

HIGH ELECTRICAL CONDUCTIVITY Cu-BASED ALLOYS. PART I

M T. Jovanović, V. Rajković

Institute of Nuclear Sciences „Vinča“, 11001 Belgrade, Serbia, tmsj@ptt.rs

Received 20.05.2009

Accepted 24.06.2009.

Abstract

Effect of thermomechanical treatment (TMT), i.e. prior plastic deformation, time and temperature of aging on microstructure, hardness, electrical conductivity and thermal stability of Cu-0.4%Cr-0.08%Zr and Cu-0.4%Cr-0.08%Zr-0.05%Mg (in wt.%) alloys has been investigated. Both alloys behave in the similar manner under TMT. The maximum value of hardness was within the range of 1520 to 1630 MPa after cold rolling for 50 and 80% followed by aging at 425 °C for 2h. The maximum of electrical conductivity which is between 89 and 92% IACS appears at 480 °C. These properties together with high thermal stability of both alloys (around 520 °C) are quite satisfactory compared to properties of commercial Cu-based alloys. Considering practical application Cu-0.4%Cr-0.08%Zr-0.05%Mg alloy might be regarded as very interesting because the TMT avoids high temperature solution annealing and quenching, without reducing the hardness and electrical conductivity.

Key words: thermal stability, recrystallization, hardness, electrical conductivity, spot welding electrodes

Introduction

Cu and Cu-based alloys are among the most commercially important metals because of their excellent properties, ease of manufacture and numerous applications. They are normally used because of their excellent electrical and thermal conductivity, resistance to corrosion and ease of fabrication. Low-alloyed Cu are used extensively for cables and wires, electrical contacts and a wide variety of other parts that are required to pass electrical current. The development of electronics industry has led to a number of new applications for Cu alloys including lead frames, connectors and other electronic components. These applications require alloys with unique combinations of strength and conductivity coupled with thermal stability [1].

Different types of high electrical conductivity alloys have been developed in research centers world wide. The literature [2] indicates that Cu-rich Cu-Cr and Cu-Zr alloys have been thoroughly investigated. On the other side, a number of commercial alloys have been developed and these are used for a variety of applications requiring

combinations of high-strength, high-conductivity and resistance to softening. In most instances a small amount of the third element additions are required to achieve optimum properties in these binary alloys. However, the chemical composition and especially technology of their processing are protected by patents or classified documents.

The electrical-resistance welding process reached full development in the production of aviation assemblies, car chassis and bodies, metallic furniture, and other applications, after World War II. This welding process uses copper and Cu-based alloys as the electrode material. Electrical-resistance welding involves passing a high current at a low voltage through a circuit closed by the pieces to be welded; these pieces are maintained in close contact with the two electrodes by means of an applied pressure (Fig. 1). The heat generated by the Joule effect is enough to produce local fusion of the pieces under pressure, leading to an autogenously forged union. Thus, electrode materials must exhibit high electrical and thermal conductivities, combined with high strength, at elevated temperatures.

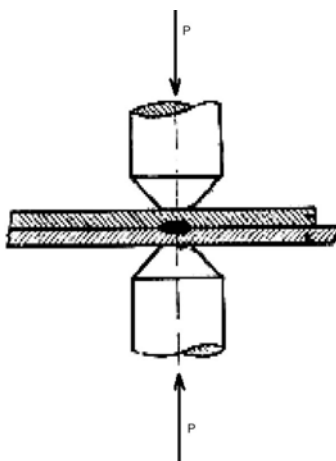


Fig. 1. Set up of welded material inserted between a pair of electrodes

Owing to a favorable combination of mechanical properties and electrical conductivity, alloys belonging to the Cu-Cr system are commonly applied for fabrication of electrodes for resistance spot and seam welding of low carbon steels.

The maximum equilibrium solubility of Cr in Cu is 0.73 wt.% at 1076.2 °C [3]. It is impractical to achieve such a high solution temperature due to the risk of formation of some liquid phase. At a safe solution treatment temperature no more than 0.7 wt.% Cr could be expected to be dissolved into solid solution. The addition of Cr more than 0.7 wt.% would serve no purpose in the precipitation hardening of the alloy. Also, very small addition of Zr (less than 0.1 wt.%) improve hardness and electrical conductivity of alloy due to very low solubility of Zr in Cu matrix at room temperature. After high temperature solution annealing these alloys are subjected to water quenching which makes their processing expensive.

