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Mechanical alloying of copper with niobium and molybdenum

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Copper has been mechanically alloyed with the bcc structure type elements Nb and Mo in order to obtain a material with high strength, good ductility and good electrical conductivity. In the case of alloying Cu with Nb a solid solution is formed during milling, whereas in the case of alloying Cu and Mo a fine distribution of Mo particles within the copper matrix is observed. The different behaviour of these two alloys is related to the large difference of the elastic constants of the bcc elements. Niobium precipitates from the solid solution and molybdenum particles coarsen during a subsequent heat treatment.

1. Introduction

The effect of insoluble phases such as oxides, carbides or bcc elements on the strength of copper-based conductor materials has been studied extensively during the last years [1–4]. In these materials the second phase is insoluble within the copper-matrix. Therefore the conductivity remains at a high level. A common problem is that these materials cannot be obtained utilising conventional cast metallurgy, but e.g., by powder metallurgy. In previous studies the mechanical alloying of Cu-Nb powder was investigated [5, 6]. During milling of Cu-Nb alloys up to 10 at.% Nb can be solved within the copper matrix, although the equilibrium phase diagram shows only a negligible solubility of Nb in Cu [5]. A heat treatment subsequent to mechanical alloying leads to the precipitation of Nb. A homogenous distribution of Nb particles, whose size depends on temperature and time of the heat treatment, is achieved [6]. In this study the properties of mechanically alloyed and subsequently heat treated Cu-Nb as well as Cu-Mo alloys are compared. The particle distribution in Cu-Mo alloys is achieved directly by mechanical alloying whereas in Cu-Nb alloys a heat treatment of a solid solution that is formed during mechanical alloying is the origin of the formation of the particles and their distribution.

2. Experimental details

The mechanical alloying of Cu-10 at.% Nb and Cu-10 at.% Mo alloys was performed in a PM 4000 Retsch planetary ball mill under argon, using a rotational speed of 200 rpm at a constant rotation direction and a powder-to-ball weight ratio of 1:14. The milling takes place almost at liquid nitrogen temperature [5]. Subsequent to mechanical alloying the powder were heat treated at constant temperatures for 1 h under argon or were consolidated by uni-axial hot pressing with 650 MPa for 20 min at 700°C. The microstructure was investigated by scanning electron microscopy (SEM) and X-ray diffractometry using Co K_α radiation. The microhardness of the powder was measured on embedded powder using a Vickers microhardness tester with a load of 245 mN and a loading time of 10 s. The mechanical properties were determined by compression test of the compacted samples.

3. Results and discussion

3.1. Mechanical alloying

After 5 h of milling the microstructure of Cu-Nb forms a coarse lamella structure which is shown in Fig. 1a, whereas in the case of Cu-Mo (see Fig. 1b) the Mo particles are homogeneously distributed. The origin of this different evolution of the microstructure is the large difference of elastic constants of Nb and Mo ($E_{\mathrm{Nb}} = 120$ GPa; $E_{\mathrm{Mo}} = 330$ GPa). The elastic constants are proportional to the Peierls stress, which is required to be applied to move any dislocation. This stress amounts to 0.8 MPa for Nb but to the much higher value of 23 MPa in the case of Mo. In consequence the dislocation movement is easier in Nb than in Mo. Thus Nb can be deformed to lamellae during milling whereas Mo breaks due to the applied stress.

X-ray powder diffraction patterns of Cu-Nb alloys show a vanishing of the Nb reflections with increasing milling time and at the same time a broadening of the Cu reflections, which is shown in Fig. 1a. This broadening is caused by the small grain size and the internal stress in copper. These effects can be separated by the Williamson-Hall plot [7], the results are shown in Fig. 2. The reduction of the intensity of the Nb reflections and the swelling of the copper lattice parameter (Fig. 2), which was calculated using the Rietveld method [8], are related to the solution of Nb within the Cu matrix.

