Supersaturated solid solution of niobium in copper by mechanical alloying

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Abstract

Alloys with both high strength and high conductivity have been produced by mechanical alloying. In the present study, copper was mechanically alloyed with 5, 10 and 20 at.% Nb using a planetary ball mill. The Cu–Nb phase diagram shows a negligibly low mutual solubility in the solid state, but high energy ball milling can largely extend the region of solid state solution. Previously, it was observed that niobium partly dissolves in the copper lattice during milling. The present investigation demonstrates that this limit can be extended to a strongly supersaturated Cu solid solution of up to 10 at.% Nb provided the appropriate mechanical alloying method is applied. The change in the powder microstructure was followed by scanning and transmission electron microscopy (TEM) as well as by X-ray diffraction (XRD) analysis. In the case of Cu–5%Nb and Cu–10%Nb a homogeneous single-phase microstructure was obtained after 30 h of milling. Elemental Nb could no more be detected, indicating the formation of a metastable supersaturated Cu–Nb solid solution.
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1. Introduction

A common way of increasing the relatively low intrinsic strength of copper while retaining its high electrical conductivity is alloying with different insoluble elements to achieve particle strengthening. Potential alloying elements can be found in the family of bcc elements (e.g. Cr, W, Ta, Nb, Mo, V) [1,2]. Among them the Cu–Nb alloys have been reported to show the best mechanical properties [1]. In thermodynamic equilibrium the mutual solubility of niobium and copper is negligibly small. Since their melting points differ strongly, conventional cast metallurgy cannot be applied on a large scale. On the other hand, alloys from an immiscible metal system can be manufactured by one of 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 a highly

supersaturated solid solution is usually not possible [3]. In contrast, due to the high energy impact during milling, MA can provide alloys with a good compositional and microstructural homogeneity and a higher content of the alloyed element in solid solution [3–8]. Previously, it has been observed that niobium dissolves partly in the copper lattice during milling [4,5]. The present investigation demonstrates that this limit can be extended to a strongly supersaturated Cu solid solution of up to 10 at.% Nb provided the appropriate MA conditions are applied.

2. Experimental

As starting material, high purity powders of copper and niobium with a particle size smaller than 35 µm were used. Three compositions, namely Cu–5at.%Nb, Cu–10at.%Nb and Cu–20at.%Nb were studied (in the following percentages are always given as at.%). Thirty grams of the powder mixture and 420 g of hardened steel balls with 10 mm diameter were filled in each milling vial, corresponding to a powder-to-ball weight ratio of 1:14. MA was performed under an inert gas atmosphere (argon) in a Retsch planetary ball mill (PM 4000) at liquid nitrogen

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temperature (77 K), using a rotational speed of 200 rev./ min at a constant rotation direction. Milling was interrupted after every 30 min to cool down the vials in liquid nitrogen. After different milling times samples were taken for microstructural investigations.

In order to observe the change in microstructure during milling, the extracted powders were embedded in conductive resin (Technovit 5000) and prepared by standard metallographic techniques. The powders were examined by scanning electron microscopy (SEM) in a JEOL JSM 6400 device and, for high-resolution SEM, in a LEO 1530. In some cases, when a higher resolution was needed, transmission electron microscopy (TEM) was carried out in a JEOL JEM 2000 FX operating at 200 kV. X-ray diffraction patterns were measured in a Philips diffractometer (PW 1830) using filtered CoKα radiation (λ=0.178897 nm). The mechanical properties of the powders were assessed using a Vickers microhardness tester with a load of 245 mN at a loading time of 10 s. The impurity content of the powder after milling was determined by chemical analysis.

3. Results and discussion

3.1. Microstructural investigations

3.1.1. SEM

During the milling process the microstructure of the powder develops from a coarse lamellar type after 5 h milling (Fig. 1a) over a fine lamellar microstructure at the limit of SEM resolution (Fig. 1b) to a very homogeneous microstructure (Fig. 1c). Energy dispersive spectroscopy (EDX) analysis of the latter powder shows a corresponding homogeneous distribution of the alloyed Nb. Only very few niobium particles with a size of about 100 nm remain after milling.