A comparative investigation on the effect of thermomechanical treatment (TMT), i.e. prior plastic deformation, time and temperature of aging on microstructure, hardness, electrical conductivity and thermal stability of Cu-0.4%Cr-0.08%Zr and Cu-

0.4%Cr-0.08%Zr-0.05%Mg alloys (designated as Cu-Cr-Zr and Cu-Cr-Zr-Mg in the following text, respectively) was carried out. The idea was to obtain a good combination of physical and mechanical properties by adding small amount of Mg in Cu-Cr-Zr alloy and optimizing heat treatment processing. The alloy with Mg addition was not subjected to the high temperature solution annealing.

Experimental

Material

Oxygen free copper (OFHC) and Cu-10% and Cu-30%Zr (in wt.%) master alloys were used for alloys preparation. Graphite mold was previously preheated to 400 °C. Ingots with 40mm in diameter and 180mm in height were produced by melting and casting in a laboratory vacuum furnace. The chemical composition of alloys is given in Table 1.

Table 1. Chemical composition of alloys (in wt.%)

Alloy	Cr	Zr	Mg
Cu-Cr-Zr	0.42	0.079	-
Cu-Cr-Zr-Mg	0.40	0.078	0.049

TMT

a. Cu-Cr-Zr

Hot rolling (to the predetermined diameter) at the temperature between 800 and 850°C→solution annealing at 960 °C for 1h→water quenching→cold rolling (degree of plastic deformation: 30, 50 and 80%)→aging (temperature of aging: 400, 425, 450, 480 and 500 °C; time of aging: 1, 2, 4, and 6h).

b. Cu-Cr-Zr-Mg

Hot rolling (to the predetermined diameter) at the temperature between 900 and 960°C→air-cooled→cold rolling followed by aging. Applied parameters of cold rolling and aging were the same as in Cu-Cr-Zr.

Samples (16mm in diameter and 10mm in height) for metallography, hardness and electrical conductivity measurements were cut from the TMT bars. One sample served for all these tests for a specified TMT parameter. Standard metallographic preparation techniques (mechanical grinding and polishing followed by etching in a mixture of 5g FeCl₃, 50ml HCl and 100ml distilled water) were applied prior to light microscope (LM) examinations. A “Zeiss Axiovert” metallographic microscope was used for microstructural characterization. Vickers microhardness was measured applying 200g load, the holding time under the load was 30s. The electrical conductivity, expressed in %IACS ($IACS_{20}^{\circ C} = 0.5800\mu\Omega^{-1}cm^{-1}$), was measured at 60 kHz on polished samples using Siemens “Sigmatest” conductometer. At least five measurements of hardness and electrical conductivity were performed on each sample.

