

## Phase Transitions in Cu-Sb Systems Induced by Ball Milling

M. Kis-Varga<sup>1</sup> and D.L. Beke<sup>2</sup>

<sup>1</sup> Institute of Nuclear Research of the Hungarian Academy of Sciences,  
P.O. Box 51, H-4001 Debrecen, Hungary

<sup>2</sup> Department of Solid State Physics, L. Kossuth University,  
P.O. Box 2, H-4010 Debrecen, Hungary

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### Abstract

Powders of  $\text{Cu}_X\text{Sb}_{100-X}$  mixtures in the composition range of  $X=0-90$  at %, and arc melted CuSb alloys with Cu=60 and 82 at % nominal concentration were ball milled in vacuum. The phase transitions and the decrease of crystallite size during milling was studied by X-ray diffractometry. Partial amorphization and formation of nanocrystalline  $\eta\text{Cu}_2\text{Sb}$  phase was observed in powder mixtures for 50 and 75 at % antimony. There was no alloying of the two components at  $X \leq 10$  at %, the XRD patterns showed the structures of nanocrystalline Sb and Cu only. By increasing the copper content up to  $X=87$  at %, the formation of nanocrystalline  $\eta\text{Cu}_2\text{Sb}$  was observed in accordance with the equilibrium phase diagram. For  $X \geq 87$  at % extended Cu-base solid solutions were obtained with average grain size of 10 nm. The XRD measurements of arc melted alloys indicated an initial mixture of phases  $\eta\text{Cu}_2\text{Sb}$  and  $\delta\text{Cu}_{4.5}\text{Sb}$  for  $\text{Cu}_{82}\text{Sb}_{18}$  as well as a mixture of  $\eta\text{Cu}_2\text{Sb}$  and Sb for  $\text{Cu}_{60}\text{Sb}_{40}$ , respectively. The milling resulted only in a nanocrystalline structure of the heterogenous alloy in both cases, and amorphization was not observed.

### Introduction

Mechanical alloying (MA) with ball mills is a well established process for achieving the formation of amorphous, metastable and nanocrystalline alloys starting from elemental metallic powders. After the first paper describing the possibility of preparing amorphous alloy from pure elemental Ni and Nb powder components [1], many other combination of elements were checked and found to form amorphous alloys during mechanical alloying [2]. The equilibrium solid solubility limits can also be extended by MA. In his review article Koch [3] gives a number of examples described in the literature for this effect.

The defects introduced by the deformation during milling must be responsible for raising the free energy of the system and thus for formation of these metastable phases. It was shown in [4,5] that by using high energy ball milling the elastic mismatch energy plays determining role in the amorphization of intermetallic compound powders. For the case of MA of elemental metallic powder mixtures a simple general condition of amorphization is given in [6]. To find this condition the authors investigated in which cases the energy of the solid solution, formed during the milling process, can be raised above the energy of the amorphous state. By studying the role of chemical, elastic and grain boundary energy contributions, the general condition for amorphization can be expressed as  $\Delta U_{\text{ssei}}/\Delta U_{\text{top}} > 0.57$ , where  $\Delta U_{\text{ssei}}$  is the internal energy difference between the reference state (two unmixed pure powders) and the solid solution, and  $\Delta U_{\text{top}}$  is a topological term expressing the energy necessary to change the structure from crystalline to amorphous, respectively. As seen in Fig. 1 the model predicts amorphization over a wide concentration range for the Cu-Sb system (where the curve is above the dashed horizontal line). The solid horizontal line corresponds to the

limit when the contribution from grain boundaries is neglected. It is worth mentioning that the crossing points of the dashed line and the  $\Delta U_{\text{ssel}}/\Delta U_{\text{top}}$  curve show the values where the free energies of the amorphous phase and the solid solution are equal. In reality there should be a region of coexistence of the two phases around the above concentration values according to the common tangent rule [6]. Furthermore, this estimation is based on the supposition that the formation of all other (stable compound) phases are excluded by kinetic constraints. The aim of the present work is to study the amorphization and phase transitions induced by ball milling for Cu-Sb mixtures at different concentration ratios.

