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Evolution of the Structure and Magnetic Properties of Composite Powder Co–Cu during Mechanical Alloying

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Abstract

Comparative investigation of the process of mechanochemical preparation of supersaturated solid solutions is carried out with the composite powders $(\mathrm{Co{-}P})_{100-x}/\mathrm{Cu}_x$, which are fine particles with the nucleus composed of amorphous $\mathrm{Co_{88}P_{12}}$ alloy or crystal alloy $\mathrm{Co_{95}P_5}$ coated with a copper layer, and a mixture of Co–P and Cu powders. The changes in structural and phase state of the powders during mechanical alloying are investigated by means of electron microscopy, X-ray diffraction, magnetic measurements and NMR spectroscopy. It is shown that mechanical alloying (MA) of the powder of composite particles with amorphous nuclei proceeds much more rapidly than with a similar powder with crystalline nuclei or mechanical mixtures of Co and Cu powders. It is established that MA in Co–P/Cu system with the mass concentration of copper 20 % (a thin Cu coating) passes through amorphization stage. In the case of composite powders $(\mathrm{Co_{88}P_{12}})_{50}/\mathrm{Cu}_{50}$ (with an increased thickness of Cu coating) crystallization of the Co–P nucleus is observed at the start of MA process, then the formation of equimolar supersaturated solid solution occurs.

INTRODUCTION

Intense development of mechanochemical synthesis of inorganic compounds, intermetallides and alloys is connected with successful investigation of the new classes of materials (amorphous alloys, nanocrystalline materials, *etc.*). When obtaining these materials with the required set of physical characteristics, it is important not only to synthesize a compound with definite chemical composition but also to form its structure purposefully. Mechanochemical methods allow one to achieve this goal. Treatment of ultrafine powders in the mills of different kinds allows one to obtain metastable phases with unique characteristics by varying the energy saturation of the system; this is often impossible when the alloys are prepared using other methods. In particular, mechanical alloying (MA) is carried out even in the systems with positive enthalpy of mixing, such as Fe–Cu, Ag–Cu, Co–Cu alloys. For instance, the Co–Cu system does not form intermetallic compounds and is characterized by negligibly low mutual solubility in the equilibrium state at temperatures below 600 °C, because it possesses large positive enthalpy of mixing (H_{mix} = 12 kJ/mol for the 50 : 50 ratio according to Miedema model [1]). The concentration range within which the formation of solid solutions is possible according to the equilibrium phase diagrams is very limited in these systems. For example, under the equilibrium conditions the solubility of copper in cobalt is about 12 at.% at 1170 °C, while that of cobalt in copper is about 8 at.% at 1090 °C. Metastable solid solutions of different concentrations (up to 50 at.%) with the crystallite size 5 to 20 nm and the level of excess energy up to 10 kJ/mol were obtained in a number of works [2–5] by means of mechanical alloying for 20–50 h (depending on activator capacity) of metallurgical Co and Cu powders (particle size 70–150 μm). In the investigations listed above, substantial consumption of mechanical work or grinding time is connected with the development of the interphase surface of contacts between particles in the reaction mixture. Indeed, mutual penetration of the atoms starts at the component contact surface, so the formation of the surface between phases (interface) is one of the important factors at the initial stage of reaction. It should be noted that a large contact surface may be created as a result of preliminary coating of the particles of one metal with another one. A similar idea was put forward in [6]; the authors used the powders of high-melting and low-melting elements. The contact surface was created during MA as a result of wetting the particles of the high-melting metal with the melt of a low-melting one as early as at the initial stages of MA. Unfortunately, this approach may be applied only to the systems containing a low-melting component. We tried to eliminate this limitation using chemical deposition at the preliminary stage to coat the particles of one reagent with a thin layer of another one. In the present work fine powders of composite particles were used as the initial reagent; particle nuclei were composed of Co–P alloy (either amorphous or crystal), coated with copper layer. So, a large contact surface was formed before the start of MA process; this had to accelerate the formation of Co–Cu metastable solid solution.

