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Cu-Ag-REAR METALS FOR WIRES: PROCESSING AND CHARACTERISATION

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ABSTRACT

Cu based alloy microalloyed with rear metals (RM) (in our case, sample with Nb) for wires were prepared by two different techniques arc-melting and mechanical alloying. Microstructure characterisation was carried out by SEM including EDX and X-ray measurements. Mechanical measurements at room temperature were performed and the results of materials obtained by different techniques are analised.

Nanocristaline microstructure it was observed and this is associated with fine graine refinament of CuAgRM material after both technologies.

KEYWORDS: Cu based alloy; arc-melting; mechanical alloying; microstructure; microhardness

1. Introduction

Cu based alloy microalloyed with Nb was produced using preparation conditions typically applied for manufacturing of bulk metallic glasses (BMGs) which is prepared by arc melting (AM) with cold drawing [1] and similar composed alloy prepared by powder metallurgical (PM) technique in order to study the microstructure and the mechanical properties

In the first technique called „in-situ” thermodynamical aspects and kinetic limitations on the specific solidification process of phase formation and it is strongly dominated by controlled diffusion mechanism [2]. A distribution of Ag dendrites in the Cu matrix can be achieved by casting. During cold drawing the Ag dendrites are deformed to fine filaments.

The second techinque, PM is a new one which combine powder metallurgy, heat treatments and deformation mechanism. Some advantages of this technique are known: the microstructural features to be developed are independent from the size of sample. In this case, almost any geometry of the sample can be obtaine depending only on the equipment that is used.

In the last period some studies shown remarkable advances have been made in the development and comprehensive understanding of Cu-Nb alloys, used for wires. Such wires can be produced by casting with a logarithmic strain $\eta=15$ and leads to a finally obtained cross section of wire with 0.2 mm depending on their forming ability [3].

To outstanding the mechanism and the mechanical properties of Cu-Ag-RM alloys, one short description about the material obtained by arc melting and similar material obtained by PM, it will be presented in this work.

However, there are no detailed informations about the manufacturing of the materials because there are a substantial difference between sample preparation under clean laboratory conditions using high purity elements and in small quantities for wires preparation.

Consequently, the aim of this paper was to prepare and to investigate a common Cu-Ag-RM composition under optimum conditions concerning the cooling rate for special phase formation and the purity of the elements in different techniques to avoid unpredictable effects and to compare the microstructure and the mechanical properties of this before preparring wires from them [4, 5].

The conditions that we used here are typically used for obtaining wires with very good properties.

2. Experimental procedure

2.1. Arc-melting technique

A 50 g ingot of this alloys with nominal composition Cu−7Ag-0.05RM (at.%), with RM = Nb, and purity > 99.9 wt.% for all elements, were prepared by arc melting in argon atmosphere. The ingots were remelted several times in order to achieve a homogeneous master alloy. From these ingots, cylindrical bulk samples with 2.5 mm diameter and 70mm length were prepared by centrifugal casting device in copper mould casting.

The structure of the samples was studied by X-ray diffraction (XRD) using a Philips PW 1050 diffractometer (CoK-radiation) and optical microscopy. Scanning electron microscop equipped with an X-ray spectrometer were employed for detailed microstructural analysis.

The microstructure was imaged using conventional SEM. The test conditions to figur out the mechanical properties should be the same like those typically used for cristaline material [6]. Measurements of mechanical properties were performed at room-temperature and quasistatic conditions. According to the ASTM standard for micro hardness testing, cylinders with a length/diameter ratio of 2.5mm diameter were prepared from the cast samples. The specimens were tested with an SHIMADZU maschine. The conditions of microhardnes measurements according to Vickers HV 0.01 were: compressive force 10 N, time of load 10 s. Data obtained from microhardness testing machine were evaluated by software LECO.