3.1.2. TEM

An investigation of the microstructure of the powder after 35 h (Cu–5%Nb and Cu–10%Nb) and 17 h (Cu–20%Nb) milling time shows a very fine nanocrystalline
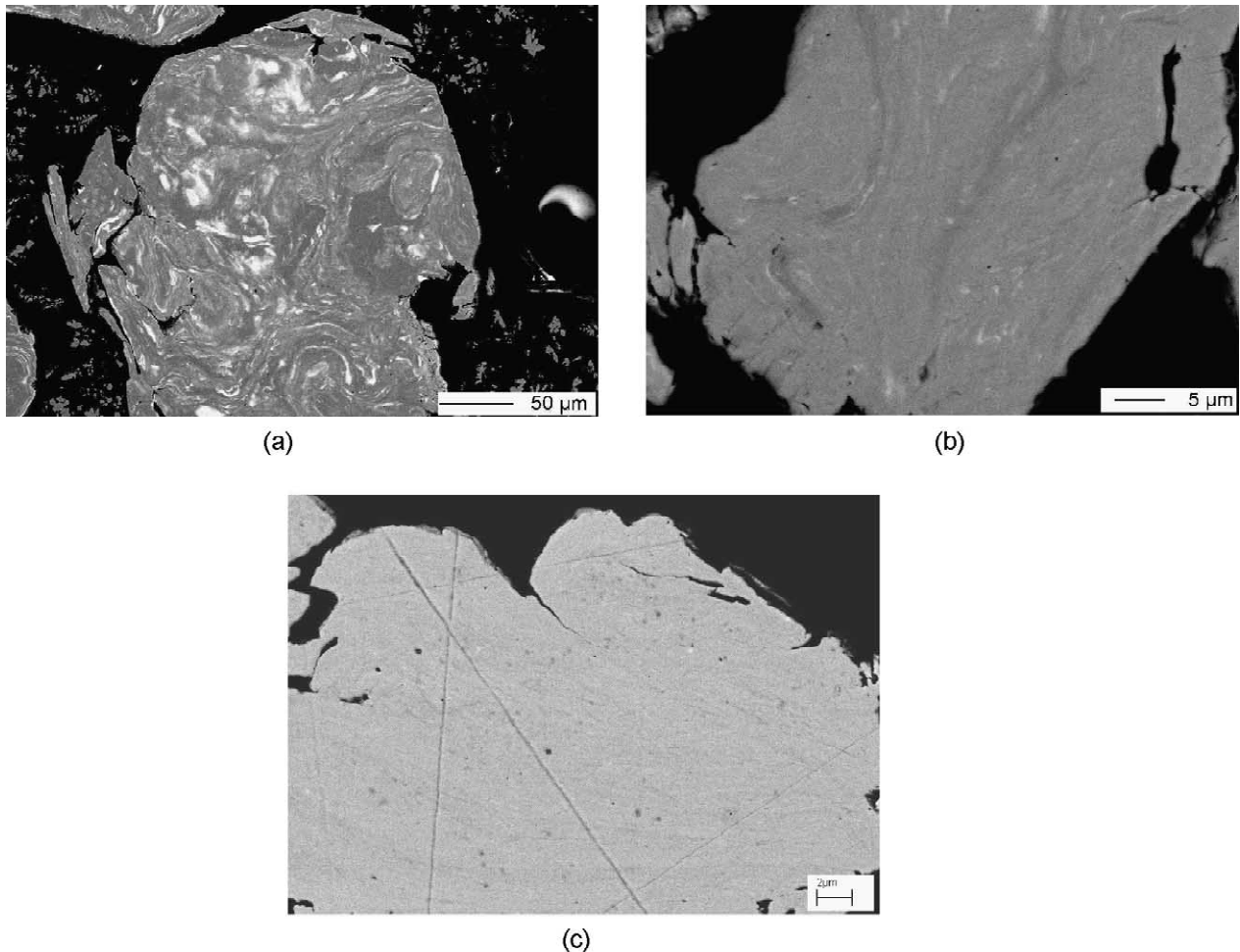

(a)

(b)

(c)