EXPERIMENTAL

The powders of all the compositions were obtained by means of chemical deposition based on metal reduction from aqueous solutions of the corresponding salts [7]. Sodium hypophosphite NaH_2PO_2 was used as a reducing agent to obtain cobalt alloys. Attention should be paid to one important feature inherent in the method of chemical deposition of metal powders and coatings with the help of hypophosphite: reduction of hypophosphite to elemental phosphorus always occurs simultaneously with metal reduction. So, a definite phosphorus admixture is always present in the resulting metal deposits. Phosphorus content depends on many factors: pH of solution, concentrations of the major reagents (hypophosphite and metal salt) and auxiliary ones (complex-forming, buffering and stabilizing additives).

When obtaining a set of $(Co{-}P)_{100-x}/Cu_x$ powders, the nucleus composed of crystal $Co_{95}P_5$ or amorphous $Co_{88}P_{12}$ was covered with a crystalline copper of different thickness. In the solutions of chemical plating for depositing a copper coating on Co–P powders, formaldehyde was used as a reducing agent; this is the only reducer that catalyses reduction of Cu^{2+} ions at room temperature.

Mechanical alloying was carried out in a ball planetary centrifugal mill AGO-2U with a volume of 150 cm^3. The cylinders and balls were made of stainless steel. Cylinder diameter was 70 mm, ball diameter was 4–5 mm. The mass of the substance loaded was 10 g, the mass of balls was 100 g. Reaction mixtures of the following composition were treated: a mechanical mixture of fine $Co_{88}P_{12}$ and Cu powders (50 : 50), fine powders of the composite particles $(Co_{95}P_5)_{50}/Cu_{50}$, $(Co_{88}P_{12})_{80}/Cu_{20}$ and $(Co_{88}P_{12})_{50}/Cu_{50}$. The material was sampled from the cylinders as the treatment of powders proceeded.

In order to determine the atomic structure of alloys obtained during mechanical activation of the powders, diffraction studies were carried out with DRON-3 diffractometer using CuK_α radiation. The morphology of powder particles was studied with JEM-100C electron microscope. The data on the field of local anisotropy $H_a = 2K/M_s$ (or on the constant of anisotropy K), as well as on the size of orientation-assigned region of anisotropy $2R_c$ were calculated from magnetization curves till saturation $M(H)$ [8] measured with a vibration magnitometer within the field range up to 14 kOe. Measurements of NMR spectra were carried out with a standard spin echo spectrometer within the frequency range 150–230 MHz at room temperature.

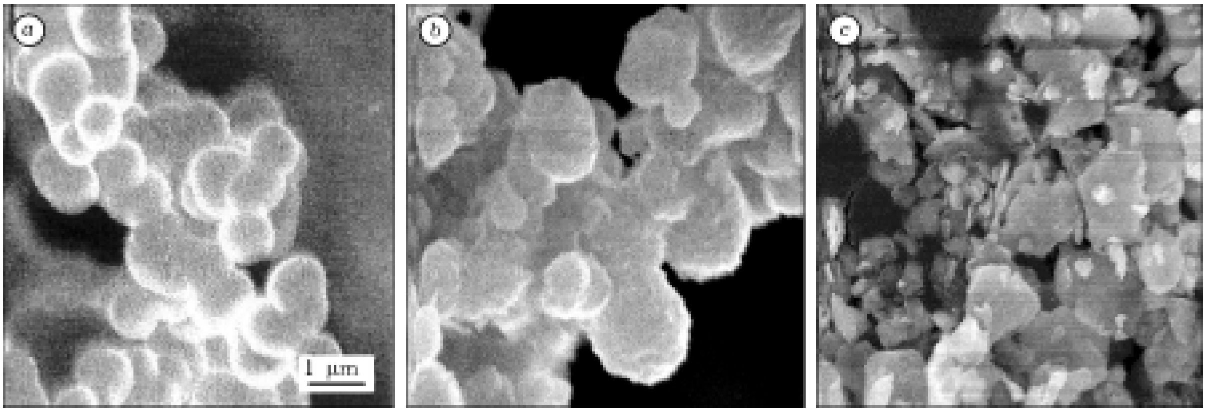

Fig. 1. Electron microscopic images of the initial powders of Co–P alloy (*a*), composite powders Co–P/Cu (*b*) and powders subjected to mechanical action (*c*).

RESULTS AND DISCUSSION

Electron microscopic images of the powders showed that the initial particles have a spherical shape for all the concentrations of phosphorus and copper. Typical electron microscopic images of the particles of initial powders of Co–P alloys, composite Co–P/Cu powders and mechanically treated powders are shown in Fig. 1.