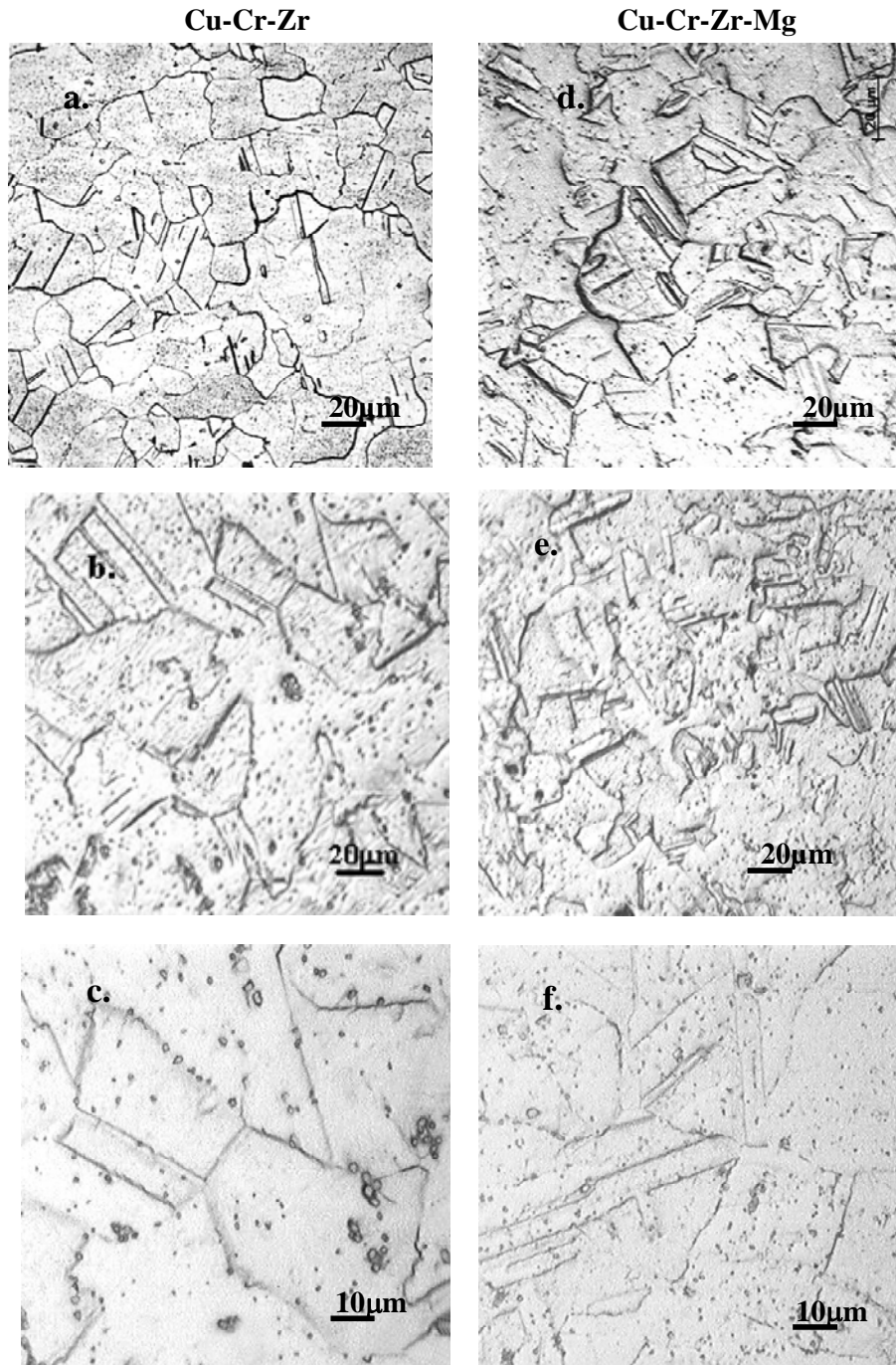


Fig. 2. LM micrographs; (a) 960 °C→water quenched; (d) hot-rolled at 960 °C→air-cooled; (b, c, e, f) cold-rolled 50%→aged 425 °C/2h

Samples with the best combination of hardness and electrical conductivity (these properties were obtained after cold rolling with 50 and 80% deformation and subsequent aging at 450 °C for 2h) were subjected to tests of thermal stability, i.e. they were post-annealed for 4h in the range of 100 and 700 °C and their hardness was measured at room temperature after every 50 °C of annealing.

Results

Microstructure

Fig. 2 shows the microstructures of alloys under different TMT conditions.

After solution treatment (Fig. 2a, d) the microstructure mainly consists of equiaxed grains with annealing twins. Presence of small particles may be seen in both alloys, but their density was higher in Cu-Cr-Zr-Mg alloy which was air-cooled after hot rolling. Fig. 2b, e shows the microstructure of peak aged condition with particles precipitated mainly inside the grains. Higher magnification of the same samples reveals particles precipitated not only inside the grains, but also at the grain boundaries (Fig. 2c, f). Coagulation of particles occurred in Cu-Cr-Z alloy (Fig. 2c). Applying LM it was not possible to detect precipitation mechanism during TMT of these alloys. TEM analysis in the Part II of this paper will supply more information concerning this phenomenon.

Hardness and electrical conductivity

Due to the large number of data only the most important results are shown. The influence of the degree of prior deformation and temperature of aging (aging time of 2h was chosen) on hardness and electrical conductivity of Cu-Cr-Zr and Cu-Cr-Zr-Mg alloys is shown in Fig. 3a, b, respectively.

