

Structure and magnetic features of nanostructured Co-Cu alloys synthesized by new modification of mechanochemical synthesis

R. ISKHAKOV, E. DENISOVA*, L. KUZOVNIKOVA, S. KOMOGORTSEV, A. BALAEV, G. BONDARENKO^a
L. V. Kirensky Institute of Physics, Akademgorodok, 660036, Krasnoyarsk, Russia
^a*Institute of Chemistry and Chemical Technology SB RAS, Akademgorodok, 660036, Krasnoyarsk, Russia*

In this work we investigate metastable inhomogeneous Co-Cu alloy produced by new modification of mechanochemical synthesis. We use both convenient structural technique (X-ray diffraction) and magnetic measurements of $M(T)$ and $M(H)$ dependences to obtain additional information about the of mechanical alloying process.

(Received March 13, 2008; accepted May 5, 2008)

Keywords: Composite powder, High energy ball milling, Magnetic properties

1. Introduction

In recent 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 [1-8]. Although cobalt and copper are immiscible due to their positive heat of mixing, it has still been proved possible to alloy them by various techniques, an example are the vapor deposition, the magnetron sputtering [1-2] and prolonged grinding of metal powders in special ball mills (mechanical alloying) [3-6]. The method of mechanical alloying has drawn special attention of researchers due to 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 were obtained from mixtures of metallurgical Co and Cu powders. The characteristic times of the Co-Cu solid solution formation amount to ~ 20 h [3-6]. In our previous work [7-8] we proposed new technique allows the Co-Cu solid solution to be obtained after milling for 2–3 hours. As a precursors we use powders form composite Co/Cu core-shell particles where Co core is amorphous and Cu coatings is nanocrystalline [9-10]. Convenient structural techniques (such as X-ray diffraction) provide rather limited information about structure of such materials at the different steps of milling process. The X-ray diffraction peaks are attributed only to Cu-rich phase. To obtain information on Co-rich phase magnetic measurements are useful.

The aim of this work is to obtain additional information on Co-Cu alloy structure formed during ball-milling process by magnetometry measurements.

2. Experiment

The investigated samples were produced by mechanical alloying (MA) of composite particle powders in hermetically sealed stainless steel containers in a planetary ball mill (AGO-2U). The reaction mixture is composed of ultra fine amorphous $\text{Co}_{88}\text{P}_{12}$ and polycrystalline Cu powders (50:50)(2); ultra fine composite particle powders $(\text{Co}_{95}\text{P}_5)_{50}/\text{Cu}_{50}$ (3) and $(\text{Co}_{88}\text{P}_{12})_{100-x}/\text{Cu}_x$ ($20 < x < 90$ at. %)(1). The $(\text{CoP})_{100-x}/\text{Cu}_x$ composite particle powders (amorphous or crystalline Co-P alloy core coated by nanocrystalline copper shell) were obtained by chemical deposition of Cu coating to the core of Co-P particles produced by reduction of metals from aqueous solutions of the corresponding salts.

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. The structure of MA-treated powders was investigated by X-ray diffraction (XRD) using $\text{CuK}\alpha$ 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, a change in the interatomic 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 ultrafine particles of one component to the crystal lattice of another (matrix) component. For this reason, the atomic structure of the obtained Co-Cu alloy was additionally characterized using the magnetization measurements. These methods provide data on the short-range order and the environment of Co atoms in the crystal lattice and some information on superparamagnetic Co-rich nanoparticles formation. 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 50 kOe.

3. Results

X-ray. The structure evolution of prepared powders with alloying is studied by X-ray technique in detail in our recent paper [11]. As a result of this study the lattice parameter for Cu-rich phase with alloying is illustrated in Fig.1, which shows the change of the fcc lattice parameters for the reaction mixtures ((Co₈₈P₁₂)₅₀/Cu₅₀ (1); (Co₉₅P₅)₅₀/Cu₅₀ (3) composite particle powders and the mixture of ultrafine Co₈₈P₁₂ and Cu powders (2)) vs milling time. The 2-h processing of the mechanical mixture of Co₈₈P₁₂ and Cu powders (symbol 2 on Fig. 1) did not result in any significant structural changes. The milling of composite particle powders with the crystalline core results in more visible changes of lattice parameter with milling time.

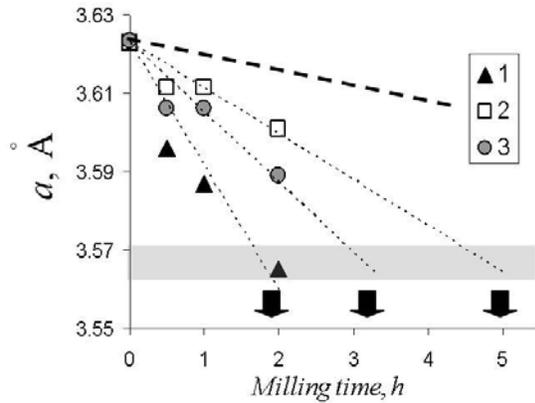


Fig. 1.