The particle size distribution for Co–P powders showed that the size is within 0.1–1.0 μm. It was established that the mean particle size increased after copper coating was deposited. However, the width of the resulting size distribution did not change. The latter fact allowed us to estimate the thickness of Cu coating in the composite powders. It was established that the thickness of copper layer (depending on its content) varied from 0.03 μm for $Co–P_{80}/Cu_{20}$ powder to 0.2 μm for $Co–P_{10}/Cu_{90}$. Spherical powder particles became irregular and scaly during MA.

According to the data of X-ray structural analysis, a nucleus composed of $Co_{88}P_{12}$ alloy has an amorphous structure, that of $Co_{95}P_5$ alloy has a crystal hcp (hexagonal close packing) structure, the structure of copper coating is face-centered cubic (fcc). When a copper coating is deposited on a crystal Co–P nucleus with HCP structure, the coating conserves fcc structure inherent in copper. The diffraction patterns of all the samples of initial powders with composite particles almost coincide with the diffraction patterns of pure copper.

The spectra of X-ray diffraction of the initial reaction mixtures to be loaded into a ball mill and the spectra of samples taken after the corresponding time of mechanical action are shown in Fig. 2.

The results of X-ray structural analysis (see Fig. 2, *d*) show that no substantial changes of the atomic structure of initial elements occur in a mixture of Co and Cu powders after mechanical treatment for 2 h (curve *1*). For example, the amorphous Co–P alloy remains amorphous, diffraction peaks of Cu broaden, their angle coordinates change only insignificantly. For the treatment of powders of composite particles with nuclei of crystal $Co_{95}P_5$ coated with copper (curve *2*), changes in the lattice parameter of Cu are more noticeable. Quite a different situation is observed with the mechanical treatment of composite particles of amorphous cobalt with copper mass concentrations 20 and 50 %. As early as after 0.5 h grinding, substantial structural changes are observed. Amorphization of the composite occurs in the Co–P/Cu system with copper mass concentration of 20 % (see Fig. 2, *d*, curve *3*) after MA for 0.5–1 h. With an increase in treatment time to 2 h, the amorphous $(Co–P)_{80}/Cu_{20}$ composite crystallizes with the formation of a supersaturated solid solution with the mass concentration of copper in cobalt 20 %. In the case of composite $(Co_{88}P_{12})_{50}/Cu_{50}$ powders (see Fig. 2, *d*, curve *4*), the reaction course is different: at the start of mechanical alloying we observe crystallization of the Co–P curve; further treatment results in the formation of equimolar supersaturated solution. So, comparison of the X-ray diffraction spectra (see