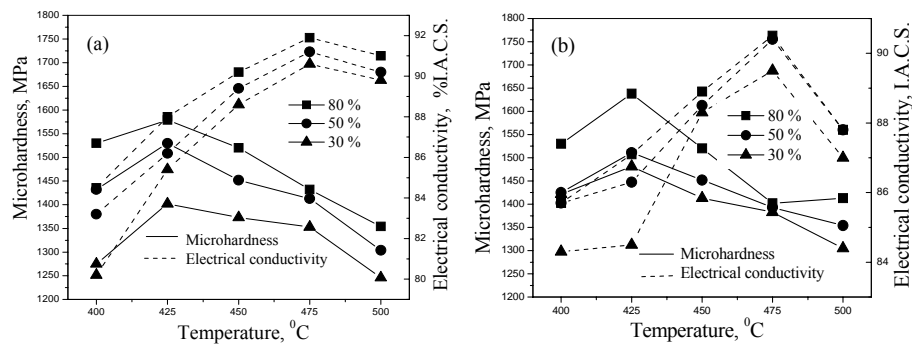


Fig. 3. Effect of prior cold deformation and aging temperature on hardness and electrical conductivity; (a) Cu-Cr-Zr; (b) Cu-Cr-Zr-Mg. Aging time-2h

Curves show characteristic bell-shape dependence with temperature and are very similar for both alloys. Hardness reaches maximum at 425 °C after 2h of aging, and then

decreases with aging temperature. The maximum value of hardness is within the range of 1520 to 1630 MPa when both alloys are deformed for 50 and 80%.

On the other hand, the maximum of electrical conductivity which is between 89 and 92%IACS appears only at 480 °C, then the conductivity decreases. Maximum of electrical conductivity corresponds to the lower hardness values and vice versa. With increased degree of deformation curves have moved towards greater values of hardness and electrical conductivity. These values correspond to many commercial high electrical conductivity Cu alloys with good mechanical properties.

Thermal stability

For the deformed alloys, which are important for practical application, it is important to know how they behave at high temperatures, i.e. at which temperature softening occurs. This temperature corresponds to the limit of alloy thermal stability. Fig. 4a, b shows changes in hardness of both alloys as a function of the temperature of post-annealing. From the curves in Fig. 4 it can be seen that the abrupt decrease in hardness occurs at about 500 °C. In the area between 500 and 600 °C hardness virtually does not change with temperature. With further increase in temperature hardness decreases again. The shape of curves is nearly the same for both alloys.

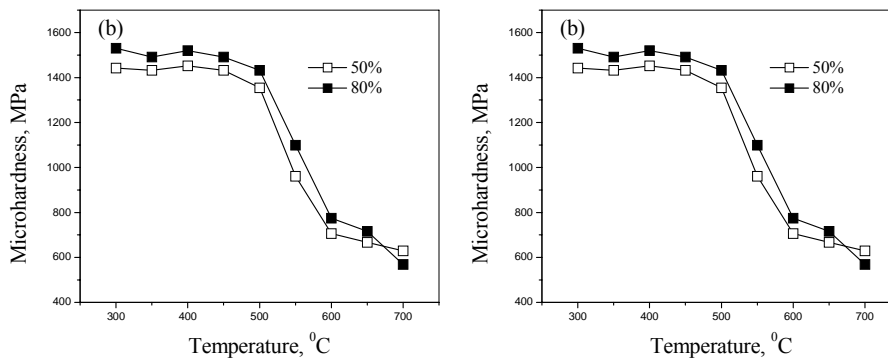


Fig. 4. Effect of post-annealing temperature (duration of annealing-4h) on hardness – determination of thermal stability; (a) Cu-Cr-Zr; (b) Cu-Cr-Zr-Mg

Discussion

Commercial Cu-Cr alloys combine high strength with high electrical conductivity in the optimally aged condition. This family of alloys (Cu-(0-1%) Cr+minor additions of other alloying elements) have a large precipitation hardening response. This is because Cr in the supersaturated Cu matrix creates a high degree of thermodynamically meta-stable nano-sized particles, thus providing a high chemical potential for the precipitation reaction which is activated by the process of subsequent aging [5, 6].