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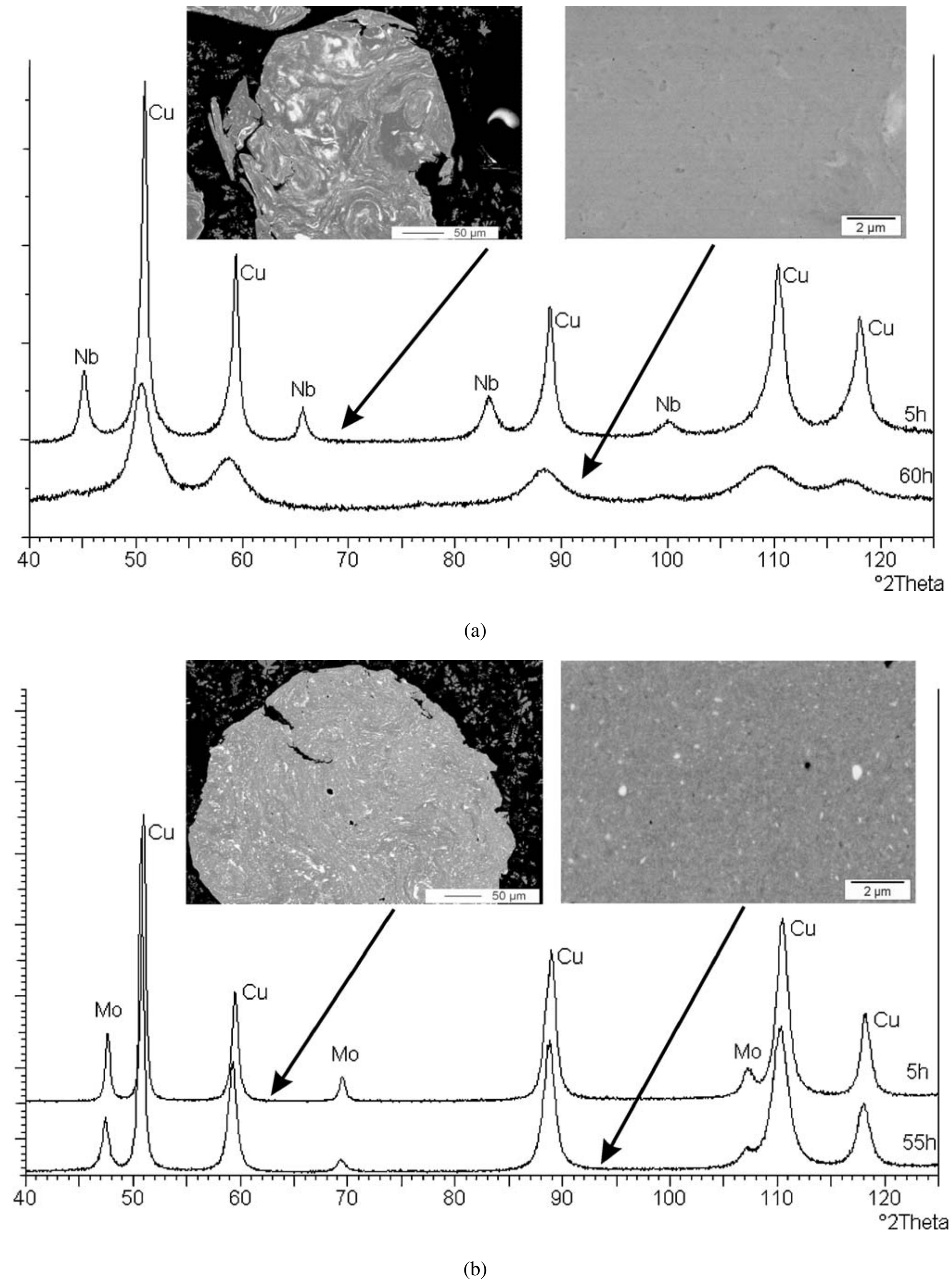

(a)

(b)

Figure 1 X-ray diffraction patterns of (a) Cu-Nb alloys and (b) Cu-Mo alloys after 5 and 60 h of milling each as well as the corresponding SEM micrographs showing the microstructure of the individual alloy.