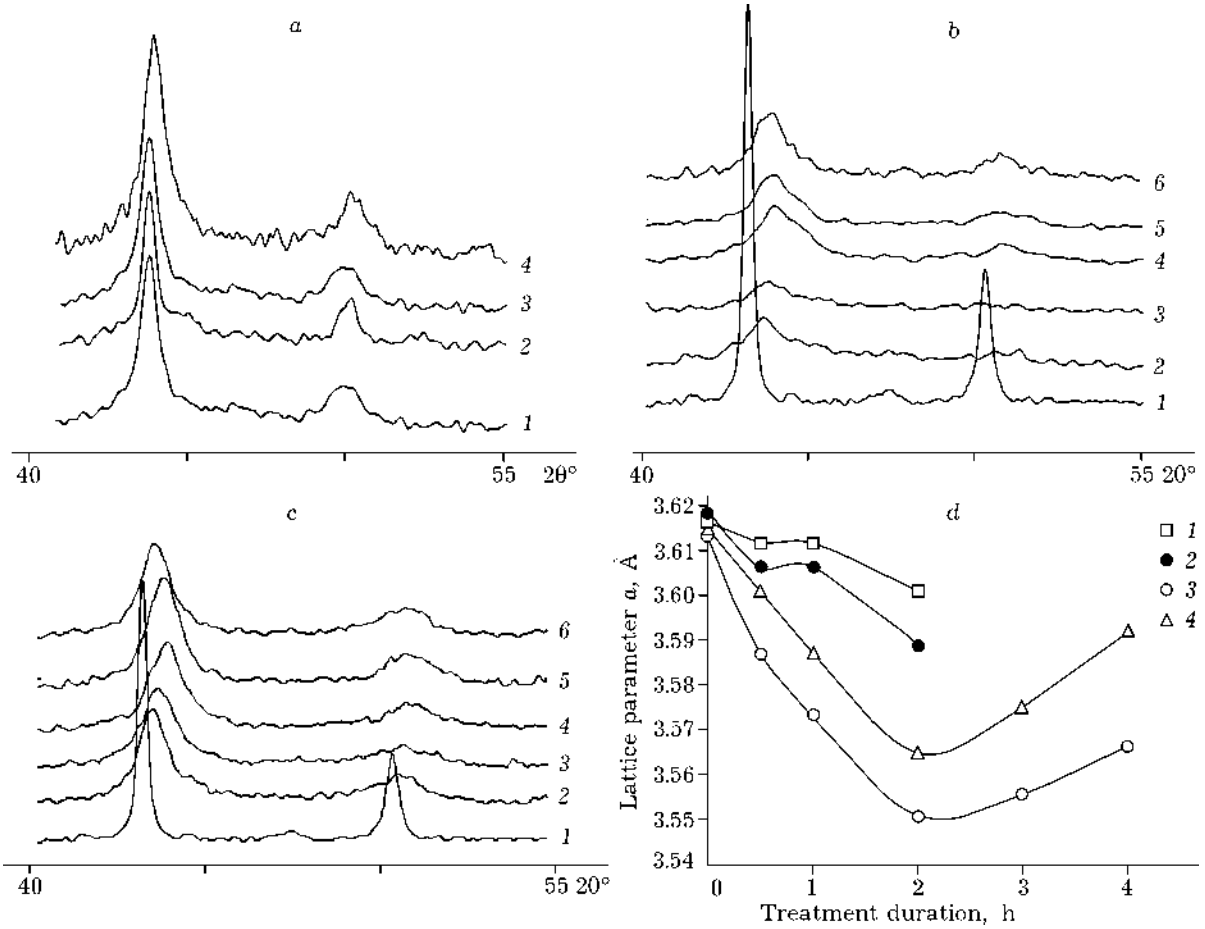

Fig. 2. Diffraction patterns of: *a* – a mixture of $Co_{88}P_{12}$ and Cu powders; *b* – composite powder $(Co_{88}P_{12})_{80}/Cu_{20}$; *c* – composite powder $(Co_{88}P_{12})_{50}/Cu_{50}$ at different stages of mechanical alloying; *d* – changes in the lattice parameter of copper during mechanical alloying; *1* – mixture of $Co_{88}P_{12}$ and Cu powders, *2–4* – composite powders $(Co_{95}P_{5})_{50}/Cu_{50}$, $(Co_{88}P_{12})_{80}/Cu_{20}$, $(Co_{88}P_{12})_{50}/Cu_{50}$), respectively; treatment time, h: initial (*1*), 0.5 (*2*), 1 (*3*), 2 (*4*), 3 (*5*), 4 (*6*).

Fig. 2, *d*) suggests that alloying of amorphous cobalt with copper occurs about two times as fast as that of crystal cobalt, that is, preliminary increase in energy saturation of the nucleus of a composite particle provides efficient acceleration of mechanical alloying. On the other hand, the same structural state is achieved in mechanical alloying of Co–Cu within much shorter time of mechanical action in the case of composite powders (even with the crystal nuclei) unlike the Co + Cu mixture.

So, MA of powders with modified particles for 2 and 3 h results in the solid solution Co–Cu, similar to the state obtained by treating a mixture of metallurgical powders of the elements for many hours [2, 4]. Thus, the basic physicochemical reason of the acceleration of mechanical alloying of powders of composite particles is the presence of interface of the components to be alloyed and high energy saturation of one of them.

However, according to the newest opinion, the data of X-ray diffraction cannot serve as an indisputable confirmation of the formation of chemically uniform solid solutions in a system of mutually insoluble components. Indeed, changes in the interplanar distances, observed in the diffraction patterns, can be due either to the formation of a solid solution or, for example, to coherent enrollment of the lattice of ultrafine particles of one pure component to the lattice of another element which is a matrix [3]. Because of this, in order to investigate the atomic structure of Co–Cu alloy, we also involved NMR and investigation of the field dependencies of magnetization *M*(*H*) allowing us to make conclusions about the short-range order and composition of the nearest surroundings of Co atoms.

