JOURNAL OF MATERIALS SCIENCE 39 (2004) 5343–5345

Formation of the microstructure in Cu-Nb alloys

J. FREUDENBERGER*, E. BOTCHAROVA, L. SCHULTZ
IFW Dresden, Institute for Metallic Materials, Helmholtzstr. 20, D-01069 Dresden, Germany
E-mail: j.freudenberger@ifw-dresden.de

In order to increase the mechanical strength of copper while retaining its high electrical conductivity the copper matrix is strengthened by Nb particles. For thermodynamical reasons the mutual solubility of Nb in copper is negligible. Therefore, a Cu-Nb alloy is prepared by mechanically alloying and subsequent hot pressing. The formation of a solid solution in a first step and of precipitates in a Cu-10 at.%Nb alloy in the second one as well as the effect of these precipitates on the mentioned properties is discussed. The influence of different temperatures during hot pressing on density, mechanical and electrical properties, etc. is investigated.

1. Introduction

In the last decade the need for conductors with high mechanical strength became more and more evident. Especially for the application in pulsed high field magnets the conductor has to meet supreme specifications as the beneficial combination of high mechanical strength, high electrical conductivity and sufficient ductility [1]. For the future, a new class of conductors shall be ready for application, namely mechanically alloyed Cu-Nb alloys [2]. Up to now the Cu-based conductors are strenghened by an addition of a second phase of up to 50 vol%. Utilising mechanically alloyed samples this fraction of second phase can be reduced to about 10% while obtaining a high strength level compared to a Cu/stainless steel macrocomposite that needs 50 vol% of steel for reinforcement [3]. Even compared to the rod-in-tube-technology which is applied at present [4] the mechanical alloying will reduce the fraction of Nb without a significant loss of strength. Due to the larger Cu fraction within the mechanically alloyed samples the conductivity is forseen to be comparable larger than in the other alloys. In previous studies it has been demonstrated, that Nb can be dissolved within the Cu matrix by mechanical alloying [2], although the phase diagram shows a negligible solubility of Nb in copper. The formation of a solid solution of Nb in Cu is explained by the dislocation pumping model of Schwarz [5]. The Nb atoms can further on be dissolved from the Cu matrix by heat treatments leading to fine and homogenous distributed Nb particles [6]. This study describes the formation of the microstructure of mechanically alloyed Cu-Nb alloys during hot pressing as well as the properties of compacted samples.

2. Experimental details

Mechanical alloying of Cu-Nb alloys was performed in a PM 4000 Retsch planetary ball mill under argon atmosphere, using a rotational speed of 200 rpm at a constant rotation direction and a powder-to-ball weight ratio of 1:14. The milling was performed at almost 77 K [2]. After 60 h of milling the alloying is found to be completed. The mechanically alloyed powder was compacted by uniaxial hot pressing at different temperatures. After compacting, the samples show a density of 95% of the theoretical density of the alloy. These samples were investigated by means of compression tests to obtain the mechanical as well as by the standard four probe technique to obtain the electrical properties. The compression tests were carried out on cylindrical samples with a height of 5 mm and a diameter of 3 mm utilising an electromechanical Instron 8562 universal testing machine with a cross head speed of 1×10^{-3} mm/s. Furthermore, the microstructure of mechanically alloyed powders and compacted samples was investigated by means of a LEO 1530 scanning electron microscope and by X-ray diffraction analysis using Co K_α radiation. The powders were analysed by chemical analysis in order to obtain their purity.

3. Results and discussion

After milling Cu and Nb powders of an atomic ratio of Cu-10 at%Nb for 60 h a solid solution is achieved. The microstructure of the powders show no sight of Nb particles. According to X-ray powder diffraction, the intensities of the Nb reflections are below the detection limit. The lattice parameter of the Cu matrix is determined from measured diffraction data using the Rietveld method [7]. An increase of the lattice parameter during milling is observed. This increase together with a lack of significant impurities—except Fe, which is caused by abrasion from the vial and balls—gives reason for the formation of a solid solution. At the same time as the lattice parameter increases the reflections of the Cu matrix broaden. Using the Williamson-Hall plot [8], the effects of grain size and internal strain on the line width of the reflections can be separated. After

* Author to whom all correspondence should be addressed.

