Technical Physics Letters, Vol. 30, No. 1, 2004, pp. 60–63. Translated from Pis'ma v Zhurnal Tekhnicheskoĭ Fiziki, Vol. 30, No. 2, 2004, pp. 43–51.
Original Russian Text Copyright © 2004 by Iskhakov, Kuzovnikova, Komogortsev, Denisova, Balaev, Mal'tsev, Bondarenko.

Accelerated Mechanical Alloying of Mutually Insoluble Metals: Co–Cu System

**R. S. Iskhakov*, L. A. Kuzovnikova, S. V. Komogortsev,
E. A. Denisova, A. D. Balaev, V. K. Mal'tsev, and G. N. Bondarenko**

*Kirensky Institute of Physics, Siberian Division, Russian Academy of Sciences,
Krasnoyarsk, Russia*
*Krasnoyarsk Branch, Irkutsk State University of Railway Communications,
Krasnoyarsk, Russia*
*Institute of Chemistry and Chemical Technology, Siberian Division, Russian Academy of Sciences,
Krasnoyarsk, Russia*
** e-mail: rauf@iph.krasn.ru*

Received May 22, 2003; in final form, July 28, 2003

Abstract—We propose a new method for accelerating the process of mechanical alloying in the Co–Cu system possessing positive enthalpy of mixing and exhibiting no mutual solubility of components under equilibrium conditions. For this purpose, highly disperse powders of composite particles representing a Co–P amorphous alloy core covered with a nanocrystalline copper shell were prepared by chemical deposition. These composite powders were mechanically alloyed by processing in a ball mill. Investigation of the atomic structure and magnetic properties of the composite powders upon milling showed that the formation of supersaturated Co–Cu solid solutions under such conditions requires a much shorter milling time as compared to that for the conventional mechanical alloying processes. © *2004 MAIK “Nauka/Interperiodica”.*

In the last decade, nanocrystalline alloys based on the combinations of elements immiscible under equilibrium thermodynamic conditions, such as (Co, Fe)–(Cu, Au, Ag), have been extensively studied. Prepared by various nonequilibrium methods, these alloys exhibit a number of anomalous physical properties with good prospects for application in practice [1–8]. An example is offered by alloys of the Co–Cu system obtained by magnetron sputtering [2, 3], rapid quenching from melt [4], and prolonged grinding of metal powders in special ball mills (mechanical alloying) [5–8].

The method of mechanical alloying has drawn the special attention of researchers due to the apparent simplicity and still unclear mechanism of alloy formation. Using this method, metastable Co–Cu solid solutions of various compositions with a grain size of 5–20 nm and an excess energy level of up to 10 kJ/mol were obtained [5–8] from mixtures of metallurgical Co and Cu powders with a particle size of 70–150 μm. The required milling time varied from 20 to 50 h, depending on the activator power. It was found that further milling does not change the alloy microstructure, which indicates that a dynamic equilibrium is established between breakage and restoration of a chemically homogeneous structure in metastable solid solutions. Considerable time and mechanical work consumed during milling are spent for the formation of a special contact interface between particles in the reaction mixture.

In this Letter, we propose a means of accelerating the process of alloy formation between cobalt and copper while obtaining metastable Co–Cu solid solutions by means of milling (mechanical alloying). Using the proposed method, the milling time can be reduced to less than one-tenth of that required for the conventional processing technology.

Reaction mixtures for the mechanical alloying of Co and Cu were prepared in the form of ultrafine powders consisting of composite particles representing a $Co_{88}P_{12}$ amorphous alloy core with a nanocrystalline copper shell. The $(Co_{88}P_{12})_{100-X}/Cu_X$ (X = 20 or 50 at. %) composite powders were obtained by method of combined chemical deposition based on the reduction of metals from aqueous solutions of the corresponding salts. In the first step, ultrafine Co–P powders were obtained from an aqueous solution of $CoSO_4$ by reduction at T = 80°C with sodium hypophosphite NaH_2PO_2 [9]. The content of phosphorus was determined by chemical analysis with an error of ±0.5 at. %. Previously [9], it was established that $Co_{88}P_{12}$ powders obtained using this method are amorphous and consist of spherical particles with diameters in the range from 0.1 to 3 μm. In the second step, $Co_{88}P_{12}$ amorphous alloy particles were coated with nanocrystalline copper shells of various thicknesses. The reducing agent in solutions for the copper plating of Co–P powder was formaldehyde.