A different situation is observed in the course of milling of the composite particle powders with amorphous core (symbol 1 on Fig. 1). Here, even 0.5-h processing result in significant structural changes. The results of X-ray diffraction measurements summarized in Fig. 1 show that a 2-3-h milling of the composite powder renders the state of the Co-Cu solid solution. However there are reflexes only from nanocrystalline Cu shell on composite powders with amorphous Co-P core before milling. The milling process would proceed through formation two different phases: Cu – rich and Cu – poor. Information on fig.1 corresponds to the former Cu – rich phase. To obtain information on Cu – poor magnetic phase the investigation of magnetic properties were carried out.

Magnetic. The low-temperature magnetization curves (4.2 K and 200 K) and temperature dependence of magnetization (measured in H=20 kOe) for the composite particle powders are shown in Fig. 2, 3. There are two contributions in $M(T, H)$ curves. The first - ferromagnetic (high and temperature independent susceptibility in small fields in $M(H)$ curves and the small temperature gradient

and positive curvature in $M(T)$ curves for $T > 50$ K). The second contribution is superparamagnetic from ultra thin ferromagnetic clusters not coupled by exchange (hard saturation in 4.2 K and negative curvature from 20 to 50 K). The experimental $M(T, H)$ (Fig. 2, 3) curves were well fitted by the following expressions (Fig. 4):

$$M(T) = a_{T0} - a_{T1} \cdot T^{3/2} + a_{T2} \cdot L\left(\frac{a_{T3}}{T}\right), \quad (1)$$

$$M(H) = a_{H0} - a_{H1} \cdot H^{-2} + a_{H2} \cdot L\left(\frac{H}{a_{H3}}\right), \quad (2)$$

where $L(x) = \text{cth}(x) - 1/x$ is the Langevin function. The first two terms in these expressions, describing the magnetization dependence vs applied field and temperature for ferromagnetic phase where $a_{T0} \approx a_{H0} = M_f v_f$; $a_{T1} = M_f v_f B$; $a_{H1} = M_f v_f H_{fa}^2 / 15$. Here 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 , H_{fa} is the local magnetic anisotropy field. The third term in (1) and (2) describes a decrease in the magnetic susceptibility of the superparamagnetic phase that corresponds to the Langevin law where $a_{T2} \approx a_{H2} = M_{sp} v_{sp}$;

$a_{T3} \equiv M_{sp} H V_{sp} / k_B$; $a_{H3} = k_B T / M_{sp} V_{sp}$. Here M_{sp} is the average 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. The values of fitting parameters were used to determine the values of average physical properties: Bloch constant $B = a_{T1} / a_{T0}$, local magnetic anisotropy field in ferromagnetic phase $H_{fa} = (15 a_{H1} / a_{H0})^{1/2}$, the number of superparamagnetic particles per unit volume $n_{sp} = a_{H2} \cdot a_{H3} / k_B T$, the absolute value of magnetization per gram Co $M_{tot} = M_{sp} v_{sp} + M_f v_f = a_{H0} + a_{H2}$ taking into account both ferromagnetic and superparamagnetic phases. The blocking temperature T_B was estimated in following way. At the some temperature near the liquid helium temperature the curvature sign of $M(T)$ curve is changed from positive (Blocking state) to negative (superparamagnetic state). We accept this temperature as the estimation of blocking temperature (insert in Fig. 4). Using blocking temperature in the form

$T_B = H_{sp_a} M_{sp} V_{sp} / k_B 50$ (where H_{sp_a} is the local magnetic anisotropy field in superparamagnetic particle) and the value of magnetic moment in superparamagnetic particle ($M_{sp} V_{sp} = k_B T / a_{H3}$) the value of H_{sp_a} is determined as $H_{sp_a} = 50 T_B a_{H3} / T$.