Fig. 1. SEM study showing the change in microstructure of Cu–10%Nb with mechanical alloying: (a) 4 h; (b) 10 h; and (c) 25 h.
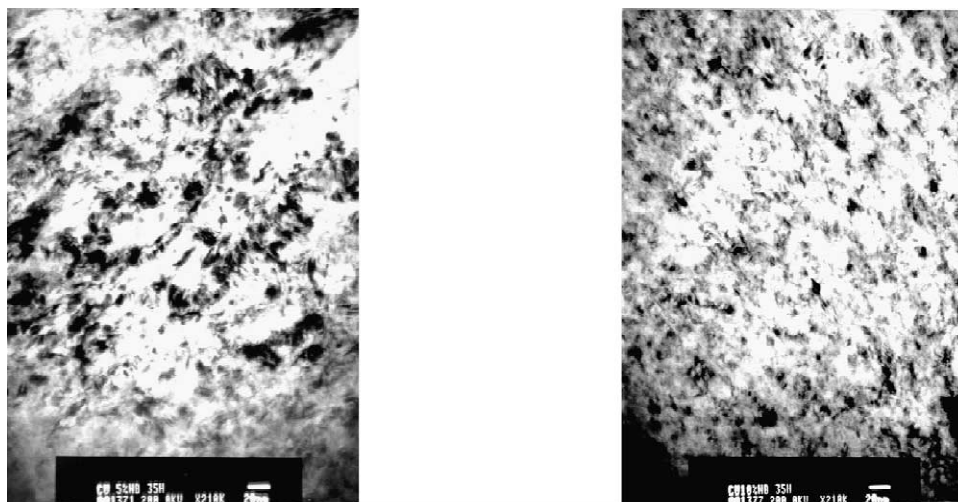
Fig. 2. TEM showing a very fine microstructure of powder Cu–5at.%Nb (a) and Cu–10at.%Nb (b) after 35 h of milling.

grain structure (Fig. 2). At comparable milling the microstructure becomes finer with increasing niobium content times. As proved by EDX analysis in the TEM, the composition of the powder is very homogeneous. Electron diffraction of the Cu–5%Nb and Cu–10%Nb powders does not show niobium reflections, but in the diffraction pattern of the Cu–20%Nb powder some residual niobium reflections can be detected (Fig. 3). In conclusion, these

investigations reveal the successful formation of a completely supersaturated and, hence, metastable Cu–Nb solid solution with nanocrystalline grain size by MA in Cu–5%Nb and Cu–10%Nb powder mixtures. In the case of Cu–20%Nb, the formation of a complete (single-phase) solid solution of niobium in copper could not be achieved. This might be due, either to the very high niobium content of 20at.% or to the too short milling time of only 17 h.
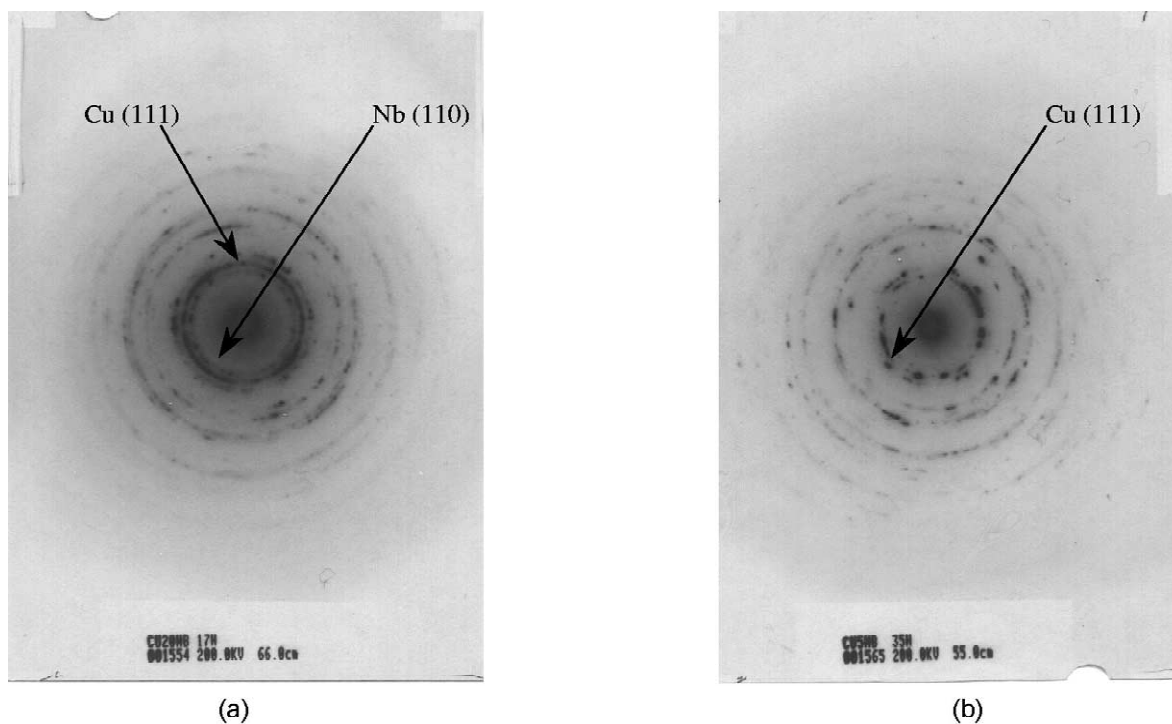