Mechanical alloying was achieved by processing composite powders in hermetically sealed containers in a planetary ball mill (AGO-2U). The duration of milling with steel balls at an acceleration of 20*g* and a ball to powder weight ratio of 10 : 1 was t_m = 0.5, 1, 2, 3, or 4 h.

The atomic structure of the alloys obtained by milling was studied by X-ray diffraction on a DRON-3 diffractometer using CuK_α radiation. Note that, according to the accepted notions, the X-ray diffraction data cannot be used for the final judgment on the formation of chemically homogeneous solid solutions in a system of mutually insoluble components. Indeed, the change in the interplanar distances determined from the diffraction patterns can be related both to the formation of a solid solution and, for example, to a coherent fitting of the crystal lattice of ultrasmall particles of one component to the crystal lattice of another (matrix) component [6].

For this reason, the atomic structure of the obtained Co–Cu alloy was additionally characterized using the nuclear magnetic resonance (NMR) and low-temperature magnetization $M(T)$ measurements. These methods provide data on the short-range order and the environment of Co atoms in the crystal lattice. The room-temperature NMR spectra were recorded on a standard spin-echo spectrometer operating in a frequency range from 150 to 230 MHz. The low-temperature magnetization measurements were performed in a temperature range from 4.2 to 200 K on a vibrating-sample magnetometer with an applied field of 20 kOe.

The X-ray diffraction patterns were obtained for the initial reaction mixtures charged into the ball mill and for the samples processed in the mills for each preset milling time t_m. The reaction mixtures were either a mechanical mixture of highly disperse Co–P and Cu powders or the $(Co_{88}P_{12})_{80}/Cu_{20}$ and $(Co_{88}P_{12})_{50}/Cu_{50}$ composite powders (Fig. 1a). The results of these measurements showed that a 2-h processing of the mixture of Co–P and Cu powders did not produce any significant change in the atomic structure: the amorphous component (Co–P) remains amorphous and the diffraction peaks of Cu exhibit broadening while retaining their angular positions.

A different situation is observed in the course of milling of the composite powders. Here, even a 0.5-h processing brings significant structural changes. As can be seen from the diffractograms of these samples (Fig. 1a shows the diffraction patterns for the $(Co_{88}P_{12})_{50}/Cu_{50}$ composite), the main phase of the material has an fcc structure with the interplanar distances (directly related to the angular positions of the diffraction reflections by the Bragg formula $d_{hkl} = \lambda/2\sin\Theta$) smaller than in fcc Cu but greater than in fcc Co. This fact is indicative of the Co–Cu alloy formation. Subsequent milling is accompanied by an insignificant decrease in the interplanar spacing (which always remains smaller than that in fcc Cu) and by broadening of the diffraction lines.