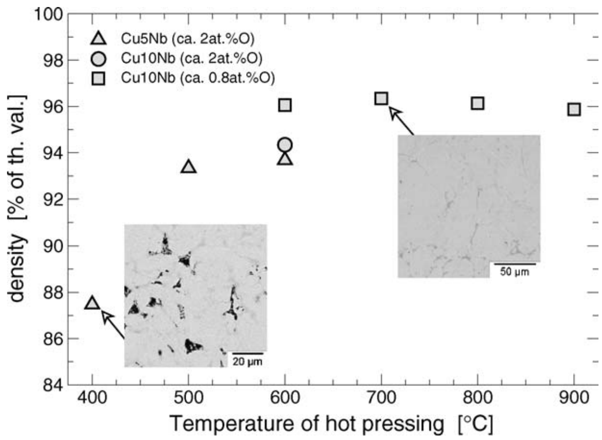

Figure 1 Density of compacted alloys in dependence on the temperature applied during hot pressing. In the insets SEM micrographs show the microstructure of an alloy compacted at 400°C (left) as well as of one pressed at 700°C (right). Pores are present in samples pressed at lower temperatures.

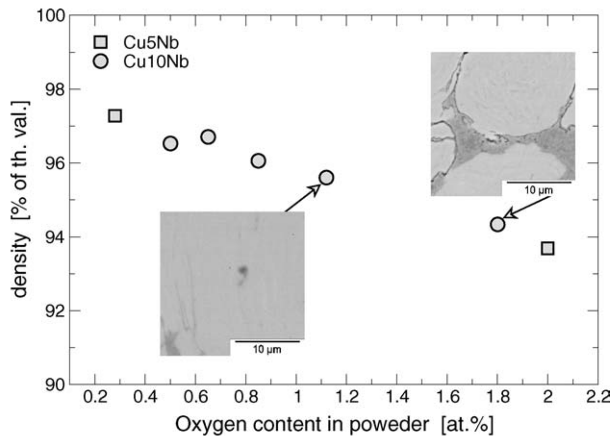

Figure 2 Density of compacted alloys in dependence on the oxygen content within the powder before pressing. The decrease of the density with increasing O content is independent on the Nb content of the alloy.

60 h of milling the grain size of the matrix is about 6 nm and the internal strain about 0.95%.

After milling, the powder was hot pressed at a load of 650 MPa for 20 min at different temperatures. Longer times lead to a coarsening of the Nb precipitates and shorter ones are not sufficient to consolidate the powder sufficiently. The density of samples compacted at 400°C is about 87% of the theoretical density of the alloy, whereas an increase of the temperature to 700°C leads to a density of about 96%. The corresponding SEM micrographs are shown in Fig. 1. For the sample compacted at 400°C many pores can be detected, whereas for samples compacted at 700°C no pores can be detected, which is correlated to the higher density. A hot pressing above 700°C does not lead to an improvement of the density, which remains almost constant at 96%.

The oxygen content in the powder strongly influences the density achieved after hot pressing. Samples with 0.8 at.%O or 2 at.%O were compacted under the same conditions at 600°C. A higher O content in the powder leads to a significantly lower density of the alloy, which can be seen in Fig. 1. It is interesting to note, that the achieved density is nearly independent on the Nb content within the alloy. Fig. 2 shows the density of compacted samples in dependence on the oxygen content in the powder. A linear decrease of the density of the compacted alloys is found for an increasing O content of the powder. Cu-5 at.%Nb and Cu-10 at.%Nb alloys fit to the same line. SEM micrographs (Fig. 2) show the microstructure of alloys with 1.0 at.%O and 1.8 at.%O, respectively. In the sample with 1.8 at.%O an impurity phase, probably copper oxide, is present at the interfaces. This oxide phase (i) prevents the bonding of powder particles during pressing and (ii) does not deform, as it is brittle. Thus the O content in the powder has to be considered while producing bulk samples with high density as a high amount leads to a lower density.

While optimising the parameters of the hot pressing, the density and, besides that, the microstructure can be adjusted. The density should be as high as possible and the microstructure should enable good electrical and mechanical properties. The compaction process is driven by shear bonding as well as diffusion bonding [9]. Shear bonding is induced by a stress state, that drives the dislocations outside the particles. Atomic clean surfaces are created which allow diffusion of matrix atoms through this surface. The remaining porosity is the consequence of a low diffusion rate.