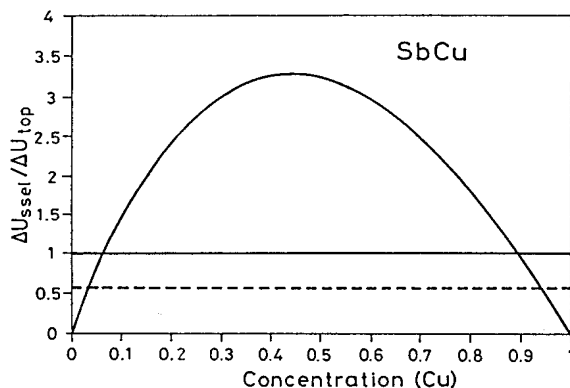


Fig. 1. Condition of amorphization for Cu-Sb binary system.

### Experimental

The ball milling of Cu-Sb powder mixtures was performed in a stainless steel cylindrical vial with a hardened steel ball, similar to that one described in [7]. A vibrating frame (type Fritsch Pulverisette 0) was used to keep in motion the vial and the ball. To prevent oxidation, the milling was performed in a vacuum of less than  $10^{-7}$  Pa. Pure Sb (99.1 %) and Cu (99.9 %) powders with particle size of less than  $150 \mu\text{m}$  were used as starting material. The ball to powder ratio was set to cca. 220 (880 g weight of ball to 4 g powder). To follow the process of MA small quantities (cca. 0.2 g) of powder were withdrawn from the vial after certain milling times for XRD studies. The XRD patterns were measured with a horizontal Siemens diffractometer by using  $\text{MoK}_\alpha$  radiation. The average grain size of crystalline powders were determined from the line broadening of XRD peaks by fitting Voigt functions to the reflections. The line widths of single peaks were calculated using the simplified deconvolution technique described in [8], while the EWA curve fitting code [9] was used for resolving the complex, overlapping reflections.

### Results and discussion

To study the phase transitions induced by ball milling, Cu-Sb mixtures were prepared from pure elemental powders with the compositions as follows:  $\text{Cu}_{10}\text{Sb}_{90}$ ,  $\text{Cu}_{25}\text{Sb}_{75}$ ,  $\text{Cu}_{50}\text{Sb}_{50}$ ,  $\text{Cu}_{75}\text{Sb}_{25}$  and  $\text{Cu}_{90}\text{Sb}_{10}$ . As shown in Fig. 1 the condition of amorphization is the most favourable for  $\text{Cu}_{50}\text{Sb}_{50}$  mixture. The sequence of XRD patterns measured after various milling times of  $\text{Cu}_{50}\text{Sb}_{50}$  is shown in Fig. 2. The starting (0 h) pattern is a superposition of the fcc Cu and the rhombohedral (A7) Sb reflections. After 50 hours milling the formation of tetragonal (C38) structure of  $\eta\text{Cu}_2\text{Sb}$  phase can be observed, in addition to the A7 structure of original Sb phase. By increasing the milling time up to

337 h, the intensities of Sb reflections decrease and their line widths significantly increase. At the same time the pattern of  $\eta\text{Cu}_2\text{Sb}$  phase shows only a slight line broadening without observable change in intensity. After 500 hours milling the Sb reflections disappear, and besides the wide bump characteristic for the amorphous phase, the peaks of  $\eta\text{Cu}_2\text{Sb}$  phase with reduced intensities and increased line widths are seen. This pattern indicates that the final product of 500 hours milling is composed of amorphous Sb and nanocrystalline  $\eta\text{Cu}_2\text{Sb}$  phases. The average grain size of the latter one is cca. 15 nm. By calculating the net peak areas of dominant reflections of the 500 h milled sample, the volume fraction of amorphous phase was estimated to be cca. 43 %. It is close to the 39 % weight fraction of Sb, which remains after the formation of  $\text{Cu}_2\text{Sb}$  compound.

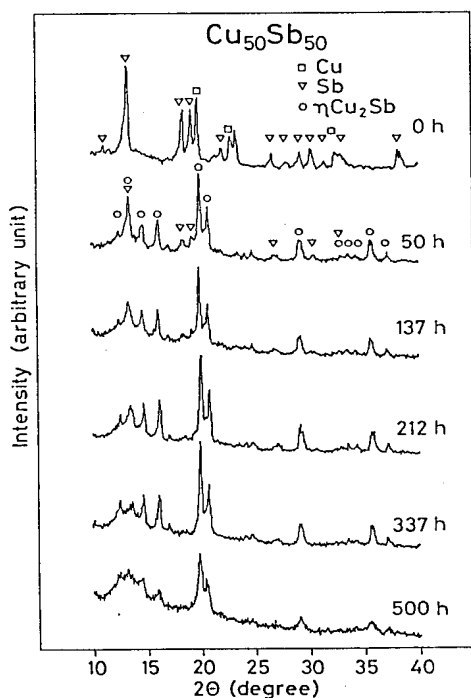


Fig.2. X-ray diffraction patterns of  $\text{Cu}_{50}\text{Sb}_{50}$  powder mixture.