In the case of the Cu-Mo alloy the intensity of the Mo reflections decrease less compared to the Cu-Nb alloy and the broadening of the Cu reflections is not as intensive. The grain size, which is calculated from the broadening of the reflections, the internal strain within the Cu matrix, the matrix lattice parameter and the microhardness are shown in Fig. 2. The matrix lattice parameter of the Cu-Mo alloy stays nearly constant with increasing milling time. Thus, molybdenum does not dissolve in the copper. The microstructure of the Cu-Mo alloy after 55 h of milling shows two size fractions of Mo particles within the Cu matrix: less than 20 nm (∼80 vol% of Mo) and bigger than 150 nm (∼20 vol% of Mo) (see Fig. 1b). For the Cu-Nb alloy, milling for 55 h leads to a solid solution as investigated in previous studies [5, 6]. A very fine grain size as well as a high dislocation density enables the formation of a solid solution of Nb in Cu [5, 9, 10]. The Nb particles are deformed to very thin lamellae and, therefore, many Nb atoms are located at the grain boundary next to the Cu grains. As these atoms are more mobile than their counterparts within the grain, they can diffuse easily along dislocation lines, which start or end at the grain boundary, to the grain interior. Thus, the area at the grain boundary is locally supersaturated with Nb atoms. In contrast to these findings Mo atoms do not show any tendency of diffusion along dislocation lines and, in consequence, Cu-Mo alloys show no sign of a formation of a solid solution, even after long milling times. The Mo particles do not form lamellae and therefore have smaller surface areas than Nb in a Cu-Nb alloy with the same Cu fraction and the same milling conditions would have. Most Mo atoms are within the grain volume and are not as movable as atoms at the grain boundary.

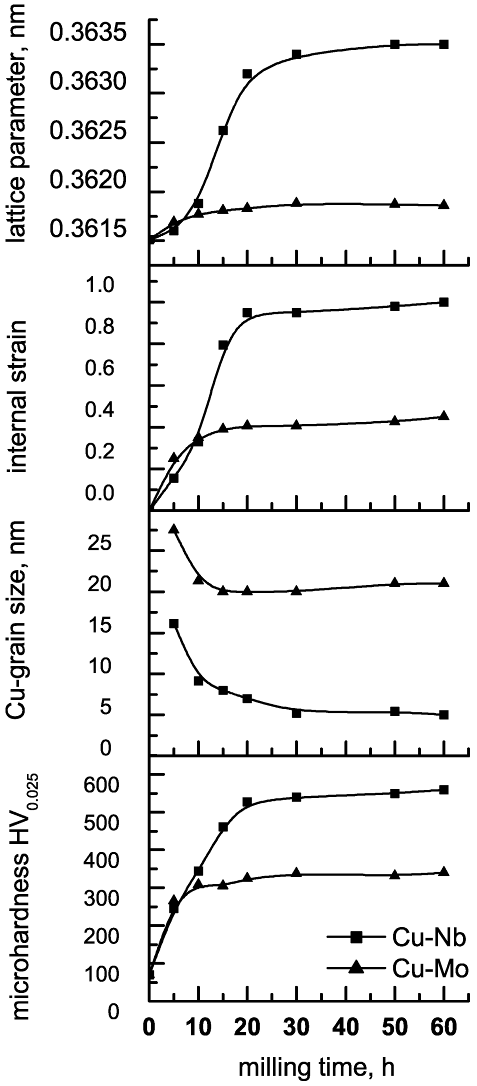

Figure 2 Matrix lattice parameter, internal strain, Cu grain size as well as microhardness of Cu-Nb and Cu-Mo alloys as a function of milling time.