Fig. 3. TEM diffraction from powder: (a) Cu–20%Nb 17 h milling time; and (b) Cu–5%Nb 35 h milling time.

3.2. X-ray investigations

X-ray diffractometry of the mechanically alloyed powder confirms the change of the microstructure of the powder during the milling process. With increasing milling time (from 4 to 35 h) the diffraction pattern of the powder shows a remarkable line broadening and an intensity reduction (Fig. 4). In addition, after long milling times (>30 h), the niobium peaks are no longer detectable. This confirms the conclusion drawn from the microstructural investigations by SEM and TEM, that niobium is completely dissolved within the copper lattice during milling. In the following, the X-ray diffraction data are evaluated to determine the grain size, the internal strain and the lattice parameter of the copper solid solution.

3.2.1. Copper grain size and internal strain in copper

Line broadening can be caused both by a small grain size or/and by internal strain. The integral line width β is given by [9]:

$$\beta = \frac{K\lambda}{d \cos \theta} + 2\varepsilon \tan \theta \tag{1}$$

where λ is the X-ray wavelength; θ the Bragg angle; d the grain size; ε the internal strain; and $K \approx 1$ the Scherrer constant.

In order to separate the two effects a quantitative analyse can be carried out by using a plot according to the Williamson-Hall method [10]:

$$\beta \cos \theta = \frac{K\lambda}{d} + 2\varepsilon \sin \theta \tag{2}$$

In case of a linear dependence of $\beta \cos \theta$ on $\sin \theta$ the slope of the straight line corresponds to the contribution of the internal strain 2ε and the intersection with the ordinate
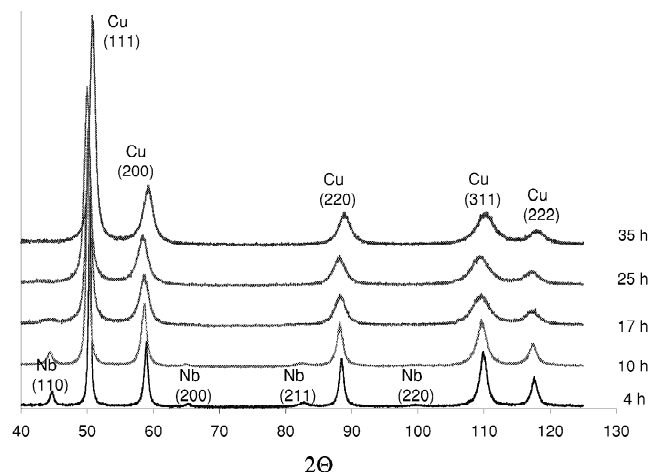
yields the contribution of the line broadening by the small grain size d.

For a suitable interpretation of this plot the elastic anisotropy of copper must be considered [11]. For this the angular data are normalised using the directional Young's modulus calculated from the elastic compliances, S_{ij} (tabulated e.g. in [12]). Young's modulus E for cubic metals is given by:

$$\frac{1}{E} = S_{11} - 2\left[(S_{11} - S_{12}) - \frac{1}{2}S_{44} \right](l^2m^2 + m^2n^2 + l^2n^2) \tag{3}$$

where l, m and n are the directional cosines of the Bragg reflections with respect to the crystallographic axes [12].