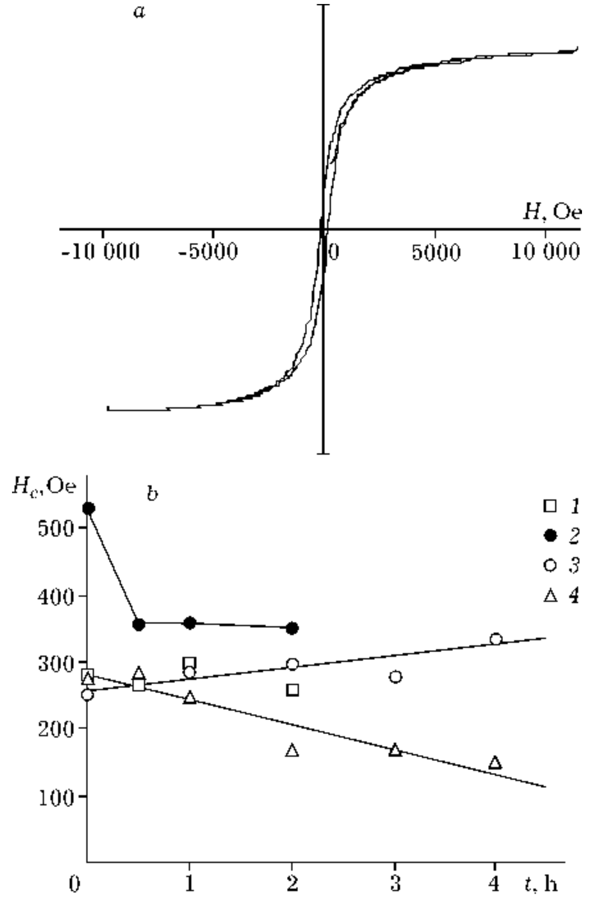

Fig. 3. Hysperesis loop for the composite $(Co_{88}P_{12})_{50}/Cu_{50}$ powder subjected to mechanical treatment for 2 h (*a*), and the dependence of coercive force on MA time (*b*): *1* – a mixture of Co and Cu powders; *2–4* – composite powders $(Co_{95}P_5)_{50}/Cu_{50}$, $(Co_{88}P_{12})_{80}/Cu_{20}$, $(Co_{88}P_{12})_{50}/Cu_{50}$, respectively.

The MA process has a substantial effect on magnetization curves of the powders under investigation. A typical hysteresis loop for the composite powder $(Co_{88}P_{12})_{50}/Cu_{50}$ subjected to mechanical treatment for 2 h is shown in Fig. 3, *a*. The dependence of coercive force on the time of MA is shown in Fig. 3, *b*. In this case, similarly to the interpretation of X-ray diffraction data, we compare the initial characteristics and their changes during MA of the composite powders $(Co_{88}P_{12})_{50}/Cu_{50}$ and $(Co_{88}P_{12})_{80}/Cu_{20}$ (composite particles with amorphous nuclei), $(Co_{95}P_5)_{50}/Cu_{50}$ (composite particles with the crystal nuclei possessing HCP structure), and a mixture of $(Co{-}P)_{am}$ and Cu powders. One can see in Fig. 3, *b* that coercive force before MA is determined by the structure of the magnetic component of the composite. During MA, coercivity of composite powders $(Co_{88}P_{12})_{50}/Cu_{50}$ and $(Co_{95}P_5)_{50}/Cu_{50}$ decreases, for $(Co_{88}P_{12})_{20}/Cu_{20}$ it increases, while for a mixture of $(Co{-}P)_{am}$ and Cu powders it remains almost unchanged. In our opinion, the most interesting observation is the difference in the behaviour of dependencies of coercive force on treatment time for composite powders $(Co_{88}P_{12})_{50}/Cu_{50}$ and $(Co_{88}P_{12})_{80}/Cu_{20}$. This difference reflects different routes of the formation of solid solution. For composite powders with copper mass concentration 20 %, as we have already shown above, the formation of alloy proceeds through amorphization stage. For powders with the mass concentration of copper 50 %, this stage is absent.

The powders under investigation belong to the class of nano-structured materials, that is, the size of characteristic structural and phase heterogeneities in them is of the order to several nanometers. Because of this, when interpreting the data on the approach of magnetization to saturation, we used special procedures developed for nano-structured magnetics [9].