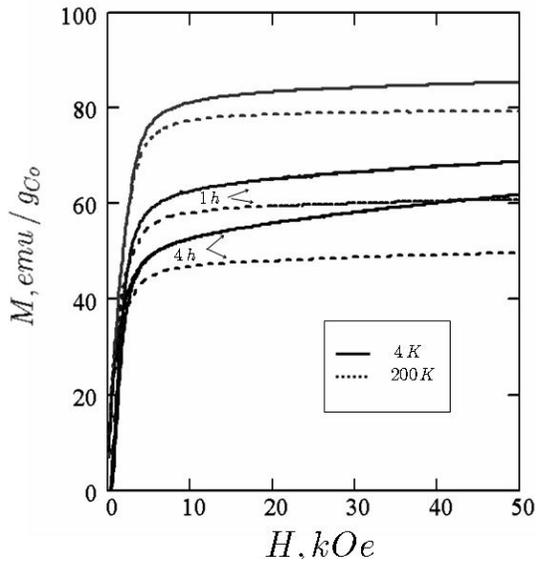


Fig. 2a.

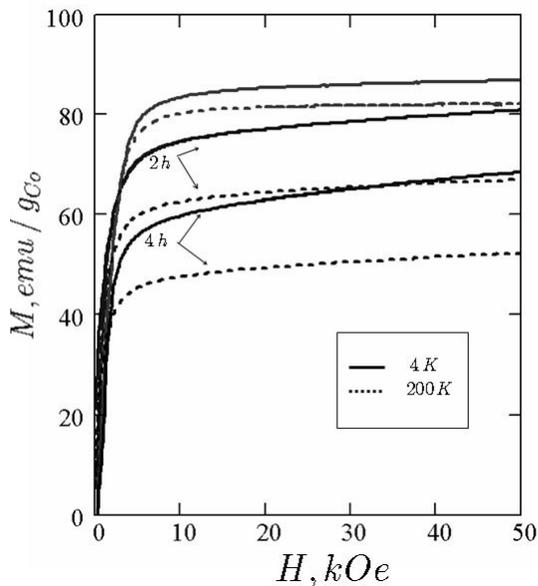


Fig. 2b.

The calculated M_{tot} and other magnetic constants for the composite particle powders milled at different times are given in the table both for ferromagnetic (H_f , B) and for superparamagnetic (T_B , n_{sp} , H_{sp_a}) phases.

In the course of milling, the value B for the initial $(Co_{88}P_{12})_{80}/Cu_{20}$ composite particle powder is almost doubled at $t_m = 1$ h (further milling does not significantly change this value). For the initial $(Co_{88}P_{12})_{50}/Cu_{50}$ composite particle powder, the Bloch constant in the course of milling exhibits a sevenfold growth at $t_m = 2$ h and then varies only slightly 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.

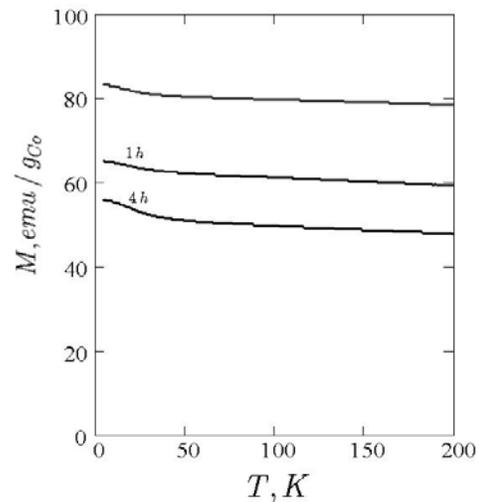


Fig. 3a.

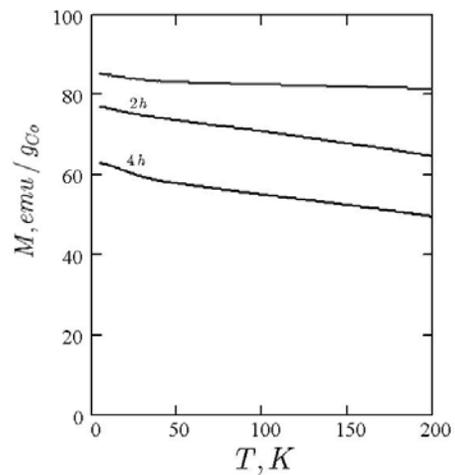


Fig. 3b.

Table.

	Ferromagnetic phase			Superparamagnetic phase		
	M_{tot} , emu/g_{Co}	B , $10^{-6} K^{-3/2}$	H_{fa} , kOe	T_B , K	n_{sp} , $10^{14} cm^{-3}$	H_{spa} , kOe
$(Co_{88}P_{12})_{50}/Cu_{50}$	88	6.5	5.16	14.0	0.50	2.53
2h	86	43.3	4.60	12.0	2.57	3.43
4h	78	48.4	4.91	19.1	4.38	5.91
$(Co_{88}P_{12})_{80}/Cu_{20}$	87	6.5	5.11	15.5	1.10	2.64
1h	74	13.9	5.19	11.6	3.75	3.18
4h	72	14.7	5.15	18.5	7.48	5.73

