The electrical conductivity of CuCrZr alloy after SPD processing

M Lipińska*, P Bazarnik, M Lewandowska
Warsaw University of Technology, Department of Materials Science and Engineering, Wołoska 141, 02-507 Warsaw, Poland

*E-mail: martal54op@gmail.com

Abstract. CuCrZr alloys exhibit very good relation between mechanical properties and electrical conductivity. However, for its use in some advanced applications improvement of mechanical strength while preserving high electrical conducting is required. Therefore, in this work a CuCrZr alloy was subjected to a series of thermo-mechanical treatments, including solution annealing and water quenching, SPD processing (using hydrostatic extrusion and ECAP) as well as aging in order to improve mechanical strength. The influence of these processing procedures on microstructure features and mechanical properties was determined by TEM observation and microhardness measurements, respectively. Electrical conductivity of the samples was measured by four-points method. The results have shown that it is possible to improve mechanical strength while preserving good electrical conductivity by a proper combination of SPD processing and heat treatment.

1. Introduction

Pure copper features excellent electrical properties, which makes it attractive for a number of industrial fields. However, its low mechanical strength is a limiting factor for many applications. To improve the strength of pure metals, many approaches can be considered, for instance alloying to form solid solution and/or second phase particles, grain boundaries or dislocation strengthening. Unfortunately, each of these approaches has a negative impact on electrical conductivity. Therefore, there is a need to compromise these two properties.

CuCrZr alloys are an example of combining mechanical strength and electrical conductivity on a very high level. Their mechanical properties are much higher than for pure copper because of the addition of alloying elements, which form precipitates during ageing of water quenched supersaturated solid solution. A very high electrical conductivity is assured by low solubility of Cr an Zr in copper matrix at room temperature [1]. CuCrZr alloys are used as electrical wires or trolley wires for fast railway. Due to the combination of excellent mechanical strength with very high electrical as well as thermal conductivity, they are considered as a prime material for fusion reactors, e.g. international thermonuclear experimental reactor, ITER [2,3]. An additional advantage of these materials is the possibility to tailor their properties using different heat treatments and manufacturing processes involving almost every known strengthening mechanisms.
The strength of CuCrZr alloys can be improved by increasing the content of alloying elements. However, this causes difficulties in manufacturing process as well as a decrease in electrical conductivity. In this work, an attempt has been made to improve mechanical strength of a CuCrZr alloy while maintaining its high electrical conductivity without changing chemical composition. This can be obtained by using severe plastic deformation (SPD) techniques. They are known as an effective way of grain size refinement below 1 micron and the production of ultrafine grained (UFG) materials. Such materials feature extremely high strength due to grain boundaries strengthening as described quantitatively by the Hall-Petch relationship [4,5]. Nowadays, the most popular SPD techniques include Equal Channel Angular Pressing (ECAP) [6] and High-Pressure Torsion (HPT) [7]. Also, Hydrostatic Extrusion (HE) was proved to be an efficient method of grain size refinement [8].

The scientific goal of the study was to quantify the influence of various microstructural elements, such as grain boundaries, dislocations, precipitates and solid solution atoms, on both mechanical strength and electrical conductivity of a CuCrZr alloy.

2. Experimental

The material studied was a copper alloy CuCrZr with chemical composition given in Table 1. The alloy was subjected to various thermo-mechanical treatments to obtain various microstructures. These are:
- solution annealing at a temperature of 1000°C for 1 h and water quenching – single phase coarse grained (CG),
- solution annealing at a temperature of 1000°C for 1 h, water quenching and ageing at a temperature of 480°C for two hours – CG precipitations hardened,
- solution annealing at a temperature of 1000°C for 1 h, water quenching, ageing at a temperature of 480°C for two hours and then processing by hydrostatic extrusion – UFG,
- solution annealing at a temperature of 1000°C for 1 h, water quenching and processing by hydrostatic extrusion – UFG,
- solution annealing at a temperature of 1000°C for 1 h, water quenching and processing by ECAP – UFG.

**Table 1.** The chemical composition (wt.%) of examined CuCrZr alloy.

| Element | Cu  | Cr  | Zr  | Fe  | Zn  | Sb  | P  |
|---------|-----|-----|-----|-----|-----|-----|----|
| Content (wt.%) | balance | 0.7 | 0.08 | 0.03 | 0.01 | 0.01 | 0.01 |

The HE was carried out at room temperature in a 4-step process with a total true strain of 3.77. The initial diameter was 30 whereas the final one 3 mm. The ECAP process was performed with two passes using B_C route in a 90° die also at room temperature. The total true strain was 2.3. The processes of HE and ECAP were carried out at the Institute of High Pressure Physics of the Polish Academy of Sciences. The microstructures were observed using optical microscope (for samples with coarse grains) and JEOL 1200EX transmission electron microscope (TEM) with an accelerating voltage of 120kV in the case of samples after SPD processing. The cross-sections were examined. The electrical conductivity was determined by measuring the electrical resistance, using the four-points method. The electrical conductivity was expressed as a relative value of the International Annealed Copper Standard (%IACS). To measure the mechanical strength of investigated materials, microhardness was measured using Vicker’s method (HV0,1).
3. Results and discussion

Figure 1 and 2 show the microstructures of CuCrZr alloy after solution annealing and water quenching as well as subsequent ageing, respectively. Both materials display coarse grained microstructure with a number of annealing twins. The average grain size is at the similar level for both samples: 38 µm and 34 µm for solution annealed and aged samples, respectively. The grain size diversity quantified using coefficient of variation (defined as a ratio of standard deviation to the mean value) is significantly higher for the sample after ageing. In addition, the sample after ageing feature high density of small precipitates homogenously distributed in grains interiors.

