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## ON MECHANISM OF NEW PHASES FORMATION DURING MECHANICAL ALLOYING OF Ag-Cu, Al-Ge AND Fe-Sn SYSTEMS

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### ABSTRACT

There are two different models for explaining a homogenization at the atomic level during mechanical alloying. The first model is based on the proposition of local melting as a consequence of ball collisions. The second one focuses on the solid-state reactions. Depending on the homogenization mechanism, the structure evolution during mechanical alloying may be different for individual systems. From this viewpoint we have studied the mechanical alloying of Ag-Cu, Ge-Al, and Fe-Sn systems. The first solid solution prepared from mechanical alloying of the Ag-Cu system has an eutectic concentration; mechanical alloying of the Ge-Al system yields metastable intermetallics and of the Fe-Sn system yields examples of decomposition of the FeSn compound. These results indicate that local contact melting occurs during mechanical alloying.

**KEYWORDS:** A. alloys, C. differential scanning calorimetry (DSC), C. X-ray diffraction, D. magnetic properties

### INTRODUCTION

In mechanical alloying, the homogenization mechanism at the atomic level can differ essentially in one of two ways for individual systems. In one case, the mechanism may involve solid-state diffusion; in the other, the mixing in melt. Depending on the homogenization mechanism, the structure and composition of the product is expected to be different. To verify this assumption we have studied mechanical alloying of the Ag-Cu, Al-Ge, and Fe-Sn systems.

The Ag–Cu system is characterized by a slight mutual solubility of the components in the solid state and the absence of intermediate compounds. The primary solutions of the elements have the f.c.c. structure. The mechanical alloying of this system produces a complete solid solution for entire compositions [1]. It is evident that no nucleation stage is required for formation of this solution by solid-state diffusion, and the concentration of solid solutions of both elements should change smoothly with time. If the formation of the product proceeds through the local contact melting and quenching, a solid solution with the eutectic concentration will occur first. In this case, the concentration of components in the product will change abruptly, not smoothly.

In the Ge–Al system, no equilibrium intermediate compounds exist; however, metastable intermetallic compounds have been obtained by quenching from the liquid [2,3]. The formation of these compounds during mechanical alloying would indicate that the formation of the products proceeds by liquid phase mechanism.

There are no congruent melting compounds in the Fe–Sn system. If local melting is probable under ball collision during mechanical alloying, the intermetallics FeSn and FeSn<sub>2</sub> must be partially decomposed according to the corresponding peritectic reactions. Such a decomposition can be most easily observed if the individual compound is taken as the starting product and mechanically treated.

## EXPERIMENTAL

To carry out our experiments, we used roughly dispersed powders of silver, copper, iron, and aluminum. Tin granules were rolled to a thickness of 0.2 mm prior to the mechanical alloying. Strips about 1 mm wide and 5 mm long were cut from the foil obtained. Germanium powders were prepared by grinding the ingots in a ball mill. A roughly dispersed fraction of particles 0.1–0.5 mm in size was used in our experiments. All the elements were at least 99.9% pure.

Mechanical treatment was carried out in an AGO-2M planetary ball mill, the main feature of which is the cooling of the vials with running water during operation. The operating conditions of the mill used in the present work were as follows: the centrifugal acceleration was  $230\text{m/s}^2$ , the rotation frequency of the vial was  $21.5\text{ s}^{-1}$ , and the calculated speed at which the balls were detached from the wall of the vial was 4.7m/s. The weight of the powders being treated was 10g. The hardened steel balls had a total mass of 200 g and a diameter of 3 mm. The cover of the vials were fitted with special valves which allowed pumping of the vials and filling them with gases up to a pressure of 1 MPa. In order to decrease the temperature of the balls during mechanical alloying, the vials were commonly filled with hydrogen or helium under the pressure of 0.5 Mpa [4]. Mechanical alloying was conducted without intermediate sampling, and excess pressure was retained in the vial throughout the process. Under these conditions and with the use of only roughly dispersed powders with small surface area, we assumed that the influence of uncontrolled impurities captured from the atmosphere on the results obtained [5] would be insignificant.