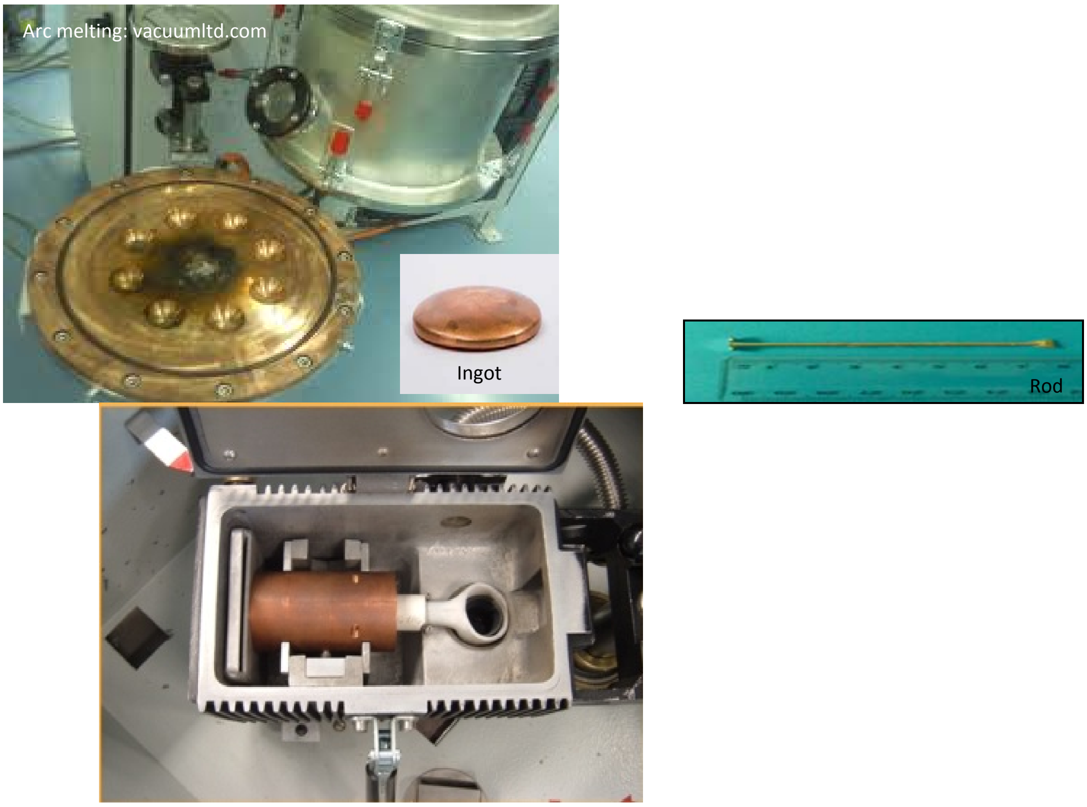


Fig.2. *Arc melting for preparring ingot and centrifugal casting for preparring rod of Cu7Ag 0.05Nb.*

2.2. PM technique

Milling experiments starting from pure elemental powder mixtures (purity >99.9 wt. %) with nominal compositions Cu−7Ag-0.05RM (at.%), with RM = Nb and Cu, Ag were performed using a Retsch PM400 planetary ball mill and hardened steel balls and vials. No process control agent was used.

The powders were milled for 30 h with a ball-to-powder mass ratio (BPR) of 13:1 and a milling intensity of 200 rpm cooling by liquid N_2 at liquid nitogen temperature (77K) [7]. To avoid or minimize possible atmosphere contamination during milling, vial charging and any subsequent sample handling was carried out in a glove box under purified argon atmosphere (less than 1 ppm O_2 and H_2O). The phases and the microstructure were characterized by X-ray diffraction (XRD) using a Philips PW 1050 diffractometer (CoK-radiation). The alloying was performed until complet solid solution of Ag and Nb within the Cu matrix has been achieved.

The microstructure of the alloys was investigated by electron microscopy using a high-resolution scanning electron microscope (REM LEO 1530) with energy dispersive X-ray analisis (EDX) after diferent time of milling. From the SEM micrographs the size of the alloying particles as well as the aspect ratio of the Nb filaments after deformation were determined. The latice structure and the lattice constants (at room temperature) as well as the phase purity of the sample were investigated with an X-ray difractometer (Philips, PW 1830) in Bragg Bretano geometry using Co radiation. Based on the X-ray data the average grain size of Cu matrix was determined using Sherrer eqution and Williamson-Hall plot. Microhardnes by Vickers was performed by SHIMADZU maschine at room-temperature and quasistatic conditions.

Fig. 3. *Retsch maschine and steel vials for preparring mixted powder of Cu7Ag 0.05Nb for compressed rods.*