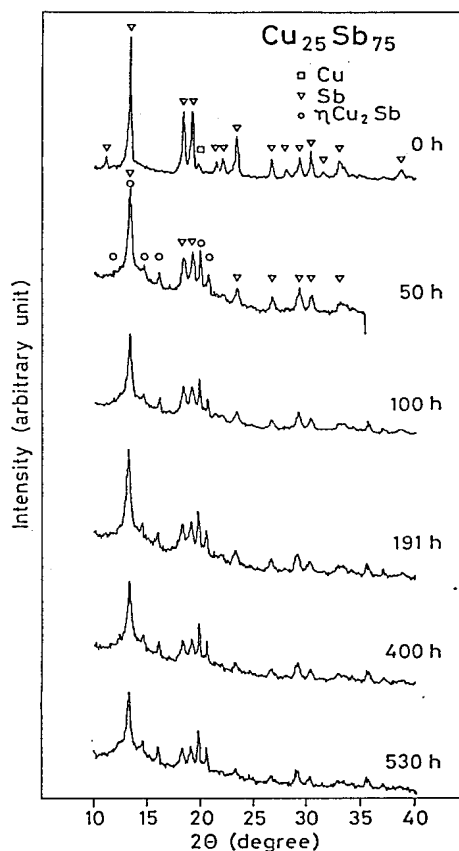


Fig.3. X-ray diffraction patterns of  $\text{Cu}_{25}\text{Sb}_{75}$  powder mixture.

Similar behaviour was observed in case of milling the  $\text{Cu}_{25}\text{Sb}_{75}$  powder mixture, as seen in Fig. 3. By increasing the milling time, the Sb and the  $\eta\text{Cu}_2\text{Sb}$  phases followed a tendency like the  $\text{Cu}_{50}\text{Sb}_{50}$  system. Due to the excess of antimony however, only partial amorphization of Sb phase

was obtained after 530 h milling. In addition to that phase, the patterns of nanocrystalline Sb (grain size cca. 15 nm) and  $\eta\text{Cu}_2\text{Sb}$  (grain size cca. 40 nm) phases can be seen in the 530 h diffractogram.

The Sb excess is more dominant at  $\text{Cu}_{10}\text{Sb}_{90}$  mixture. The ball milling of this material was made only for 230 hours, because the trend was the same as above: the decrease of height and increase of width of A7 structure Sb phase, and less observable changes at the weak reflections of  $\eta\text{Cu}_2\text{Sb}$  phase, respectively. There were no shift of reflections detected, indicating the lack of formation of extended solid solution on the Sb rich side. Furthermore, from the diffractograms we could not confirm the existence of amorphization.

Fig. 4 shows the XRD patterns of  $\text{Cu}_{75}\text{Sb}_{25}$  at various milling times. It is clear from the figure that the intensive reflections of the original crystalline Sb have been disappeared after 25 h milling, and the formation of  $\eta\text{Cu}_2\text{Sb}$  phase has been completed. By further milling this compound the lines

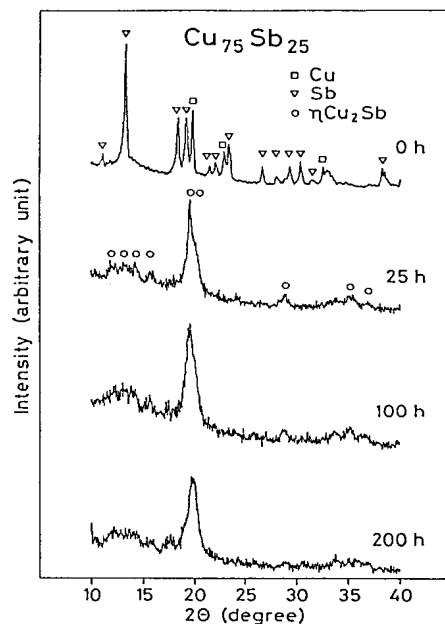


Fig. 4. X-ray diffraction patterns of  $\text{Cu}_{75}\text{Sb}_{25}$  powder mixtures.

are broadening significantly, and a nanocrystalline phase with grain size of cca. 20 nm is achieved at 200 h milling time. This is in accordance with the simple rule [5,6] that intermetallic compounds with ordering temperature less than the melting point can not be amorphized by ball milling.