As can be seen from Fig. 2 the matrix grain size of Cu-Nb alloys is smaller than in Cu-Mo alloys. A formation of a nanocrystalline microstructure is based on the formation of dislocation cells. These transform into subboundaries and further on into grain boundaries [11]. This process is repeated and thus refines the cells until a very fine nanostructure is built up. The higher the dislocation density in this material is, the more dislocation cells are formed and, in consequence, the finer they are. The interface of elongated Nb lamellae is a more effective barrier against the dislocation movement than the interfaces of the round Mo particles just as a consequence of the surface area. This results in a higher dislocation density in the Cu-Nb powder and finally in a smaller copper grain in the Cu-Nb alloys. Additional the internal strain in Cu-Nb alloys is higher than that in Cu-Mo (see Fig. 2), which is directly proportional to the dislocation density.

The microhardness of Cu-Nb powder particles is higher than that of Cu-Mo powder particles. After milling for 60 h the microhardness of particles of the Cu-Nb alloy is about 570 $HV_{0.025}$, whereas Cu-Mo only shows a value of 340 $HV_{0.025}$. The large difference of the microhardness of both alloys has several reasons. (i) The matrix grain size in the Cu-Nb alloy is smaller, (ii) the internal strain in this alloy is higher and (iii) within the Cu-Nb alloy the effect of solid solution hardening is present. (iv) The Mo particles do not essentially contribute to the hardness of the Cu-Mo alloy due to the small grain size of the copper matrix as this size is about the same size or even less than that of the Mo particles. Thus the hardening due to the Orowan mechanism cannot be taken into account for the Cu-Mo alloy.

3.2. Heat treatment

After milling, the powders of both alloy types were heat-treated. The microstructures change during this heat treatment. In the case of the Cu-Nb alloy the niobium precipitates from the solid solution at temperatures above 600°C. Consequently, the matrix lattice parameter decreases to the value of pure copper (Fig. 3). Above 600°C the Nb particles start coarsening. In the case of Cu-Mo alloys a coarsening is observed for those temperatures, too, but the coarsening itself is much slower than in the case of Cu-Nb (see Fig. 4). A growth of the Cu grains is observed, too. The starting temperature depends on the type of the alloy. In the case of Cu-Nb the growth is observed to start at 500 to 600°C,

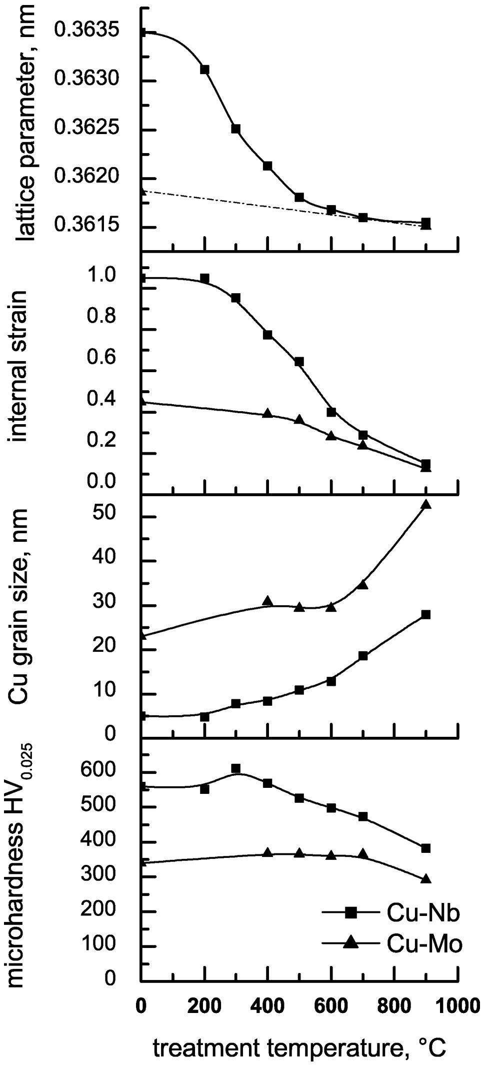

Figure 3 Matrix lattice parameter, internal strain, Cu grain size as well as microhardness of Cu-Nb and Cu-Mo alloys as a function of the heat treatment temperature.