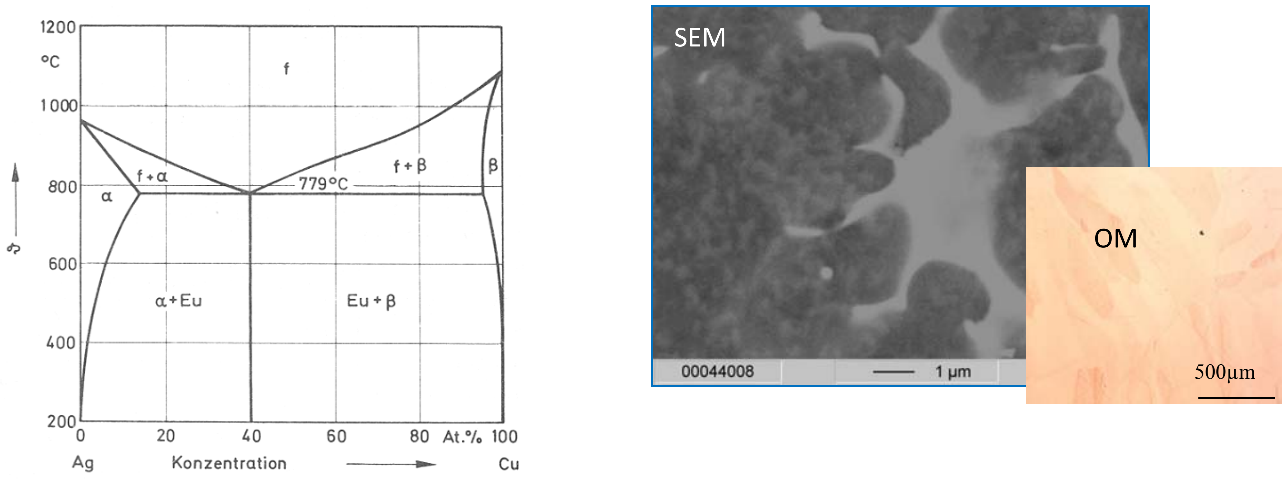
3. Results and discussions

By arc-melting, CuAg forms a simple eutectic phase diagram with limited solubility. At binary Cu-7Ag alloy are detected two phases, namely a saturated Cu(Ag) solid solution and regions which show a reduced amount of Cu in comparison to the matrix. This situation changes for the Cu-7Ag-0.05Nb alloy.

The addition of Nb leads to a slower decomposition reaction which in this case is found to be only continuous.

The grain boundary it was modify by the addition of a insoluble element like Nb.

This suppresses the diffusion along the grain boundary and hence enhances the formation of continuous precipitates [8]. Because of the specific solidification conditions in the arc-melter (relatively high cooling rate) and the particular composition with high carbon content a phase formation it can be obtained. The reasons for the astonishing ductility of the arc-melted Cu-Ag alloy are likely manifold, which together give the capability for plastic deformation.



a) b) c)

Fig.3. *Phase diagram (a) of CuAg and precipitation modes as well as structure (c) and microstructures (b) of Cu7Ag 0.05Nb by arc melting with discontinous precipitates (80-100HV).*

Composition profiles measured by EDX (Fig. 3-b) show that the chemical composition frequently changes within a short distance (about once per 1µm), indicate the formation of different very finely dispersed phases, which give the material its high strength and large ductility. Copper based materials leads to distinctively values of microhardnes in surface.

At the second technique it was observed an intense mechanical alloying among all three phases (Cu, Ag, Nb) because of the high energy of ball milling. During milling time Nb shows a negligibly solubility in the solid state and it was observed niobium partly dissolves in the copper lattice during milling (fig. 4) [6].

The present investigation demonstrates that this solubility can be improuved to a strongly supersaturated Cu solid solution provided the appropriate mechanical alloying method is applied, by cryomilling. Scanning electron microscopy reveal a homogeneous single-phase microstructure after more then 10 hours of milling.

Elemental Nb could no more be detected, indicating the formation of a metastable supersaturated Cu-Nb solid solution.

Cryomilling time influences the the graine size of elements and their miscibility. After cryomilling the structure of powder mixed is uniform. Microhardness increase with number of hours milling. (Fig. 5).