![Figure 1. Microstructure of the CuCrZr alloy after solution annealing and water quenching.](image1)

![Figure 2. Microstructure of the CuCrZr alloy after solution annealing, water quenching and additional aging.](image2)

SPD processing brings about significant microstructure refinement, as illustrated in figures 3 to 5. However, the SPD microstructures differ significantly due to the fact that HE and ECAP differ in the strain components, which have a major impact on microstructure evolution. In ECAP there is a pure shear, meanwhile in HE a three-dimensional compressive strain state is characteristic.

TEM observations of the sample after two passes of ECAP revealed the structure consisting of highly elongated subgrains with high density of dislocations, as illustrated in figure 3. The average distance between subgrain boundaries was measured as 222 nm. The structure with very high density of dislocations is typical for SPD copper based materials processed to relatively low accumulated strain. CuCrZr alloys exhibit rather low stacking fault energy (SFE). As a result, during plastic deformation dislocations are separating which induce more dislocation tangles. They baffle dislocations to move and with further deformation they behave like a dislocation sources which leads to accrue the dislocations. As a result the morphology with high density of dislocations is obtained [9].

The microstructures of the samples, which were HE processed before and after ageing are shown in figures 4 and 5, respectively. The grains observed on the cross-section have more equiaxial shape compared to those after ECAP. The density of the dislocations is relatively high, but still smaller than for the samples after ECAP. Comparing the samples, one may notice difference in the grains size, which is smaller for the sample HE processed directly after solution annealing and water quenching (166 nm) whereas larger for the sample HE processed after ageing (202 nm). In both samples, small precipitates (of the size of few nm) homogenously distributed in the microstructure are visible. Therefore, the same combination of phases has been obtained, which is in agreement with other
studies [10]. However, it should be noted that the precipitates in the sample processed before ageing appear during HE processing. Although it has been demonstrated that the temperature rise is negligible during SPD processing [11], HE features very high strain rate (up to 100 s\(^{-1}\)). As a result, the temperature rise is expected due to adiabatic heating phenomena.

Figure 3. Microstructure of the CuCrZr alloy after two passes of ECAP.

Figure 4. Microstructure of the CuCrZr alloy solution annealed, water quenched and HE processed.

Figure 5. Microstructure of the CuCrZr alloy after ageing and HE processing.

The results of the electrical conductivity, microhardness measurements and average values of grain size are summarized in table 2. The single phase CG sample exhibits the lowest hardness and electrical conductivity. Ageing leads to a significant improvement in both microhardness and electrical conductivity, which is the highest (70.2% IACS) among all samples investigated. However, the most pronounced microhardness increase takes place for the samples processed by SPD methods. Comparing HE and ECAP processing, one can notice higher microhardness and electrical conductivity measured for HE processed samples. Among the SPD processed samples, those aged and HE processed possesses the best combination of microhardness and electrical conductivity.

The major microstructural elements influencing the mechanical strength of materials are grain boundaries, which are described by the Hall-Petch relationship. This relationship predicts linear dependence between strength (or hardness) and inverse square root of the grain size. The results of grain size and microhardness measurements of the CuCrZr alloy were plotted in the Hall-Petch coordinates, as illustrated in figure 6. They are far from the linear dependence due to overlapping of
grain boundary and precipitation strengthening. The samples subjected to ageing exhibit significantly higher microhardness than those corresponding to single phase material with the same grain size. It can also be noticed that the HE processed sample has slightly higher microhardness than that predicted by the Hall-Petch relationship. This can be attributed to partial decomposition of supersaturated solid solution during HE, which proceeds with very high strain rate, causing temperature rise due to adiabatic heating phenomena.

Table 2. The electrical conductivity, microhardness and average grain size of CuCrZr alloy in different stages.

|                  | Conductivity (%IACS) | Microhardness (HV0,1) | Grain size (nm) |
|------------------|----------------------|-----------------------|-----------------|
| CG single phase  | 48,2                 | 144                   | 38010           |
| CG aged          | 70,2                 | 152                   | 34190           |
| aged + HE        | 56,6                 | 179                   | 202             |
| HE               | 51,9                 | 171                   | 166             |
| ECAPx2           | 48,1                 | 160                   | 222             |

Figure 6. Hall – Petch plot for CuCrZr alloy subjected to various thermo-mechanical treatments.