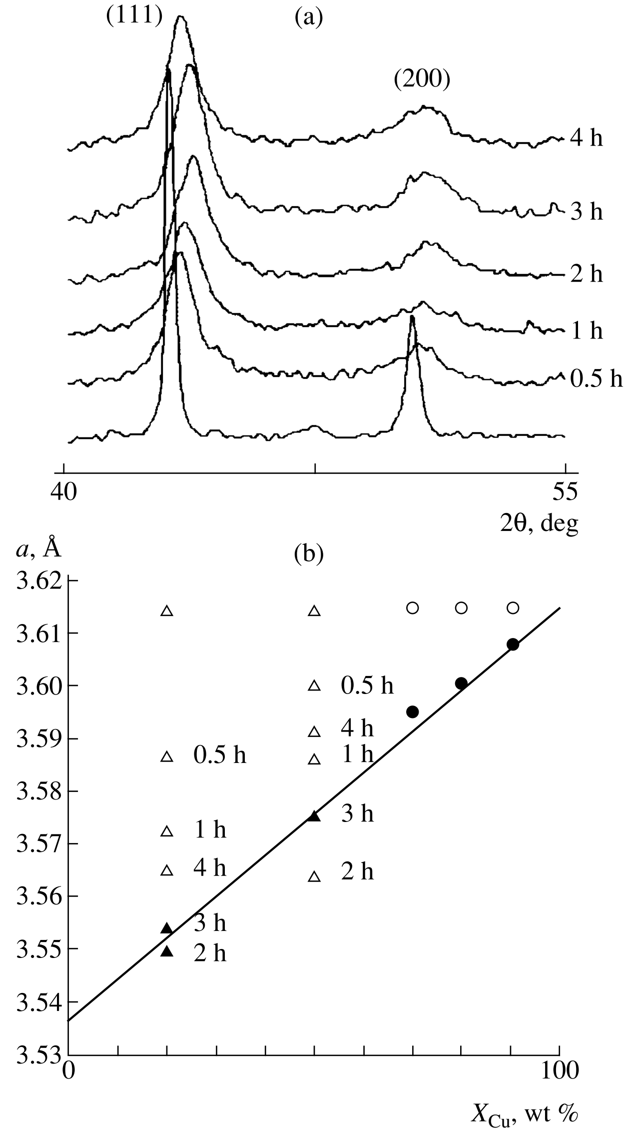

Fig. 1. X-ray diffraction study of a $(Co_{88}P_{12})_{50}/Cu_{50}$ composite powder: (a) diffractograms measured in various stages of mechanical alloying (figures at the curves indicate the milling time t_m); (b) variation of the lattice parameter of copper *a* in the course of mechanical alloying (Δ, this study; ○, data of [8] (initial and after 50-h milling); solid line corresponds to the Vegard law; black symbols correspond to alloys most close to the state of solid solution.

The results of X-ray diffraction measurements are summarized in Fig. 1b. As can be seen, the alloys obey the Vegard law. Note that a 2- to 3-h milling of the composite powder renders the state of the Co–Cu solid solution analogous to that observed after a 50-h conventional mechanical alloying of a mixture of metallurgical powders.

Thus, the main physicochemical factors responsible for the accelerated mechanical alloying of composite

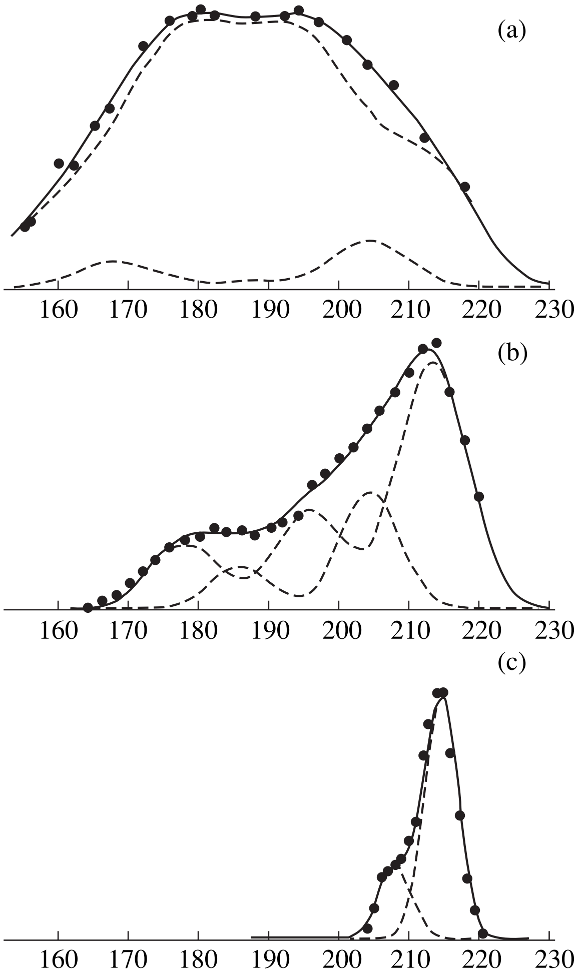

Fig. 2. Variation of the NMR spectra of a $(Co_{88}P_{12})_{50}/Cu_{50}$ composite powder: (a) initial powder; (b) after milling for t_m = 0.5 h; (c) after milling for t_m = 4 h and annealing for 1 h at T = 500°C (dashed curve show the results of deconvolution into components).

powders is the special character of interface between alloy components in these particles. This conclusion follows from a comparison of the diffractograms of the mechanical mixture of Co–P and Cu powders and the patterns observed for the composite powders.