In the preparation of FeSn intermetallic compound, the elements were preliminarily alloyed mechanically in stoichiometric amounts, and pellets were pressed from the mechanical alloy obtained. These pellets then were annealed in a hydrogen atmosphere at 700°C for 10 h.

Mechanically milled powders were characterized by X-ray diffraction measurements in a DRON-4 diffractometer with a graphite monochromator (using  $\text{CoK}\alpha$  radiation for the samples containing iron, and  $\text{CuK}\alpha$  radiation for the other samples). Differential thermal analysis, differential scanning calorimetry (Setaram DSC-111) and magnetization were measured for these specimens.

## RESULTS

**Ag–Cu System.** Figure 1 shows a sequence of X-ray diffraction (XRD) patterns for the  $\text{Ag}_{60}\text{Cu}_{40}$  powder mixture. From curves b and c, it can be seen that the peak positions of Ag and Cu hardly change with milling time. New diffraction peaks appear between peaks of pure elements. The new peaks become larger with milling time. After milling for 5 h, the peaks of pure Ag and Cu almost disappear and only the new f.c.c. peaks are detected.

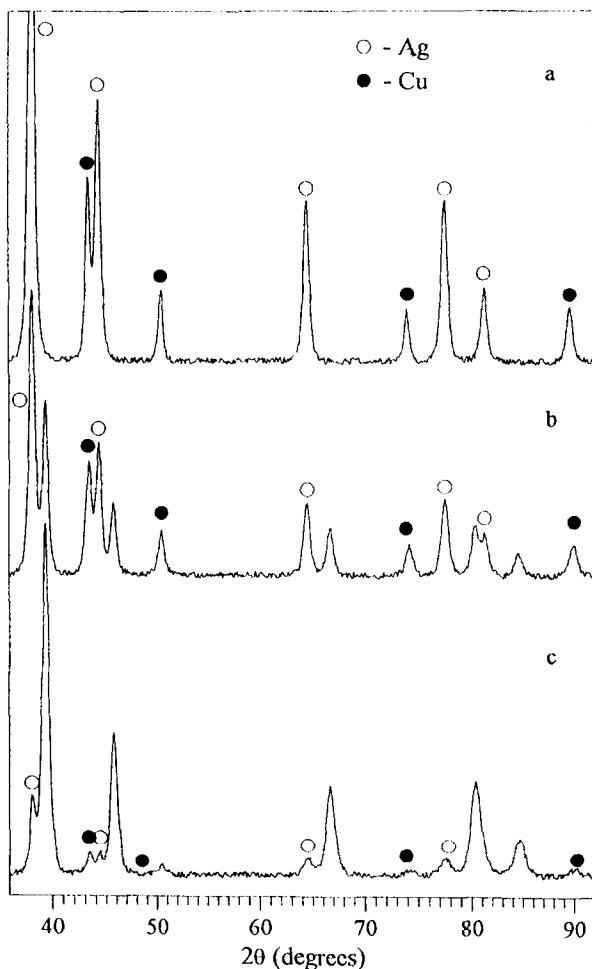


FIG. 1

Evolution of X-ray diffraction patterns of  $\text{Ag}_{60}\text{Cu}_{40}$  after (a) 0.1, (b) 0.5, and (c) 3 h of milling.