The Nb, which is dissolved within the Cu matrix, precipitates from it again during hot pressing. The size of the Nb precipitates in a sample that was compacted at 600°C for 20 min amounts to 50 nm (see Fig. 3). Fig. 3 shows the phase formation during hot compaction on the basis of X-ray powder diffraction patterns. At the same time as Nb particles are formed, several phase impurities appear, such as Cu and Nb oxides and Fe-Nb intermetallic phases. With increasing temperature during hot pressing the Nb precipitates coarsen and their size amounts to 70 nm (700°C) or 80 nm (800°C), respectively. After annealing the samples at 900°C for 1 h and subsequently pressing them at 600°C for 20 min the precipitates are about 250 nm in size. This procedure

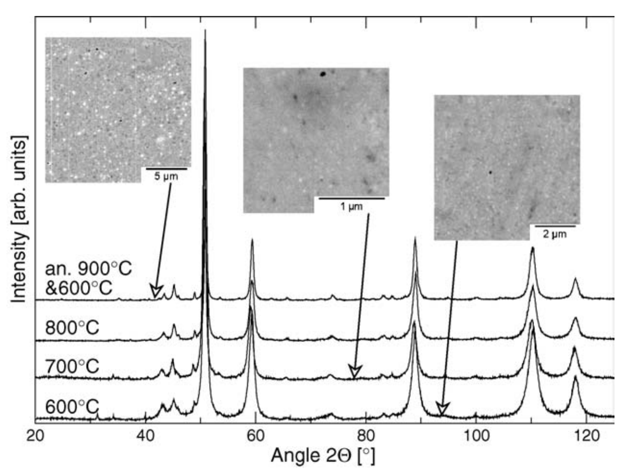

Figure 3 X-ray powder diffraction patterns of samples that were compacted with a load of 650 MPa at 600, 700 and 800°C for 20 min as well as one alloy annealed at 900°C for 1 h and hot pressed at 600°C. In the insets SEM micrographs show representatively the microstructure of three of the alloys. From the SEM micrographs precipitation and coarsening of the Nb precipitates in dependence on the temperature can be seen.

was applied since the hot pressing equipment is limited to about 800°C. The copper grain size also grows during hot pressing. The size is about 13, 17 and 19 nm for samples pressed at 600, 700 and 800°C, respectively, and about 27 nm, when annealed at 900°C and pressed at 600°C. The internal strain in the Cu matrix decreases to about 0.3% after compaction, which is nearly independent on the pressing temperature.

The temperature applied during hot pressing strongly influences the microstructure of the compacted alloy [6]. It gives the dislocations a higher movability, which means that more dislocations end at the surface and thus generate a larger atomic clean surface. Furthermore a higher temperature rises the diffusion rate of Cu atoms, which on the one hand enlarges the area supporting the clean surface and, on the other hand, welds pores by diffusion bonding. Since the temperature needed for the activation of dislocation movement is lower than that needed for diffusion activation, the process to compact powder at 400°C is based on shear bonding. For higher temperatures the diffusion of copper is active, too. If both processes are active a maximum density of the sample can be obtained. This is the case for temperatures above 600°C. The density of the alloys will not increase for higher temperatures and 600°C will be the minimum temperature required during hot pressing. On the other hand Nb precipitates from the solid solution and coarsens at higher temperatures and the grain size of the Cu matrix also grows.

The mechanical and electrical properties of compacted Cu-10 at%Nb alloys are shown in Fig. 4. The ultimate compression stress (UCS) of the sample compacted at 600°C is about 1625 MPa. With increasing temperature during hot pressing the UCS decreases and for the sample annealed at 900°C and compacted at 600°C a UCS-value of about 1265 MPa is reached. The electrical conductivity of the alloys changes considerably from 13% IACS (International Annealing Copper Standard, i.e., the conductivity of pure copper) for the sample compacted at 600°C to 33% IACS for the sample annealed at 900°C for 1 h and compacted at 600°C. The mechanical strength on the other side falls off with increasing temperature. The Nb precipitates from the solid solution during hot pressing, even at 600°C. The size of the Nb precipitates is larger than that of the Cu-grains and, therefore, the hardening mechanism present in these alloys is based on grain- or phase-boundaries according to the Hall-Petch relation. On the other hand, the high number of grain-boundaries, which is enhanced for a small grain size, cause a high electrical resistivity, as electrons scatter at these boundaries [10]. The growth of the Cu-grain size by increasing the temperature during pressing leads to an enhancement of the electrical conductivity and, at the same time, to a loss in strength.