Figure 2 shows the NMR spectrum of the initial $(Co_{88}P_{12})_{50}/Cu_{50}$ composite powder and changes in this spectrum upon the first 0.5-h milling and after a 4-h milling followed by annealing for 1 h at 500°C. The NMR spectrum of pure Co contains two main components corresponding to the resonances at 213.5 MHz (fcc Co) and 221 MHz (hcp Co). The nearest environment of Co in both fcc and hcp lattices includes 12 neighbors. When the magnetic neighbors are replaced by nonmagnetic ones, the NMR spectrum displays equidistant satellites. Deconvolution of the NMR spectrum of the initial powder into components shows that Co atoms occur primarily in an fcc environment including one or two nonmagnetic neighbors (Fig. 2a).

Already the first 0.5-h milling of the $(Co_{88}P_{12})_{50}/Cu_{50}$ composite powder leads to a significant change in the NMR spectrum (Fig. 2b): the main resonance now corresponds to pure fcc Co (which is evidence for the crystallization of the initially amorphous Co) and there appears a satellite reflecting the hcp Co environment. After a 1-h processing, the total NMR signal intensity decreases, but the shape of the spectrum also indicates the presence of Co in both fcc and hcp environments. After 2-h and 4-h milling, the room-temperature NMR signal vanishes and appears again only after a 1-h annealing at 500°C, representing a sum of two resonance components (Fig. 2c). One of these components corresponds to pure fcc Co (213.5 MHz), and the other (208 MHz), to a Co-based solid solution with an hcp structure featuring one nonmagnetic atom in the first coordination sphere of Co. Since phosphorus atoms in the sample annealed at T = 500°C enter a phosphide phase (Co_2P) and do not contribute to NMR, the role of a nonmagnetic neighbor in the environment of Co is played by Cu. The component at 208 MHz corresponds to a $Co_{92}Cu_8$ solid solution with an hcp structure.

The above NMR data indicate that milling is accompanied by a polymorphous transformation (fcc–hcp) in the nearest environment of cobalt. These local martensitic shifts probably favor a significant increase in the coefficients of heterodiffusion of the alloy components. In addition, an analysis of the NMR spectra suggests the possible formation of copper phosphide (Cu_2P) together with cobalt phosphide (Co_2P).

The typical low-temperature magnetization curve $M(T)$ of the $(Co_{88}P_{12})_{100-X}/Cu_X$ composite powder (Fig. 3) shows that the alloy contains both the regions of solid solution rich in Co (ferromagnetic phase) and the regions where separate Co atoms and small clusters are not coupled by exchange (superparamagnetic phase). The experimental $M(T)$ curve can be approximated by the following expression:

$$M(T) = a_0 - a_1 T^{3/2} + a_2 L\left(\frac{a_3}{T}\right), \qquad (1)$$

where $L(x) = \coth(x) - 1/x$ is the Langevin function. The first two terms in this expression, describing a decrease in the magnetization of the ferromagnetic (FM) phase related to the spin waves, correspond to the Bloch “3/2” law: $a_0 - a_1T^{3/2} \equiv M_f v_f(1 - BT^{3/2})$, where M_f is the average magnetization of the ferromagnetic component, v_f is the volume fraction of this component, and $B \sim A^{-2/3}$ is the average Bloch constant related to the effective exchange coupling constant A [10]. The third term in Eq. (1) describes a decrease in the magnetic susceptibility of the superparamagnetic phase that corresponds to the Langevin law [11]: $a_2L(a_3/T) \equiv M_{sp}v_{sp}L(M_{sp}HV_{sp}/(kT))$, where M_{sp} is the average