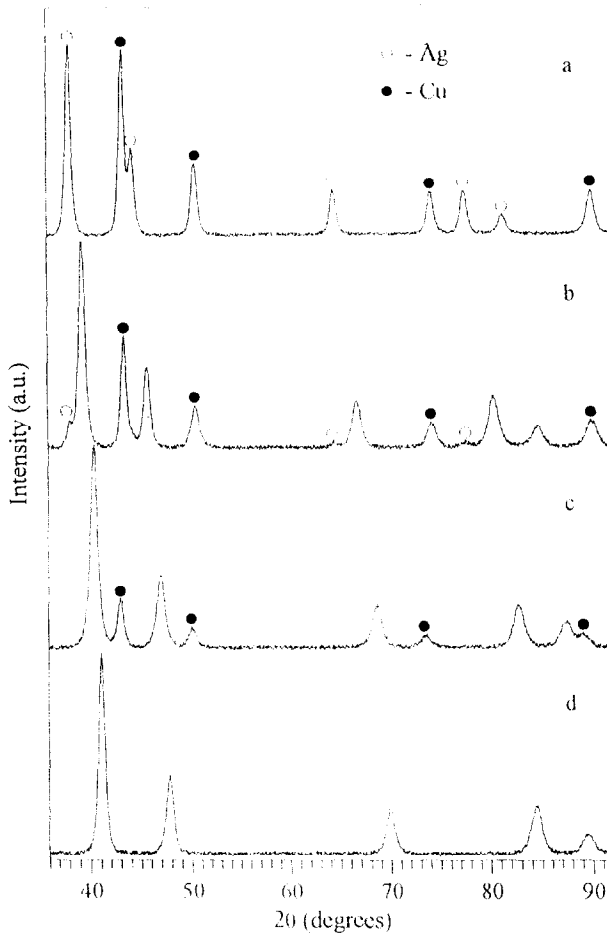


FIG. 2

Evolution of X-ray diffraction patterns of  $\text{Ag}_{30}\text{Cu}_{70}$  after (a) 0.1, (b) 1.5, (c) 3, and (d) 5 h of milling.

However, the peak positions of the phase resulting from the mechanical alloying do not change during the milling process. The lattice parameter of the synthesized phase was 0.395 nm. This value corresponds to a Ag–Cu supersaturated solid solution with the eutectic concentration [6].

When mechanical alloying was conducted for mixtures of another Ag–Cu composition,  $\text{Ag}_{30}\text{Cu}_{70}$ , the following sequence of changes was observed (Fig. 2). First, a solution with eutectic concentration was always obtained (Fig. 2, curve b), and the concentration of the solution began to change gradually only after one of the components was exhausted (Fig. 2, curves c and d). As a result, a crystalline solid solution was obtained in the entire composition range.

Thus, the formation of solid solution in Ag–Cu systems shows peculiarities that count in favor of local contact melting. It should be noted that the higher the heat conductivity of the components being alloyed, the lower the local temperature at collisions (see ref. 7 for

details). Of all the metals, silver and copper show the greatest heat conductivity. If local melting is possible for this pair of metals, this mechanism is plausible in other systems.

**Ge–Al System.** Only the mechanical alloying of a mixture of the powders of the eutectic composition were studied. Figure 3a shows the XRD pattern of the mixture  $\text{Al}_{70}\text{Ge}_{30}$  after milling for 4 h. Besides Bragg's reflection from the starting components, this figure shows additional peaks.

There is a great variety of data concerning the crystalline structure of metastable phases obtained by quenching of Ge–Al melts in the literature (see ref. 2 for review). According to Jones [2], a possible reason for these differences is that the metastable phases resulted from the solid-state transformations subsequent to rapid solidification (martensitic, massive or disorder-to-order). Such transformations can lead to the formation of complex metastable phases. The extreme sensitivity of any solid state transformation to small variation of