To extract the contribution of the sample (β) from the total line broadening β_g a Wagner relation was assumed:

$$\beta = \beta_g - \frac{\beta_i^2}{\beta_g} \tag{4}$$

where β_i is the instrumental line broadening [9,13,14].

The internal strain in copper (Fig. 5) increases with increasing milling time and increasing Nb content (compare the Cu–10%Nb with the Cu–5%Nb alloy). Both facts can be explained by the higher content of dissolved niobium in the copper solid solution at the same state of milling.

Fig. 6 shows the evolution of the copper grain size during milling as evaluated from the XRD measurements. The prediction from the microscopic investigations concerning the formation of a nanocrystalline grain structure in the powder during the milling process can be confirmed. The copper grains after 35 h milling have a diameter of about 11 nm in the Cu–5%Nb alloy and 7 nm in the Cu–10%Nb alloy. Thus, the copper grain size decreases with increasing niobium content in the solid solution.

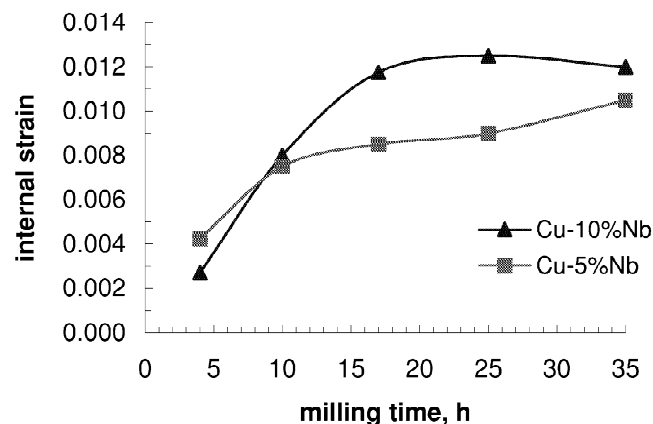The formation of an extended solid solution of niobium in the copper matrix can be explained by means of the

Fig. 4. X-ray powder diffraction patterns of Cu–5%Nb with mechanical alloying.

Fig. 5. Internal strain with respect to alloying time for Cu–5%Nb and Cu–10%Nb systems.
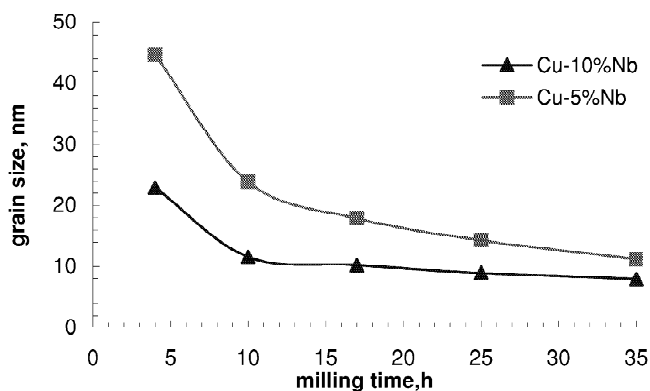
Fig. 6. Copper grain size respect to alloying time for Cu–5%Nb and Cu–10%Nb systems.

dislocation solute-pumping mechanism introduced by Schwarz [15]. According to this model the dislocation core acts as a pump for the solutes. Niobium atoms are larger than copper atoms, therefore the lattice near the niobium atoms is compressed and the dislocation situated in an expended lattice. Thus the niobium atoms interact with the dislocations. The solutes diffuse along the dislocation line two times faster compared to that of the inner grain regions without any lattice defects. Thus niobium atoms can arrange in the form of chains along the dislocation line within the copper matrix. The stress in the powder particles exceeds the flow stress of copper due to the impact of the balls and hence the dislocations start to glide. As the niobium solutes cannot move easily they will be left behind the dislocation line. The niobium atoms remain a few nanometer within the copper grain whereby the matrix is locally supersaturated. In order to achieve the supersaturated state in the whole volume, the grain size has to be reduced to the nanometer scale, too. This means that the achievement of the extended solid solution is closely related to the formation of a nanocrystalline structure [6,16]. Furthermore, a high dislocation density is needed to

achieve a supersaturated solid solution. Therefore, a nanocrystalline structure and a high density of dislocations (high internal strain) is present in the powder as indicated by from the X-ray analysis.