The formation of extended solid solution was observed on the Cu rich side. As seen in Fig. 5, after 100 hours milling of the  $\text{Cu}_{90}\text{Sb}_{10}$  mixture, the broad peaks characteristic to nanocrystalline fcc Cu are detected. The peaks are shifted towards lower angles indicating the existence of extended solid solution. The Sb atomic fraction of the solution was estimated by using the Vegard's rule and found to be 3.7 %. This suggests that the remaining antimony can be in amorphous state. From Fig. 5 the small, wide bump between 10 and 15 degree is also in accordance with this. The average grain size of the 100 h milled powder is cca. 10 nm. The solubility of Sb was not increased by further

milling the sample up to 300 h. Similar result was obtained for a mixture with composition of  $\text{Cu}_{87}\text{Sb}_{13}$ .

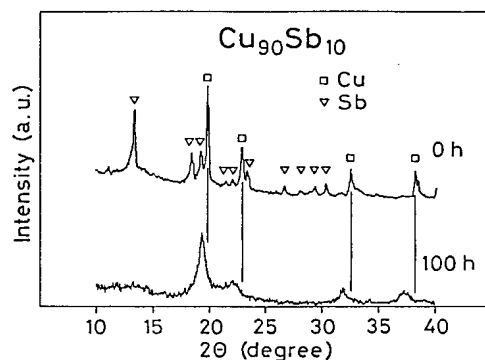


Fig. 5. X-ray diffraction patterns of  $\text{Cu}_{90}\text{Sb}_{10}$  powder mixture.

Two arc melted alloys with nominal compositions of  $\text{Cu}_{60}\text{Sb}_{40}$  and  $\text{Cu}_{82}\text{Sb}_{18}$  was also ball milled. (Originally, compositions of  $\text{Cu}_{50}\text{Sb}_{50}$  and  $\text{Cu}_{75}\text{Sb}_{25}$  were intended to prepare, but due to the volatility of Sb, the composition was changed during the melting process.) As indicated in Fig. 6, the

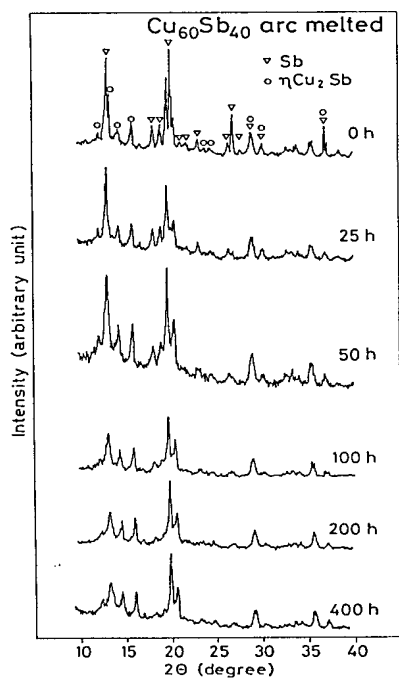


Fig. 6. X-ray diffraction patterns of  $\text{Cu}_{60}\text{Sb}_{40}$  arc melted alloy.

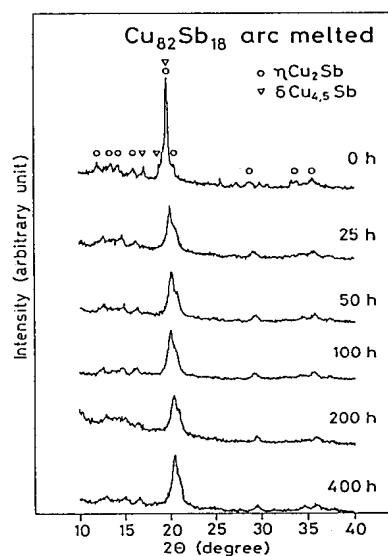


Fig. 7. X-ray diffraction patterns of  $\text{Cu}_{82}\text{Sb}_{18}$  arc melted alloy.