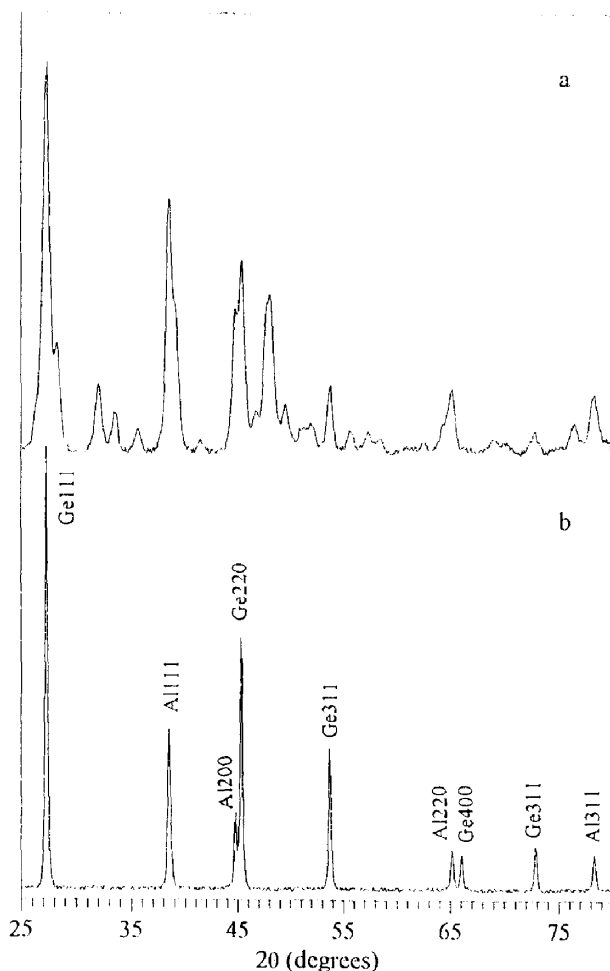


FIG. 3

X-ray diffraction patterns of  $\text{Al}_{70}\text{Ge}_{30}$  (a) milling and (b) after milling and annealing for 0.5 h at  $400^\circ\text{C}$ .

quenching conditions may explain why results of different workers are sometimes in apparent disagreement.

Our data are similar to those of Ramachandrarao *et al.* [3]. Figure 4 provides a comparison of the interplanar spacings determined from extra peaks in Figure 3a with the data for  $\delta_1$  and  $\delta_2$  phases obtained in work [3] on alloys of this system rapidly quenched from liquid. It can be seen that in the powder mixture treated mechanically both these metastable intermetallic compounds are presented. Some differences in the intensities of reflections and interplanar spacings may be associated with variable composition of metastable phases, with visual method of intensities determination in the work [3] and also with the different texture of our powder and splat-cooled foils.

An increase in the duration of mechanical alloying to 14 h brought no detectable changes in the composition of the product (the lines of both the starting elements and metastable compounds were retained on XRD patterns as before) and the relative intensity of reflections markedly changed only for the first 2 h of the mechanical treatment. These results suggest that during the prolonged mechanical alloying of this system, the steady state is established between the processes of the formation and the decomposition of intermediate metastable compounds.

Figure 5 gives the DSC spectrum of the samples obtained. We detected only one exothermic peak in our work, whereas Ramachandrarao *et al.* [3] recorded three exothermic peaks as heating quenched samples. We think this difference is associated with the differences in the composition and particle size of metastable phases obtained in the work by Ramachandrarao *et al.* and in our work. In our work, the value of the heat evolution was 4–5 J/g. Because the samples contain two metastable phases simultaneously, and their amounts

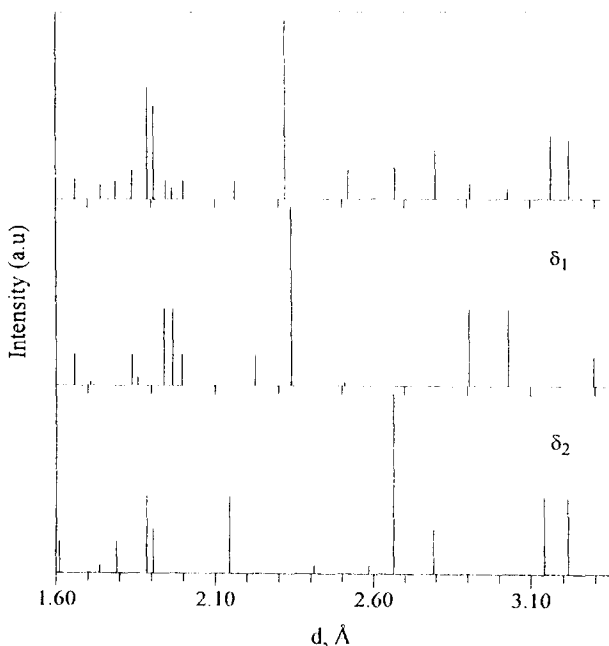


FIG. 4

Comparison of interplanar spacings and intensities determined from extra peaks on  $\text{Al}_{70}\text{Ge}_{30}$  X-ray diffraction patterns with data for  $\delta_1$  and  $\delta_2$  phases [3].