Due to the chaotic distribution of the axis of local anisotropy and small size of heterogeneities with the conservation of strong exchange correlation in the spin system of a nanocrystalline ferromagnetic, new parameters arise; they are determined by the constant of exchange interaction A, constant of local anisotropy K and the region of its homogeneous orientation $2R_c$ [8]. Magnetic structure of nanocrystalline ferromagnetics can be represented as an assembly of stochastic domains (magnetic blocks) [9, 10]. Mean anisotropy $<K> \sim K^4 R_c^6 / A^3$ and correlation extension $R_f \sim A^2/(K^2 R_c^3)$ serve as the characteristics of these magnetic blocks.

For heterogeneous ferromagnetics characterized by local magnetic anisotropy of any origin and symmetry, the law of magnetization approaching saturation can be written down as

$$\langle M_z \rangle / M_s \approx 1 - d_m(H) \qquad (1)$$

where d_m is normalized mathematical dispersion of the transverse components of magnetization [10]. It was shown in [10] that the dependence of magnetization dispersion on field is:

$$d_m = (aH_a)^2 \begin{cases} H^{-2}, & H >> H_R \\ H^{-1/2} H_R^{-3/2}, & H << H_R \end{cases} \qquad (2)$$

Here H_a is the field of local anisotropy equal to $2K/M_s$; a is symmetry coefficient, which is equal to $1/15^{1/2}$ for a one-axis anisotropy; H_R is the correlation field equal to $2A/(M_s R_c^2)$; R_c is the correlation radium of anisotropy heterogeneities. In the coordinates lg d_m − lg H, this corresponds to a characteristic bend of the experimental $M(H)$ curve in the vicinity of $H \sim H_R$.

Dispersion of magnetization $d_m = \Delta M/M_s$ of the samples under investigation is shown in Fig. 4 in double logarithmic coordinates *versus* external magnetic field. The dependencies $\Delta M/M_s(H)$ are characterized by crossover of the curves from $\Delta M \sim H^{-2}$ to $\Delta M \sim H^{-1/2}$ in the region of H_R field. The dependencies of aH_a, R_c, $a\langle H_a\rangle \sim (aH_a)^4/H_R^3$ and R_f (calculated from experimental dependencies using the above equations) for the composite powder $(Co_{88}P_{12})_{50}/Cu_{50}$ on the time of mechanical action are shown in Fig. 5, *a*, *b*. One can see that the treatment of the powder in the planetary mill, as expected, resulted in a decrease in R_c, that is, in enhancement of structural disorder. The dependence of aH_a on the time of mechanical treatment has a more complicated character.

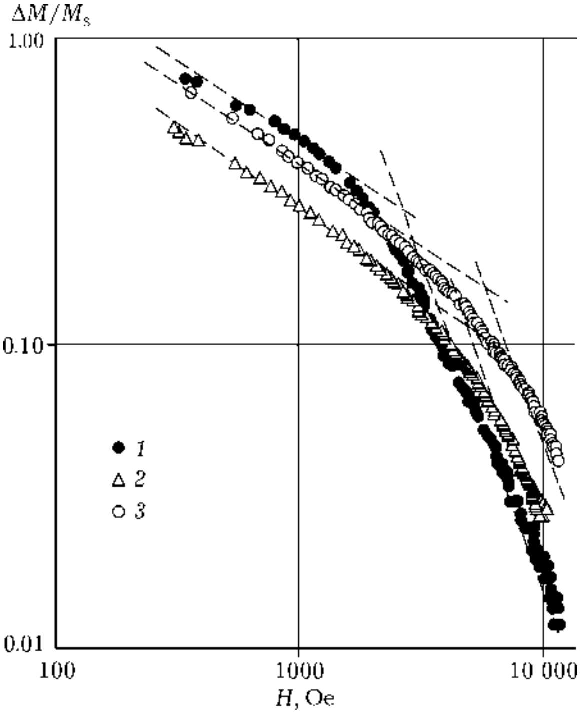

Fig. 4. Dispersion of magnetization d_m depending on the external field for the composite powder $(Co_{88}P_{12})_{50}/Cu_{50}$ before (*1*) and after MA for 2 (*2*) and 4 h (*3*).