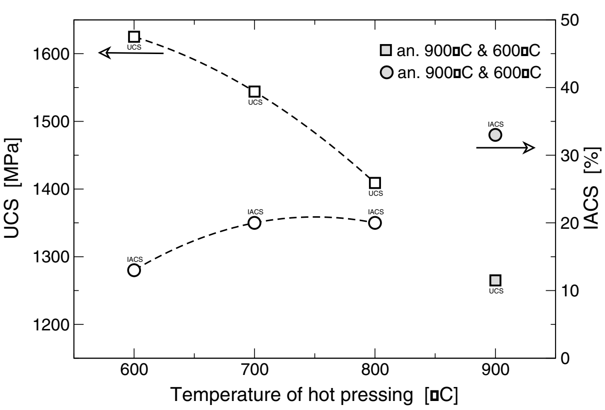

Figure 4 Ultimate compressive strength (boxes) and conductivity (IACS, circles) in dependence on the temperature applied during hot pressing. With incresing temperature the strength decreases and at the same time the conductivity increases.

4. Summary

Cu-Nb alloys are prepared by mechanical alloying and subsequent hot pressing. Up to 10 at.% Nb can be solved within a Cu matrix by milling and form a solid solution. At a later step it can be dissolved again by annealing (hot pressing) and Nb precipitates are formed. During hot pressing above 600°C the processes of shear and diffusion bonding are present, which are both required to obtain samples with a density of about 96% of the theoretical density of these alloys. During hot pressing at high temperatures oxides are formed at the surface of the powder that hinders the compaction. In consequence the samples end up with a lower density. At the same time Nb precipitates coarsen and thus lower the strength of the alloy. An ultimate compressive strength of 1625 MPa is obtained for a sample compacted by a load of 650 MPa at 600°C for 20 min. The conductivity of this alloy is about 13% IACS. With increasing temperature during hot pressing the conductivity can be enhanced to 33% IACS, but with a significant loss in strength (1265 MPa). This is mainly related to the grain growth of the copper matrix and, with a minor effect, to the coarsening of the Nb precipitates.

This work was supported by the german Bundesministerium für Bildung und Forschung by grant no 03SC5DRE. Furthermore we would like to thank V. Hoffmann and H. Klauß for experimental support.

References

1. J. FREUDENBERGER, W. GRÜNBERGER, E. BOTCHAROVA, A. GAGANOV and L. SCHULTZ, *Adv. Engng. Mater.* **4** (2002) 677.
2. E. BOTCHAROVA, M. HEILMAIER, J. FREUDENBERGER, G. DREW, D. KUDASHOW, U. MARTIN and L. SCHULTZ, *J. Alloys Comp.* **351** (2003) 119.
3. W. GRÜNBERGER, M. HEILMAIER and L. SCHULTZ, *Mater. Lett.* **303** (2001) 127.
4. L. THILLY, M. VERON, O. LUDWIG and F. LECOUTURIER, *Mater. Sci. Eng.* A **309–310** (2001) 510.
5. R. B. SCHWARZ, *Mater. Sci. Forum* **269–272** (1998) 665.
6. E. BOTCHAROVA, J. FREUDENBERGER and L. SCHULTZ, *J. Alloys Comp.* (in press).
7. H. M. RIETVELD, *J. Appl. Cryst.* **2** (1969) 65.
8. G. K. WILLIAMSON and W. H. HALL, *Acta Metall.* **1** (1953) 22.
9. P. R. SONI, "Mechanical Alloying: Fundamentals and Applications" (Cambridge, Cambridge Internat. Science, 2000).
10. A. SEEGER and G. SCHOTTKY, *Acta Metallurgica* **7** (1959) 495.

Received 11 September 2003
and accepted 27 February 2004