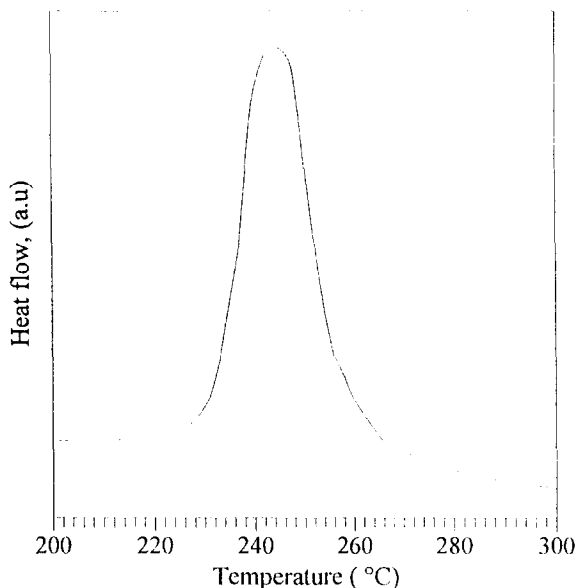


FIG. 5

DSC scan of mechanically alloyed  $\text{Al}_{70}\text{Ge}_{30}$  at heating rate of  $10 \text{ Kmin}^{-1}$ .

are unknown, the molar heats of the decomposition of these compounds into the elements could not be determined.

After the DSC studies, the XRD patterns of the samples show no phases other than their equilibrium solid solutions on the basis of the elements (Fig. 3b). No marked amounts of ferromagnetic impurities (from the materials of the balls and the vials) was detected by measurement of magnetic susceptibility on a Gouy balance. On the basis of these results, a conclusion can be drawn that the formation of the metastable intermediate compounds is not associated with the influence of impurities.

**Fe–Sn System: Demixing of FeSn.** Figure 6 shows XRD patterns of the FeSn intermetallic prior to and after mechanical treatment. In the XRD pattern after milling, the most intensive reflections of the  $\text{FeSn}_2$  are easily observed. Such samples initially exhibit no ferromagnetic property, but they become ferromagnetic after milling. This indicates the formation of compounds with an iron content higher than in FeSn (in the Fe–Sn system, the FeSn and  $\text{FeSn}_2$  compounds are antiferromagnetic, and the compounds with the iron content higher than in FeSn are ferromagnetic [8]). Samples completely lose their ferromagnetic properties after heating above  $400^\circ\text{C}$ . The XRD pattern of the samples after heating does not differ for the XRD pattern of the initial FeSn intermetallic. Thus, the data obtained suggest that under ball milling, the FeSn compound decomposes to form  $\text{FeSn}_2$  and one or several compounds with higher iron contents.

We think that the results obtained support the assumption that local melting is possible during impaction of the powder. Several processes should be considered. Incongruent melting of FeSn leads to the formation of a solid compound (compounds) with an iron content higher than in FeSn and a liquid solution of iron in tin. The reasonable estimate for high local temperature lifetime is the time of collision, i.e., approximately  $10^{-5}$  s. After collision, the temperature  $T$  of melted regions decreases rapidly. When  $T$  is between  $770^\circ\text{C}$