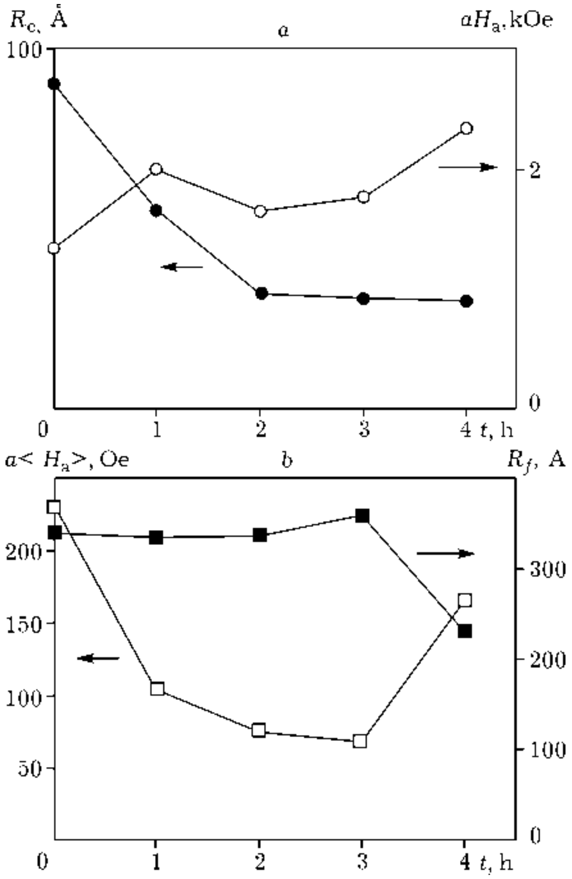

Fig. 5. Dependencies of aH_a and R_c (*a*) and $a\langle H_a\rangle$ and R_f (*b*) for the composite powder $(Co_{88}P_{12})_{50}/Cu_{50}$ on time of mechanical treatment.

The $a\langle H_a\rangle$ and R_f values depend at the same time on A, R_c and aH_a, or on experimentally recorded values H_R, aH_a. Analysis of the dependencies of $a\langle H_a\rangle$ and R_f on MA time taking into account the dependencies of R_c and aH_a (see Fig. 5, *b*) shows that changes in magnetic structure (characterized here by $a\langle H_a\rangle$ and R_f values) in the samples under investigation during the first two hours of treatment are determined by enhancement of structural disorder. An increase in the time of mechanical treatment causes modification of magnetic structure due to an increase in local magnetic anisotropy, which, as suggested by the X-ray diffraction data, accompanies phase layering (separation) process (and is likely to be due to it) in the composite powders under investigation.

The NMR spectrum of the initial powder $(Co_{88}P_{12})_{50}/Cu_{50}$, modification of the spectrum after MA for half and hour and 1 h, and the

NMR spectrum of this powder after treatment for 4 h followed by annealing at 500 °C for 1 h are shown in Fig. 6. The NMR spectrum for pure Co at room temperature can be characterized by two main NMR frequencies: 213.3 MHz for *fcc* Co and 221 MHz for hcp Co. The nearest surroundings of fcc and hcp cobalt contains 12 neighbours; equidistant satellites will be observed when magnetic atoms will be substituted with non-magnetic ones. Decomposition of the NMR spectrum of initial powder into satellites shows that Co atoms in the powder are characterized mainly by the fcc nearest surroundings with one and two non-magnetic neighbours (see Fig. 6, *a*). After mechanical action for only half an hour, substantial changes are observed in the NMR spectrum: the basic resonance is due to pure fcc Co, which points to crystallization of amorphous Co; a satellite of hcp surrounding of Co is formed (see Fig. 6, *b*). After treatment for an hour (see Fig. 6, *c*), total intensity of the signal increases but the shape of NMR spectrum points to the presence of a mixture of fcc and hcp surroundings of Co. After mechanical alloying for 2–4 h, the NMR signal at room temperature disappears due to substantial broadening of the lines and appears again only during annealing (500 °C, 1 h) (see Fig. 6, *d*). Now the NMR spectrum is described by a sum of two resonance lines; one of them corresponds to pure fcc Co (213.3 MHz), another (208 MHz) to the solid solution based on Co with HCP structure in which one non-magnetic atom is present in the first coordination sphere of Co atom. Since phosphorus atoms after annealing at 500 °C do not make any contribution into NMR spectrum due to the formation of Co_2P phosphide, it is evident that the role of non-magnetic neighbour in the surroundings of Co atom belongs to Cu atom, and the spectral line at the frequency of 208 MHz corresponds to the solid solution $Co_{92}Cu_8$ with HCP structure.