3.2.2. Copper lattice parameter

In order to pursue the dissolution of niobium in the copper lattice, i.e. the formation of the copper–niobium solid solution, the copper lattice parameter a, was determined. For an accurate determination of a, the measured data were refined by the RIETVELD method [17]. Fig. 7 shows the dependence of the copper lattice parameter on milling time. At the beginning of milling, a increases to a maximum of 0.36406 nm in the Cu–10%Nb alloy and 0.36315 nm in the Cu–5%Nb alloy after 17 h milling. On further milling a decrease of a to 0.36268 nm in the Cu–10%Nb alloy and to 0.36224 nm in the Cu–5%Nb after 35 h milling is observed. The dependence of the copper lattice parameter on milling time can be explained by the observed dissolution of niobium, which can be assumed to take place by a substitutional mechanism. This leads to an increase of the copper lattice parameter due to the larger atomic radius of niobium compared to copper.

The decrease of the copper lattice parameter after 17 h milling time is difficult to rationalize. Several hypotheses are conceivable: first, precipitation of niobium from the supersaturated solid solution may occur. However, these precipitates have to be so small that neither peaks in the XRD diagrams are visible nor direct observation in TEM is possible. Another possibility is the formation of stacking faults during intense milling. Copper is known to have a low stacking fault energy, hence, a high density of stacking faults can be expected. Consequently, these stacking faults may cause a peak shift opposite to that caused by the dissolved niobium in copper [6]. However, our TEM investigation could not prove that a high density of stacking faults exists in the mechanically alloyed powder. A third explanation for the reduction of the copper lattice parameter is related to the oxygen content of the powder.
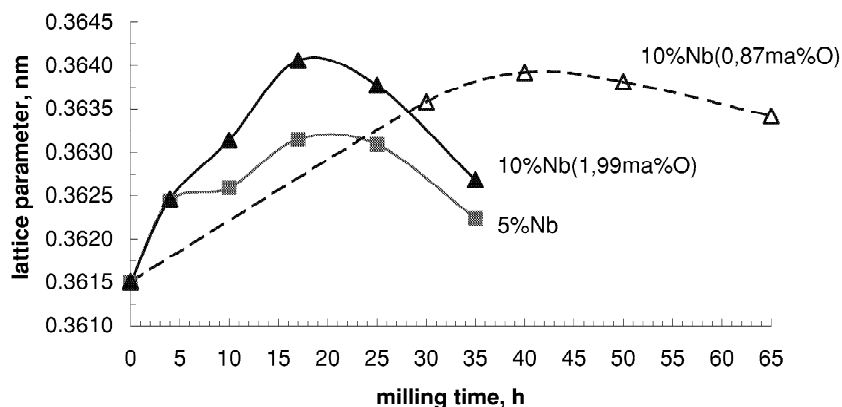

Fig. 7. Lattice parameter for copper with respect to alloying time for Cu–5%Nb and Cu–10%Nb systems.

3.2.3. Influence of the oxygen content of the powder on the copper lattice parameter

Although the powder handling occurs in a protective atmosphere, a contamination by oxygen during milling cannot be avoided completely. The oxygen content in the powder increases constantly with increasing milling time (Fig. 8). Fig. 7 shows that the dependence of the copper lattice parameter on milling time varies strongly with the oxygen content of the powder. For a low oxygen content the copper lattice parameter in the powder increases more slowly and decreases later.

Considering the presence of oxygen in the powder, two assumptions to explain the decrease of the copper lattice parameter at longer milling times can be taken into account. First, a change of the dissolution mechanism of oxygen after a certain saturation concentration might be conceivable. It can be assumed that only a limited amount of oxygen atoms may be dissolved on interstitial sites of the copper lattice because of their limited number. Further oxygen atoms have to occupy lattice sites according to the substitutional mechanism. This would lead to a strong decrease of the lattice parameter due to the large difference in the atomic radii (atomic radius of oxygen being substantially smaller than that of copper). Thus, the simultaneous increase of the copper lattice parameter due to the dissolution of niobium in copper is compensated by the decrease of the copper lattice parameter due to a substitutional dissolution of oxygen. After 17 h milling the decrease of the copper lattice parameter even dominates due to the larger difference in the atomic radii between copper and oxygen than between copper and niobium.

