac{L}{l}R_{dist} \quad (1)$$

Fig. 5 EBSD orientation images of the 8 pass specimens after isochronal annealing (10 min) at (a) 110°C, at (b) 150°C and at (c) 170°C.

where κ_{bulk} is the bulk heat conductivity and R_{disl} is the thermal resistance due to dislocations, other contributions to resistivity being neglected. To evaluate R_{disl} , one can assume that the electrical and thermal conductivity for an electron gas are proportional to each other according to the Wiedemann–Franz law. As the majority of the dislocations are organised in cell walls (which at sufficiently large strains will have transformed to grain boundaries), published estimates^{11,12)} of the grain boundary electrical resistance may be used:

$$R_{disl} = \frac{4\lambda}{3A\kappa_{bulk}(1-r)} \quad (2)$$

Here λ is the electron mean free path, A the contact area and r the electron reflectivity. This parameter takes into account the fact that the electrons reflected from the grain boundary dislocations do not take part in the transfer process.

The grain surfaces exhibit a complex geometry, and the effective partial contact area may be expressed as $A = xS$, with $x < 1$. Combining (1) and (2) gives:

$$R = \frac{L}{S\kappa_{bulk}} \left(1 + \frac{4\lambda}{3xl(1-r)} \right) \quad (3)$$

The experimentally measured effective thermal conductivity κ_{exp} (which is presented in Fig. 7) can be introduced via the equation

Fig. 6 Tensile deformation behaviour of ECAP processed copper (8 passes) after isochronal annealing.

Fig. 7 Variation of thermal conductivity with increasing number of ECAP passes.⁶⁾

$$R = \frac{L}{S\kappa_{\text{exp}}} \quad (4)$$

leading to

$$\kappa_{\text{exp}} = \frac{\kappa_{\text{bulk}}}{1 + \frac{4\lambda}{3xl(1-r)}} \quad (5)$$

As l can be identified with the grain size, and $\kappa_{\text{bulk}} = 400 \text{ W/mK}$ and $\lambda = 39 \text{ nm}$ at room temperature¹³⁾ are given, the only remaining variable influencing the thermal conductivity is the electron reflectivity. According to,⁶⁾ differences in r correspond to differences in the width of grain size distribution functions, as this influences the matching between boundaries of neighboring grains.

3.4 Effect of ECAP on corrosion resistance

Another aspect which is important for the application of copper is its corrosion resistance. The question arises of how the grain refinement, which improves the strength of the material very well, may influence the overall corrosion behaviour. Therefore, potentiodynamic investigations of the corrosion behaviour of copper before and after 8 ECAP passes were carried out.^{7,14)} We summarise the results of these studies here. Potentiodynamic polarisation curves of the coarse grained (CG) and the ECAP processed, ultrafine grained (UFG) copper in the $1 \text{ kmol/m}^3 \text{ H}_2\text{SO}_4$ solution are presented in Fig. 8. Both specimens exhibit similar polar-

Fig. 8 Potentiodynamic curves ($1 \text{ kmol/m}^3 \text{ H}_2\text{SO}_4$) of technical purity copper before and after ECAP processing.

Fig. 9 Potentiodynamic curves (3% NaCl) of technical purity copper before and after ECAP processing.

isation behaviour showing a single active-passive transition between 350 and 450 mV_{SCE} . Upon reaching the passivation potential, a steady state anodic current is observed.

The corrosion behaviour in a 3% NaCl solution ($\text{pH} = 7.01$) is shown in Fig. 9. In this case, two distinct active-passive transition potentials were observed. The potential E_{p1} can be attributed to the formation of a CuO film on the specimen surface,¹⁵⁾ while E_{p2} may be associated with copper oxidation to Cu_2O_3 . Again, both materials exhibit very similar curves indicating that there is no pronounced effect of ECAP on the overall corrosion behaviour.

A more detailed comparison in terms of commonly used corrosion parameters, *viz.* the corrosion potential E_{corr} , the corrosion current density i_{corr} and the already mentioned active-passive transition potentials, cf. Table 1, also shows that there is almost no difference in the corrosion behaviour between the ECAP processed and the coarse grained copper.