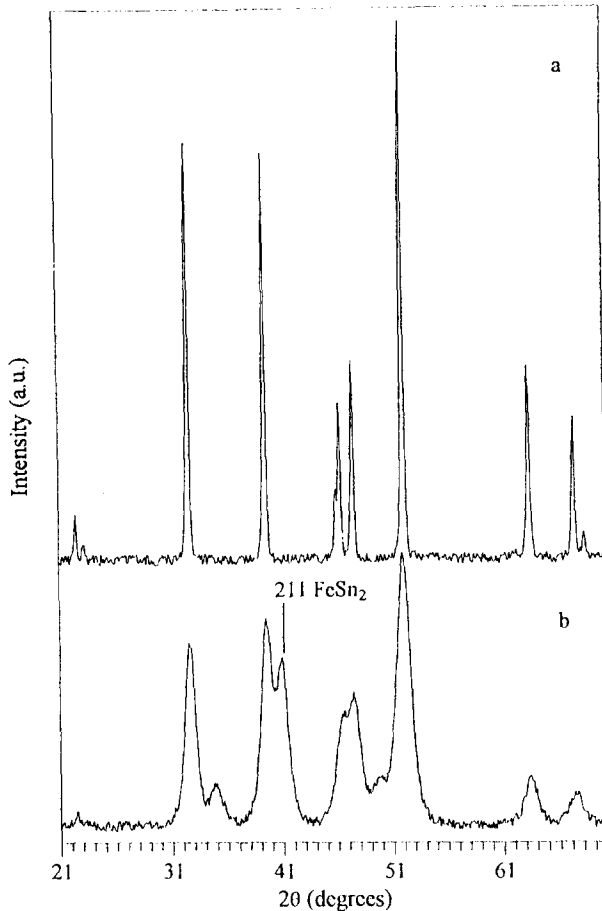


FIG. 6

X-ray diffraction patterns of FeSn intermetallic (a) before and (b) after milling.

(the temperature of decomposition of FeSn) and 513 °C (the temperature of decomposition of FeSn<sub>2</sub>), the reverse process of formation of FeSn becomes possible by two mechanisms: (1) solid + liquid reaction and (2) decay of liquid solution due to decrease of solubility with cooling. When the temperature is under 513 °C, FeSn<sub>2</sub> can be formed by the same two mechanisms. After solidification, tin may be oversaturated with iron and the solid solution may decay, giving FeSn<sub>2</sub>. If our proposition on local melting is valid, it is evident that FeSn<sub>2</sub> intermetallic should decompose under impaction, giving FeSn and liquid; whereas during cooling, the reverse process (i.e., the formation of this compound) should occur. All these processes must come into steady state after some time. As a result, the product of milling of FeSn must contain all the phases existing in the Fe–Sn system. The amount of different phases may vary considerably, and only some of the phases may be detected in an experiment.

Complete decomposition of FeSn by increasing the milling time has not been observed. The relative intensities of the FeSn and FeSn<sub>2</sub> phases cease to change after milling for 2 h.

During the mechanical alloying of the mixture Fe<sub>50</sub>Sn<sub>50</sub>, the FeSn<sub>2</sub> compound forms very rapidly (in about 0.5 h). The formation of FeSn proceeds substantially slower: a small



amount of this phase is detected by XRD only after treatment for 2 h. However, if the mechanical alloying is carried out for 10 or more hours, the product formed is of the same composition as that obtained by the treatment of FeSn.

Both the solid-state diffusion mechanism and the mechanism involving participation of melting can account for the formation of intermediate phases in the Fe–Sn system during mechanical alloying. In the latter case, FeSn<sub>2</sub> forms on reaction of melted tin with solid iron, and FeSn on peritectic decomposition of FeSn<sub>2</sub>. The decomposition of FeSn compound can be most simply accounted for by high local temperatures at collisions.

### CONCLUSION

The data obtained indicate that local melting can occur during mechanical alloying. The mechanism involving participation of a liquid phase cannot be regarded as the only possible mechanism for mixing at the atomic level. Mixing at the atomic level depends on many factors and is determined by both the properties of the starting components and the condition of the mechanical treatment.

### ACKNOWLEDGMENTS

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