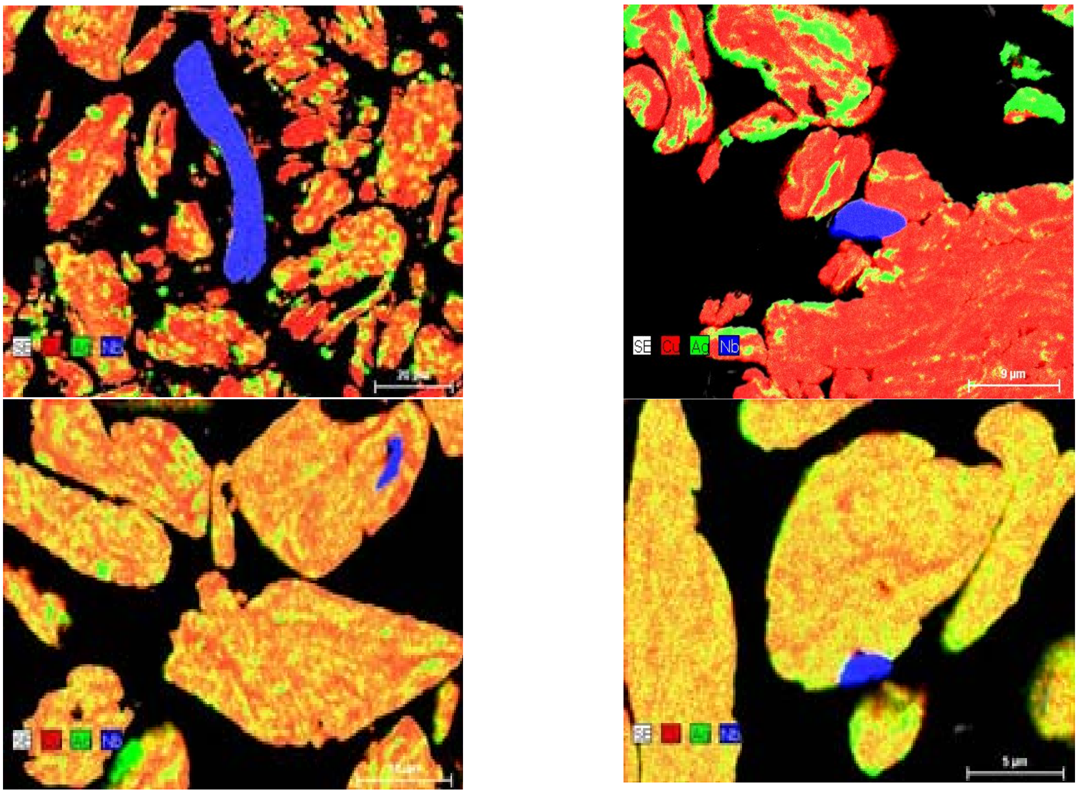


Fig. 4. *SEM study of microstructure of Cu-7%Ag-0.05%Nb powder with mechanical alloying after 1h (a), 3h (b), 5h(c) and 10h(d) milling time.*

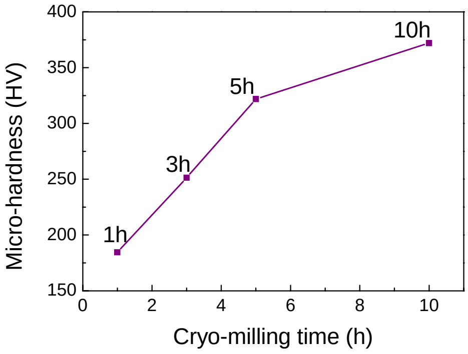


Fig. 5. *Room-temperature microhardness curves for CuAgNb mecahnical alloying samples. The inset shows how increas cryomilling time with microhardness curves of the alloy.*

4. Conclusions

Conventional cast metallurgy cannot be applied on a large scale. Manufacturing of alloys from immiscible metal system can be carried out by using the following two techniques: rapid solidification (RS) and mechanical alloying (MA). By RS a fine distribution of two phases can be produced, but the formation of solid solution with a high content of the alloyed element is not possible. In contrast, by mechanical alloying, alloys with better homogeneity and a higher content of the alloyed element in solid solution can be manufactured. Due the high energy impact during milling, the region of solid state solution extends and alloys with very high homogeneity in the microstructure can be achieved by the use of under the appropriate conditions. In conclusion, applying preparation conditions typically used for the fabrication of bulk metallic glasses to the manufacturing of the Cu based alloy, superior mechanical properties have been achieved, due to the formation of a cristaline structure, with a ductile phase and finestructured Nb filamentary phase.

Also the work hardening behaviour of the crystalline alloy made by PM is excellent. Therefore, the most important benefit of this material is its distinct of uniform distribution of fine Nb particles in Cu-Ag matrix with very good plasticity, which is, as is known, a strong requisite for engineering applications.

Comparing the microhardness properties of crystalline metallic alloys obtained after two different techiniques, arc-melting and PM, also the latter ones offer very interesting perspectives for novel applications as functional and structural materials for a variety of engineering applications when processed under appropriate conditions. This opens new opportunities for the “processing for properties” of advanced materials with superior properties.

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References

[1]. V.I. Pantsyrnyi, A.K. Shikov, A.D. Nikulin, A.E. Vorobova, E.A. Dergunova, A.G. Silaev, N.A. Bel’akov, I.I. Potapenko, IEEE Trans. Magn. 32 (4) (1996) 2866

[2]. A. Inoue, T. Zhang, A. Takeuchi: Appl. Phys. Lett. 71 (1997) 464

[3]. E. Botcharova, J. Freudenberger, A. Gaganov, Materials Science and Engineering A 416 (2006) 261–268

[4]. X.H. Lin, W.L. Johnson, W.K. Rhim: Mater. Trans. JIM 38 (1997) 5

[5]. A. Gebert, J. Eckert, L. Schultz: Acta Mater. 46 (1998) 5

[6]. K. Werniewicz, U.Kuhn, N. Mattern, B. Bartusch, J. Eckert, J. Das, L. Schultz, T. Kulik: Acta. Mater. 55 3513 (2007)

[7]. S. Ichikawa, K. Miyazawa, H. Ichinose, K. Ito, Nanostruct. Mater. 11(1999) 1301

[8]. E.Bocharova, Ph.D. Thesis, TU Dresden, Germany, www.ifw-dresden.de/imw/theses/Dr Bocharova.pdf.