To investigate the local patterns of the corrosion attack, SEM pictures were taken after the corrosion experiments (Fig. 10). On the left-hand side, where the surface of the ECAP processed copper is presented, it is seen that a uniform corrosion attack had occurred, no preferential corrosion attack at the grain boundaries being recognisable. In contrast, the surface of a non-ECAP processed specimen (right-hand side micrograph in Fig. 10) shows distinct localisation of corrosion attack at the grain boundaries, while significantly

Table 1 Corrosion characteristics of the coarse grained and the ECAP processed copper in the two solutions used.¹⁴⁾

1 kmol/m³ H₂SO₄	E_{corr} [mV]	i_{corr} [$\mu\text{A}/\text{cm}^2$]	i_{an} [$\mu\text{A}/\text{cm}^2$]	E_p [mV]
coarse grained	−79	45	159	470
8 ECAP passes	−54	30	142	361
3% NaCl	E_{corr} [mV]	i_{corr} [$\mu\text{A}/\text{cm}^2$]	i_{an} [$\mu\text{A}/\text{cm}^2$]	E_{p1}/E_{p2} [mV]
coarse grained	−234	23	6–12	37/195
8 ECAP passes	−206	30	5–10	27/185

Fig. 10 SEM micrographs after the corrosion tests showing the difference in the character of corrosion attack, left: after 8 ECAP passes, right: coarse grained copper.

lower corrosion damage is seen in the grain interior regions. The more homogeneous corrosion damage in case of ECAP processed copper in contrast with the localised corrosion attack in conventional copper can obviously be seen as an advantage.

In assessing the overall effect of grain refinement by ECAP on the corrosion properties of copper, the following major outcomes of the tests can be reported. From the thermodynamic viewpoint both potentials (the corrosion and the passivation one) of UFG copper are shifted to positive values with respect to the corresponding potentials of CG copper, which signifies an improvement in corrosion resistance. From the kinetic viewpoint the influence of ECAP on the corrosion current density and the steady state current density in the passive state is not so obvious, however. The results of the electrochemical tests reported here characterise the surface of the material in a *short-term*. From the character of the corrosion attack on the surface of the UFG and the CG copper seen in Fig. 10 one may conjecture that the long-term progress of the corrosion attack will be affected by the formation of a layer of corrosion products (passive and/or pseudopassive layer). This layer will be more homogeneous in the ECAP processed copper due to its ultra fine grain size. It can thus be expected that in long-term corrosion resistance tests the corrosion rate will drop below the levels for the coarse-grained copper. Such behaviour was, indeed, found by other authors for ECAP processed titanium.¹⁶⁾ They found unambiguously that in all corrosive media tested the corrosion rate of UFG specimens was lower than that of the coarse-grained reference material.

4. Conclusion

In this paper several aspects of the effect of ECAP on the properties of technical purity copper have been reviewed and summarised. Having in mind industrial applications of copper, *e.g.* in connectors or sputtering targets, the material's portrait presented in this paper is quite promising. ECAP leads to extreme structural refinement of copper, down to the grain size of about 200 nm. This gives rise to a huge increase in strength, but causes a low ductility level. It was shown that a suitable heat treatment can partly restore ductility, while still maintaining a very high strength.

At moderate temperatures the ECAP processed copper was found to retain its grain structure and properties, while at about 150°C and above recrystallisation was observed.

The overall favourable assessment of the effect of ECAP on the properties is also based on the fact that ECAP does not lead to any sizeable deterioration of thermal conductivity. It can be conjectured that electrical conductivity is not strongly affected in a negative way either.

Finally, it was shown that ECAP has no detrimental effect on the overall corrosion behaviour in 1 kmol/m³ H₂SO₄ and 3% NaCl solutions. Localisation of the corrosion attack at the grain boundaries was only observed in coarse grained copper. ECAP processed copper exhibited a more homogeneous corrosion behaviour.

It can thus be concluded that a very favourable combination of properties of technical purity copper can be obtained by equal channel angular pressing, which—together with subsequent heat treatment—permits tailoring of the properties within a certain range of practical interest.

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