Cold working is often carried out between the solid solution treatment and aging to assist in the age hardening by introducing a high density of dislocation [4]. The high

hardness of Cu-Cr-Zr alloys is due to precipitation on dislocations and precipitation strengthening of the Cu matrix. The excellent electrical conductivity is attributed to the very low solubility of Cr and Zr in Cu matrix. In order to control the microstructure and improve the properties of Cu-Cr-Zr(Mg) alloys, it is of great value to identify the composition of the precipitates. There has been no unanimous agreement on the chemical composition of precipitated phases in the alloy. The precipitates within the grains were indexed to be Hoesler phase $\text{CrCu}_2(\text{Zr},\text{Mg})$, whereas grain boundary particles were identified as Cu_4Zr . Most researchers consider the composition of precipitates as cubic fcc Cu_5Zr [8]. Huang and Ma [9] found $\text{Cu}_{51}\text{Zr}_{14}$ in the matrix of Cu-Cr-Zr alloy. In a recent paper it was shown that three phases Cr-rich, Hoesler phase $\text{CrCu}_2(\text{Zr},\text{Mg})$ and Zr-rich should exist in the system [10].

A small number of fine particles visible in Cu-Cr-Zr alloy (Fig. 2a) is the result of a relatively low solutionizing temperature with the result that some amount of Cr and Zr was not converted into the solid solution. Due to a very high temperature for maximum solubility of these elements in Cu the lower solution temperature was deliberately chosen. On the other side, higher density of small particles in Cu-Cr-Zr-Mg alloy matrix (Fig. 2d) suggests that these particles were precipitated during air cooling after hot rolling. However, this alloy reached the same level of hardness at peak aged condition as Cu-Cr-Zr alloy irrespective it was not subjected to the solution annealing. In this respect the role of Mg to enhance and preserve capacity for supersaturation of Cu solid solution is still unknown.

Considering these facts, the hardness reached at 425 °C corresponding to peak aged condition is derived from the distribution of nano-sized Cr-rich precipitates in the Cu matrix. Particles visible in samples of both alloys in peak aged conditions (Fig. 2 b, c, e, f) are obviously too large to contribute to the strengthening of Cu matrix.

The highest conductivity obtained at somewhat higher aging temperature (480°C) may be regarded as a result of activation of overaging process.

The decrease in hardness during post-annealing treatment (determination of thermal stability) can be explained by the process recrystallization and increase in the grain size (Fig. 5a, b).

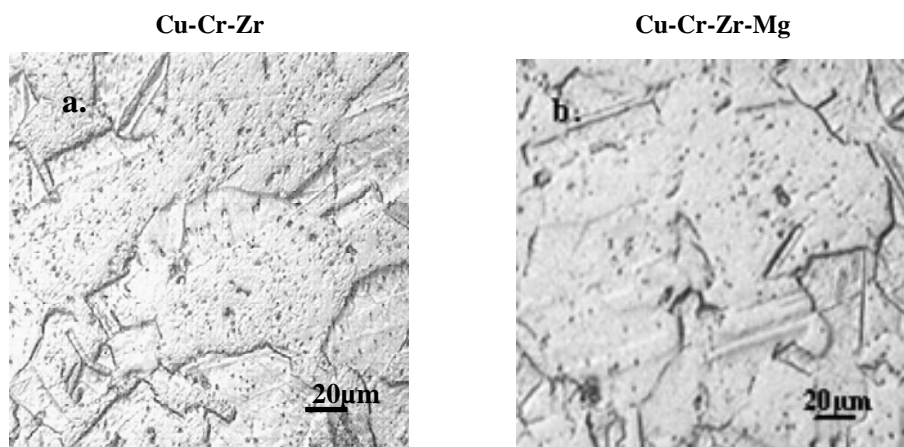


Fig. 5. LM micrographs; (a, b) after post-annealing at 700 °C/4h

According to the standard [11] thermal stability is determined by the highest temperature at which the hardness decreases for 15% in relation to the initial hardness. Data on the temperature of the thermal stability, T_s , determined from Fig. 4a, b are given in Table 2. Almost no difference between Cu-Cr-Zr and Cu-Cr-Zr-Mg alloys exists.