The NMR data presented here point to the polymorphous transformation of the nearest surroundings of Co (*fcc* → *hcp*) during mechanical alloying. These local martensite shifts may stimulate a substantial increase in the coefficients of heterodiffusion of the elements. Further, analysis of NMR spectrum admits the possibility of the formation of copper phosphide (Cu_2P) along with the formation of cobalt phosphide (Co_2P).

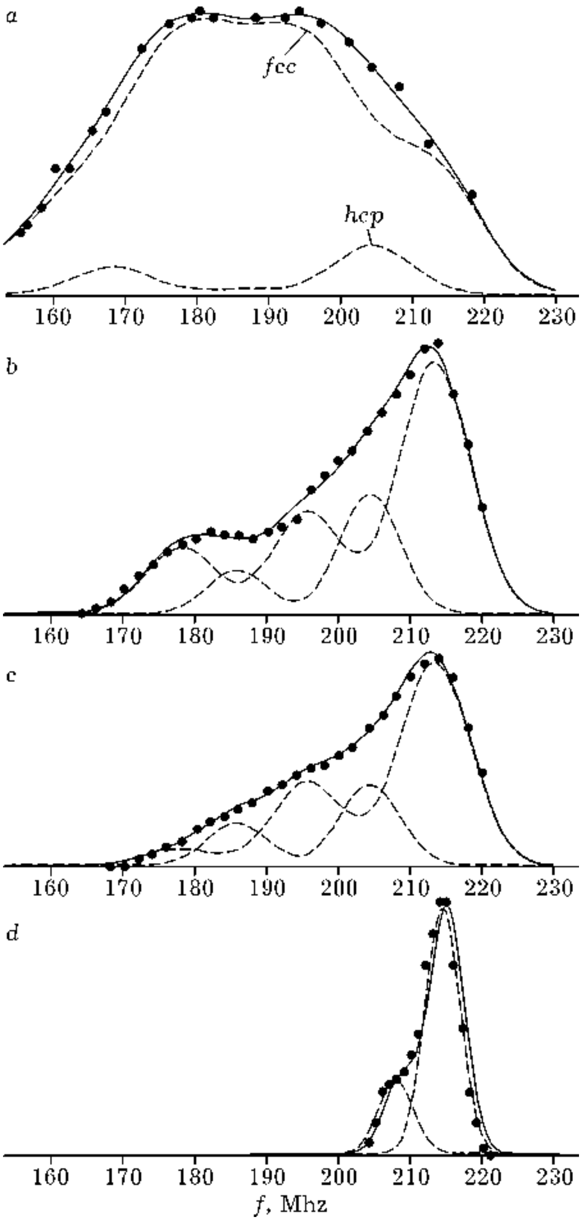

Fig. 6. NMR spectra of composite $(Co_{88}P_{12})_{50}/Cu_{50}$ powders: *a* – initial; *b* – after treatment for 0.5 h; *c* – after treatment for 1 h; *d* – after treatment for 4 h followed by annealing at a temperature of 500 °C.

CONCLUSIONS

It is established that mechanical alloying in the system Co–P/Cu with the mass concentration of copper 20 % proceeds through amorphization stage (treatment for 0.5–1 h).

With an increase in time of mechanical action to 2 h, composite amorphous $(Co{-}P)_{80}/Cu_{20}$ powder crystallizes with the formation of supersaturated solid solution with the mass concentration of copper in cobalt equal to 20 %. During mechanical synthesis of composite powders $(Co_{88}P_{12})_{50}/Cu_{50}$, at the verys tart of MA crystallization of the amorphous Co–P nucleus is observed; only after that MA causes the formation of equimolar supersaturated solid solution. The discovered difference is exhibited also in the behaviour of the dependencies of coercive force of the composite on the time of treatment in the planetary mill.

Comparative investigation of MA of supersaturated solid solutions from mixtures of Co–P and Cu powders and composite $(Co{-}P)_{100-x}/Cu_x$ powders showed that mechanical alloying of the composite powders with amorphous nuclei proceeds much more rapidly than that of similar powder with crystal nuclei, or mechanical mixtures of Co–P and Cu powders. So, the main physicochemical reason of acceleration of mechanical alloying of the powders with composite powders is the pre-existing large interface between the components to be alloyed and high energy saturation of one of the components.

Acknowledgement

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