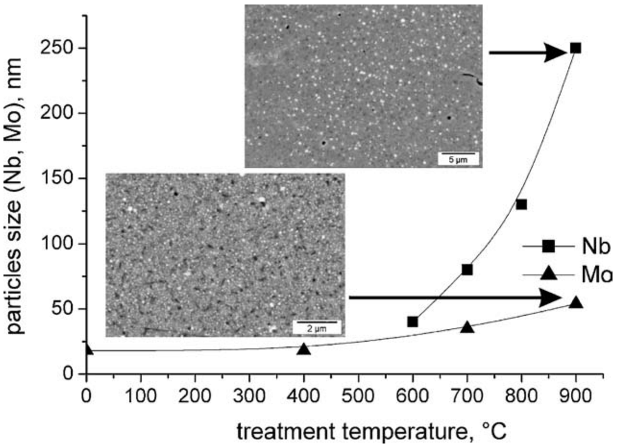

Figure 4 Particle size of Nb and Mo in Cu-Nb and Cu-Mo alloys in dependence on the heat treatment temperature. The SEM micrographs were taken on samples that were heat treated at 900°C.

whereas the temperature has to be higher than 800°C for Cu-Mo alloys to initiate grain growth. This is related to the very fine Mo particle distribution, which suppresses the grain growth. The internal strain decreases in Cu-Nb alloys faster than in Cu-Mo, due to a higher dislocation density in the Cu-Nb alloy after milling (Fig. 3).

The microhardness of Cu-Nb power shows a small peak at a heat treatment temperature of 300°C and a decrease further on with increasing temperature. After treating the alloy at 900°C, a hardness of about 400 HV is reached (Fig. 3). This behaviour is caused by the precipitation of Nb from the solid solution, the decrease of the internal strain and the growth of the copper grains. In the case of Cu-Mo the microhardness remains nearly constant with the annealing temperature as the microstructure does not change significantly and the internal strain remains almost constant. For temperatures above 800°C the Cu grains start to grow and, therefore, a decrease of the hardness to about 300 HV is observed. The Nb or the Mo particles do not contribute significantly to the hardening of the alloys as their size is larger than that of the Cu grains and thus the Orowan mechanism has no relevance.

3.3. Compacted samples

After milling, the powder was compacted by uniaxial hot pressing at 700°C. About 96% of the theoretical density of the alloy is reached. The microstructures of the Cu-Nb and Cu-Mo alloy show a homogeneous distribution of particles within the nanocrystalline matrix. Hereby, the Nb is already precipitated from the solid solution due to the temperature of 700°C applied during the compaction. Compression tests show an ultimate compression stress (UCS) of about 1544 MPa for Cu-Nb alloys and about 1142 MPa for Cu-Mo. The higher ultimate stress of the Cu-Nb alloy can only be related to the difference in the grain size of the copper matrix, as the internal strain and matrix lattice parameter are roughly the same and the size of the Nb particles is even larger than the Mo particle size.

4. Summary

Cu-Nb and Cu-Mo alloys were prepared by mechanical alloying. The microstructure and the properties of the alloys were adjusted by a subsequent heat treatment or by hot compression. In the case of Cu-Nb, mechanical alloying leads to a solid solution of Nb within the Cu matrix, whereas in the case of Cu-Mo a distribution of fine Mo particles, about 20–30 nm, in size is achieved. The different deformation behaviour of Mo and Nb is related to their different elastic constants. Additionally, a smaller copper grain size, a higher internal strain and the presence of solid solution hardening can be observed for the Cu-Nb alloy. In consequence of the different microstructures, a nearly two times larger hardness is found for the Cu-Nb alloy after milling, namely about 570 $HV_{0.025}$ (Cu-Mo: about 340 $HV_{0.025}$). During heat treatments the microstructure changes more significantly in Cu-Nb alloys than in Cu-Mo. Compression tests of compacted samples also show that the Cu-Nb alloy has a higher ultimate compression strength of 1544 MPa than Cu-Mo (UCS = 1142 MPa). As the Mo particles were found to be smaller than the Nb particles the hardening in these alloys is induced by the small copper grain size and not by the strengthening mechanism of fine particles (Orowan mechanism).

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