Table 2. Dependence of thermal stability (T_s) on chemical composition of alloy and prior cold deformation

Alloy	T_s , °C	
	50%	80%
Cu-Cr-Zr	520	524
Cu-Cr-Zr-Mg	526	524

This result is rather unexpected considering the fact since that small additions of certain elements such as Ag, Cd, Mg, P and Sn delay the process of recrystallization. These elements are located on dislocations and grain boundaries reducing their mobility [12]. The results of this work showed, however, that the effect of Mg on the temperature of recrystallization was practically negligible. It should be pointed out that with regard to the commercial alloys whose thermal stability is between 380 °C (alloys of Cu-Cr system) and 550 °C (some Cu-Cr-Zr alloys) thermal stability of alloys investigated in this work was quite satisfactory. Comparing the results of both alloys it can be concluded that, although with addition of Mg the increase of recrystallization temperature has not been achieved, Cu-Cr-Zr-Mg alloy might be regarded as very interesting from the stand point of practical application because the TMT avoids high temperature solution annealing and quenching, without reducing the hardness and electrical conductivity.

According to these results Cu-Cr-Zr and Cu-Cr-Zr-Mg alloys might be considered for application at high temperatures when a good combination of mechanical properties and electrical conductivity is the most important prerequisite: as electrodes for electrical resistance spot and seam welding, electric contacts, molds for steel casting etc.

Conclusions

Effect of thermomechanical treatment (TMT), i.e. prior plastic deformation, time and temperature of aging on microstructure, hardness, electrical conductivity and thermal stability of Cu-0.4%Cr-0.08%Zr and Cu-0.4%Cr-0.08%Zr-0.05%Mg (in wt.%) alloys was carried out.

- Both alloys behave in the similar manner under TMT.
- Hardness reaches the maximum at 425 °C, and then decreases with aging temperature. The maximum value of hardness is within the range of 1520 to 1630 MPa after cold rolling for 50 and 80% followed by aging at 425 °C for 2h.
- The maximum of electrical conductivity which is between 89 and 92% IACS appears at 480 °C. This maximum corresponds to the lower hardness values.

- Thermal stability (around 520 °C) of both alloys is quite satisfactory compared to stability of commercial alloys.
- Cu-0.4%Cr-0.08%Zr-0.05%Mg alloy might be regarded as very interesting from the stand point of practical application because the TMT avoids high temperature solution annealing and quenching, without reducing the hardness and electrical conductivity.
- According to their properties Cu-0.4%Cr-0.08%Zr and Cu-0.4%Cr-0.08%Zr-0.05%Mg alloys may possibly find application as electrodes for electrical resistance spot and seam welding, electric contacts, molds for steel casting etc.

Acknowledgement

This investigation was financially supported by the Ministry of Science and Technological Development through the project 142027.

References

- [1] J.W. Davis, G.M. Kalinin, *J. Nucl. Mat.*, 258-263 (1998) 323.
- [2] A. Atrens, J. Nairn, H. Fernee, G. Skennerton, A. Olofinjana, *Materials Forum*, 21 (1997) 57.
- [3] Alloy Phase Diagrams, ASM Handbook, vol. 3, tenth ed., ASM publishers, New York, 1992.
- [4] J.H Su, Q.M. Dong, P.Liu, H.J. Li, B.X. Kang, *Mat. Sci. Eng.*, A 392, 1-2 (2005) 422.
- [5] S. Nagarjuna K.K. Sharma, I. Sudhkar, D.S. Sarma, *ibid.*, A313 (2001) 251.
- [6] S. Nestorovic, D. Markovic, Lj. Ivanic, I. Rangelov, *Metalurgija*, 11 (2005) 309.
- [7] W.X. Qi, J.P. Tu, Y.Z. Yang, *ibid.*, A343 (2003) 89.
- [8] E. Kneller, Y. Khan, U. Gorres, *Z. Metallkunde* 77 (1986) 43.
- [9] F.X. Huang, J.S. Ma, *Scr. Mat.*, 48 (2003), 97.
- [10] Holzwarth and H. Stamm, *J. Nucl. Mat.*, 279 (2000) 31.
- [11] JUS Standard, JUS C.H.3, 074
- [12] J.W. Cahn, *Acta Met.*, 10 (1962) 789.