According to the Matthiessen’s rule, the electrical resistivity ($\rho$), the inverse of electrical conductivity, depends on several microstructural features [1]:

$$\rho = \rho_0 + \Delta \rho_S + \Delta \rho_P + \Delta \rho_V + \Delta \rho_D + \Delta \rho_B$$  \hspace{1cm} (1)

where: $\rho_0$ describes resistivity of pure solvent metal, and $\Delta \rho$ corresponds to the rise of electrical conductivity due to atoms in solid solution (S), precipitates (P), vacancies (V), dislocations (D) and grain boundaries (B). Two out of all samples investigated exhibit the lowest conductivity, namely single phase CG and UFG one after ECAP processing. Both samples have single phase microstructure with alloying elements dissolved in Cu matrix. This indicates that atoms in solid solution have the most detrimental effect on electrical conductivity. A similar value of %IACS for single phase CG and UFG samples also suggests that the grain size has minor effect on this property. This is in an agreement with other studies, whose results revealed that structure refinement reduces electrical conductivity only by few %IACS or sometimes even get it higher [9,12,13]. The highest electrical conductivity was measured for the solution annealed, water quenched and aged sample, which can be attributed to its coarse grained structure and a large degree of decomposition solid solution, as a result of which small precipitates in pure copper matrix are produced.
Among UFG samples, the highest conductivity was measured for the sample aged and then HE processed. It can be explained by the fact that most of the atoms of alloying elements are in the form of precipitates, which are homogenously distributed in the matrix. Slightly higher electrical conductivity of HE processed sample than compared to ECAP one is caused by the partial decomposition of solid solution as discussed above. The sample after ECAP exhibits the biggest grain size, however, the increase in electrical resistivity caused by grain boundaries is negligible as compared with the benefit caused by precipitation. Experiments show that bigger decrease of electrical conductivity can be observed for greater effective strain [14,15].

In many applications, a good combination of high strength and high electrical conductivity is required. However, all microstructural elements which cause strengthening reduce at the same time conductivity. On the other hand, some elements act as strong factors whereas the others have weaker impact. This is illustrated in figure 7, which presents the plot of microhardness as a function of electrical conductivity. The results show that grain size refinement allows to improve hardness to conductivity balance far beyond the line characteristic for coarse grained materials. Although it was not possible to achieve the value of %IACS as high as for aged CG sample, there is a clear tendency that grain size refinement accompanied by decomposition of solid solution offers a great potential to produce high strength materials with a relatively good electrical conductivity.

![Figure 7. Microhardness versus %IACS for CuCrZr alloy subjected to various thermo-mechanical treatments.](image)

4. Conclusions

Satisfactory combination of high mechanical properties and good electrical conductivity is possible employing processes which lead to precipitation hardening and grain refinement. Both of them cause the scattering of electrons, which results in a decrease in electrical conductivity comparing to pure solvent metal. Nonetheless this drop is significantly smaller than the one caused by solid solution. The precipitates even increase the electrical conductivity of the alloy after age hardening.

Age hardening combined with SPD processing make it possible to obtain a material with very high mechanical properties together with relatively high electrical conductivity which can be attractive for many industrial applications.
Acknowledgements

This work was carried out within a NANOMET Project financed under the European Funds for Regional Development (Contract no. POIG.01.03.01-00-015/08).

References

[1] Zhou H T, Zhong J W, Zhou X, Zhao Z K and Li Q B 2008 Materials Science and Engineering A 498 225-230.
[2] Barabash V R, Kalinin G M, Fabritsiev S A and Zinkle S J 2011 Journal of Nuclear Materials 417 904-907.
[3] Lorenzetto P, Peacock A, Bobin-Vastra I, Briottet L, Bucci P, Dell’Orco G, Ioki K, Roedig M and Sherlock P 2006 Fusion Engineering and Design 81 355-360.
[4] Hall E O 1951 Proc. Phys. Soc. London B 64 747.
[5] Petch N J 1953 J. Iron Steel Inst. 174 25.
[6] Langdon T G 2007 Materials Science and Engineering A 462 3-11.
[7] Zhilyaev A P and Langdon T G 2008 Progress in Material Science 53 893-979.
[8] Kurzydlowski K J 2006 Materials Science Forum 503-504 341-348.
[9] Feng H, Jiang H, Yan D and Rong L 2013 Materials Science & Engineering A 582 219-224.
[10] Straumal B B, Kilmametov A R, Ivanisenko Y, Kurmanaeva L, Baretzky B, Kucheev Y O, Zieba P, Korneva A, Molodov D A 2014 Materials Letters 118 111-114.
[11] Straumal B, Korneva A, Zieba P 2014 Archives of Civil and Mechanical Engineering 14 242-249.
[12] Takata N, Lee S-H and Tsuji N 2009 Materials Letters 63 1757-1760.
[13] Zhilyaev A P, Shakhoiva I, Belyakov A, Kaibyshev R and Langdon T G 2013 Wear 305 89-99.
[14] Ko Y G, Namgung S, Lee B U and Shin D H 2012 Journal of Alloys and Compounds 504S S448-S451.
[15] Habibi A, Ketabchi M and Eskandarzadeh M 2011 Journal of Materials Processing Technology 211 1085-1090.