Cu<sub>60</sub>Sb<sub>40</sub> alloy shows similar phase transitions to the Cu<sub>50</sub>Sb<sub>50</sub> and Cu<sub>25</sub>Sb<sub>75</sub> powder mixtures: decrease of intensity and strong line broadening of Sb reflections as well as moderate change in the pattern of  $\eta$ Cu<sub>2</sub>Sb phase. The result of 400 hours milling is a homogenous mixture of these two nanocrystalline phases. The crystallite sizes are cca. 16 nm for Sb and cca. 30 nm for  $\eta$ Cu<sub>2</sub>Sb phase.

The starting (0 h) pattern of Cu<sub>82</sub>Sb<sub>18</sub> arc melted alloy composed from the reflections of  $\eta$ Cu<sub>2</sub>Sb and  $\delta$ Cu<sub>4.5</sub>Sb (see Fig. 7). The reflections of  $\delta$  phase disappear at 25 hours milling and the  $\eta$ Cu<sub>2</sub>Sb phase can only be seen. At longer milling times the diffractograms are similar to ones measured from the Cu<sub>75</sub>Sb<sub>25</sub> powder mixture: the milling results in a nanocrystalline structure of this phase after 400 h.

### Conclusions

Cu<sub>X</sub>Sb<sub>100-X</sub> binary mixtures were prepared from pure elementary metallic powders in the range of X=0-90 at %. Phase transitions and decrease of crystallite size induced by ball milling was studied by X-ray diffractometry. Formation of nanocrystalline  $\eta$ Cu<sub>2</sub>Sb phase and partial amorphization of Sb was observed in samples with Sb content at and above 50 at %. The XRD patterns of the two phases showed different behaviour with increasing milling time, i.e. a rapid decrease of intensity and increase of line width of Sb phase, while a moderate change in the pattern of  $\eta$ Cu<sub>2</sub>Sb phase was obtained during a milling period of cca. 500 hours. By increasing the copper content, the formation of  $\eta$ Cu<sub>2</sub>Sb phase completed within shorter milling time, and a nanocrystalline structure of that phase was achieved after 200 hours milling of Cu<sub>75</sub>Sb<sub>25</sub>. For X  $\geq$  87 at % Cu concentrations, extended Cu-base solid solutions were obtained with average grain size of cca. 10 nm. The ball milling of arc melted Cu<sub>60</sub>Sb<sub>40</sub> alloy resulted in similar structure to the Sb-rich powder mixtures. After 400 hours milling, nanocrystalline Sb and  $\eta$ Cu<sub>2</sub>Sb phases with different grain sizes were obtained. The XRD patterns of arc melted Cu<sub>82</sub>Sb<sub>18</sub> alloy showed the same phase transition like the Cu<sub>75</sub>Sb<sub>25</sub> sample prepared from elemental components.

Our experimental results are in a qualitative accordance with the prediction of [6] (see also Fig. 1) allowing the coexistence of the amorphous phase with solid solution or with the stable  $\eta$  compound. At powder compositions of 10 < X < 90 at % Cu, ball milling resulted in the formation of mixtures of the amorphous phase plus the  $\eta$  phase or extended solid solution. The formation of the  $\eta$  phase is very favourable under milling conditions used.

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### References

1. C.C. Koch, O.B. Cavin, C.G. McKamey, J.O. Scarbrough, *Appl. Phys. Lett.* **43**, 1017 (1983)
2. A.W. Weeber, H. Bakker, *Physica B* **153**, 93 (1988)
3. C.C. Koch, *Proc. of Int. Conf. on Mechanical Alloying, Kyoto 1991* (Ed. P. Shingu) *Mat. Sci. Forum* **88-89**, 243 (1992)
4. D.L. Beke, P.I. Loeff, H. Bakker, *Acta metall. mater.* **39**, 1259 (1991)
5. D.L. Beke, H. Bakker, P.I. Loeff, *Acta metall. mater.* **39**, 1267 (1991)
6. D.L. Beke, S. Szabó, *Scripta Metallurgica et Materialia* **31/10**, 1365 (1994)
7. H. Bakker, L.M. Di, D.M.R. Lo Cascio, *Solid State Phenomena* **23-24**, 253 (1992)
8. Th.H. de Keijser, J.I. Langford, E.J. Mittemeijer, A.B.P. Vogels, *J. Appl. Cryst.* **15**, 308 (1982)
9. J. Végh, Thesis, Debrecen (1990)