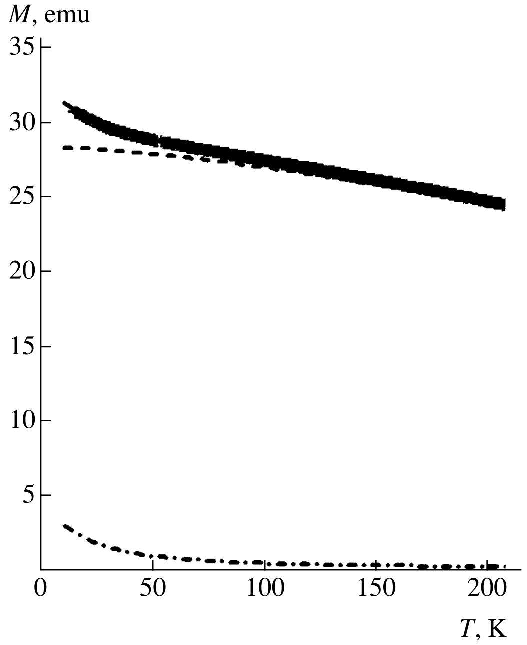

Fig. 3. The typical low-temperature magnetization curve $M(T)$ of a composite powder measured in an external magnetic field of $H = 20$ kOe. Solid curve shows the approximation according to formula (1); dash and dot-dash curve correspond to the ferromagnetic and superparamagnetic components in formula (1). This example refers to a $(Co_{88}P_{12})_{50}/Cu_{50}$ composite powder milled for $t_m = 4$ h.

magnetization of the superparamagnetic component, v_{sp} is the volume fraction of this component, and V_{sp} is the average volume of a superparamagnetic particle.

Expression (1) describes the experimental $M(T)$ curve well (Fig. 3). The values of parameters a_0, a_1, a_2, and a_3 were determined, but detailed analysis of the low-temperature magnetization behavior is beyond the scope of this paper. Here, let us consider the Bloch constant $B = a_1/a_0$. For the initial $(Co_{88}P_{12})_{80}/Cu_{20}$ composite powder, this quantity amounts to $B = 6.5 \times 10^{-6}$ K$^{-3/2}$. In the course of milling, this value is almost doubled to reach $B = 13.9 \times 10^{-6}$ K$^{-3/2}$ at $t_m = 1$ h (further milling does not significantly change this value: $B = 14.7 \times 10^{-6}$ K$^{-3/2}$ at $t_m = 4$ h). For the initial $(Co_{88}P_{12})_{50}/Cu_{50}$ composite powder, the Bloch constant also equals $B = 6.5 \times 10^{-6}$ K$^{-3/2}$. In the course of milling, this value first exhibits a sevenfold growth to reach $B = 43.3 \times 10^{-6}$ K$^{-3/2}$ at $t_m = 2$ h and then varies only slightly to reach $B = 48.4 \times 10^{-6}$ K$^{-3/2}$ at $t_m = 4$ h. Since the magnitude of the exchange coupling constant A (determining the B value) is related to the nearest environment of Co atoms, the changes in B observed for the composite powders during the initial milling for 1–2 h are naturally attributed to the formation of Co–Cu solid solutions.

According to the published data on the mechanical alloying of Co and Cu, the characteristic times of milling after which the formation of a Co–Cu solid solution takes place amount to ~20 h and above [5–8]. The new method proposed in this paper allows the solid solution to be obtained after milling for $t_m = 2$–3 h, which significantly reduces the energy consumption for the mechanical alloying of Co and Cu.

REFERENCES

1. S. D. Kaloshkin, I. A. Tomilin, E. V. Shelekhov, *et al.*, Fiz. Met. Metalloved. **84** (3), 68 (1997).
2. H. Errahmani, N. Hassanain, A. Berrada, *et al.*, J. Magn. Magn. Mater. **241**, 335 (2002).
3. J. R. Childress and C. L. Chien, Phys. Rev. B **43**, 8089 (1991).
4. P. Panissod, M. Malinowska, E. Jedryka, *et al.*, Phys. Rev. B **63**, 014408 (2000).
5. C. Gente, M. Oehring, and R. Bormann, Phys. Rev. B **48**, 13244 (1993).
6. M. A. Uimin, A. Ye. Yermakov, V. V. Serikov, *et al.*, Phys. Status Solidi A **165**, 337 (1998).
7. J. Y. Huang, Y. K. Wu, A. Q. He, *et al.*, Nanostruct. Mater. **4**, 293 (1994).
8. Y. Ueda, S. Ikeda, and S. Chikazawa, Jpn. J. Appl. Phys. **35**, 3414 (1996).
9. R. S. Iskhakov, L. A. Chekanova, and E. A. Denisova, Fiz. Tverd. Tela (St. Petersburg) **41**, 464 (1999) [Phys. Solid State **41**, 416 (1999)].
10. R. S. Iskhakov, G. V. Popov, and M. M. Karpenko, Fiz. Met. Metalloved. **56** (1), 85 (1983).
11. S. V. Vonsovskiĭ, *Magnetism* (Nauka, Moscow, 1971; Wiley, New York, 1974).

Translated by P. Pozdeev