The second assumption is the formation of niobium oxide clusters. This would lead to a decrease of the lattice parameter of the copper matrix as niobium as well as oxygen are precipitated from the copper matrix. This hypothesis is supported by the fact that the affinity to oxygen is much higher for niobium than that for copper. Consequently, the formation of niobium oxide is favoured over that of copper oxide. As the diffusivity of the atoms at
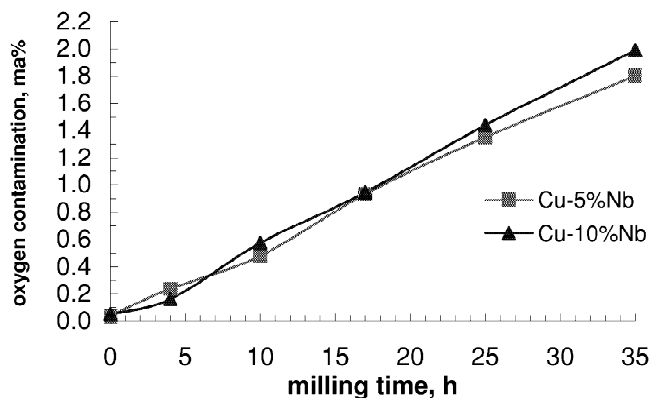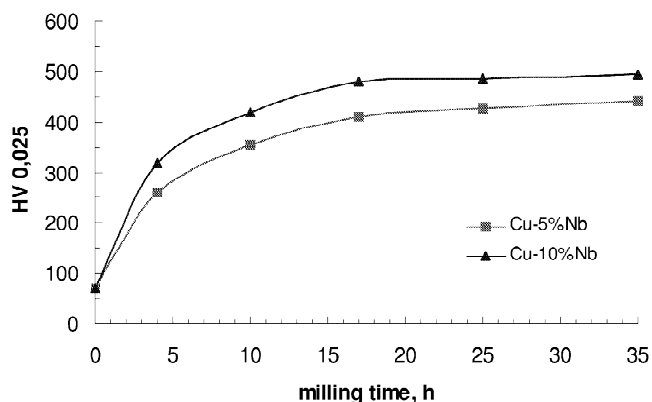

Fig. 9. Microhardness of powder with milling time.

the milling temperature is quite low, the distance between the niobium and oxygen atoms has to be small enough in order to form niobium oxide. This requirement is fulfilled only up to certain concentrations of both elements in the copper matrix. Hence niobium oxide clusters can only form at a later stage of milling. They do not grow further due to the absence of any driving force and they are thermodynamically stable. Due to their small size the clusters can neither be detected by X-ray diffraction, nor by standard TEM investigations.

However, proof of this hypothesis would require the preparation of Cu–Nb powders with a substantially reduced oxygen contamination which should not then exhibit the lattice parameter reduction upon long milling times. This possibility will be examined in future investigations.

3.3. Microhardness measurements

Fig. 9 shows the change of the microhardness during the milling process. First, the microhardness of the powder increases strongly followed by an only moderate increase after 17 h of milling time. This corresponds exactly to the milling time dependence of the internal strain in copper (Fig. 7) as discussed previously. The microhardness shows values of about 450 HV in the Cu–5%Nb alloy and about 500 HV in the Cu–10%Nb alloy. Obviously, the higher hardness values in the Cu–10%Nb alloy can be attributed to the higher amount of dissolved niobium in copper and to the resulting larger internal strain in the solid solution.

4. Conclusions

In contrast to previous studies [4,5] the present study demonstrates a complete dissolution of niobium in the copper lattice up to 10at.% Nb. MA results in a supersaturated solid solution of niobium in copper due to the high energy impact during milling. The influence of oxygen impurities on the formation of the supersaturated solid solution by milling is not yet well understood. The

Fig. 8. Contamination by oxygen in powder of Cu–5%Nb and Cu–10%Nb systems.

resulting homogeneous Cu solid solution is nanocrystalline in nature with a (steady state) grain size of about 10 nm. Due to the dissolution of niobium in the copper matrix and due to the strong plastic deformation exerted during milling the value of the internal strain in the powder is very high. This results in an increase of the powder hardness to 500 HV.

Acknowledgements

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