The absolute value of magnetization per gram Co reveals decreasing with milling. For the initial $(Co_{88}P_{12})_{80}/Cu_{20}$ and $(Co_{88}P_{12})_{50}/Cu_{50}$ composite particle powder magnetization per gram Co are well corresponded with magnetization of amorphous $Co_{88}P_{12}$ powders [9-10]. Decreasing magnetization with milling is result from both recrystallization of amorphous $Co_{88}P_{12}$ to fcc $Co + Co_2P$ [12] and Co-Cu solid solution formation. Decreasing magnetization from recrystallization of amorphous $Co_{88}P_{12}$ would be no more than 5 emu/g_{Co} . Thus observing lack of magnetization about 10÷14 emu/g_{Co} is the evidence of Co-Cu solid solutions too.

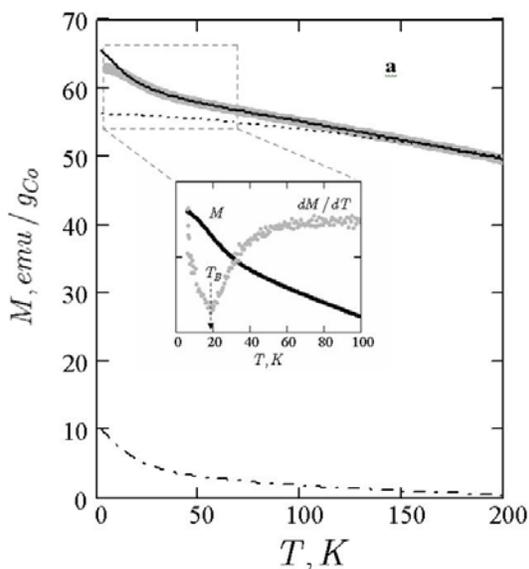


Fig. 4a.

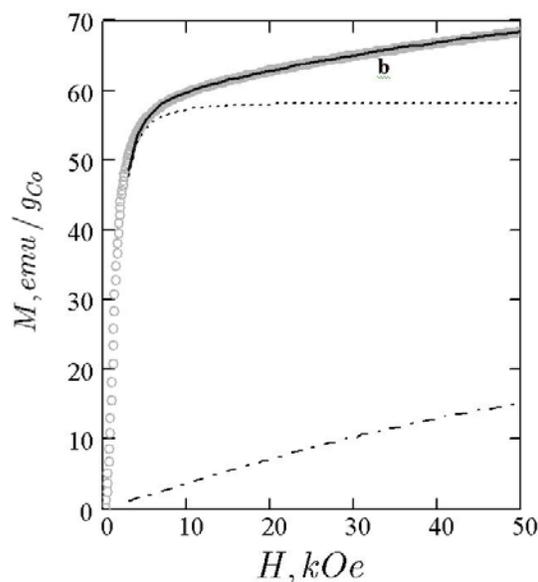


Fig. 4b.

The value of H_{fa} with milling is changed slightly. The value of T_B varies nonmonotonously. The milling of $(Co_{88}P_{12})_{50}/Cu_{50}$ composite particle powder during 2 hours results in decreasing T_B by 2 K and further milling during 4 hours results in increase it by 7 K. The milling of $(Co_{88}P_{12})_{80}/Cu_{20}$ composite particle powder during 1 hour results in decreasing T_B by 4 K and further milling during 4 hours results in increase it by 7 K. The value of n_{sp} is significantly increased in the course of milling process. The volume concentration of superparamagnetic particles n_{sp} for $(Co_{88}P_{12})_{80}/Cu_{20}$ composite particle powder both before and after milling is more than n_{sp} for

(Co₈₈P₁₂)₅₀/Cu₅₀. We suppose that it is result from the buffer function of copper with more plastic than cobalt. The copper makes the grinding process of Co slower and thus more Cu in composite particle powder results in pure grinding of Co clusters. The value of T_B varies slowly in comparison with n_{sp} . This means that during milling process the superparamagnetic clusters with approximately equal size are broke off from the coarse magnetic particles. The local magnetic anisotropy field of superparamagnetic particles H_{sp_a} is twice smaller than magnetic anisotropy in ferromagnetic phase H_{f_a} but it is increased with milling and reached the same value as in ferromagnetic particles.

In summary we investigate metastable inhomogeneous Co-Cu alloy produced by new modification of mechanochemical synthesis. 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. New information on magnetic anisotropy, blocking temperature and concentration of superparamagnetic particles formed during the milling process is obtained.

This work was supported by the RFBR and KRSF, project no.07-03-96808.

- Rev. B **63**, 014408 (2000).
- [3] C. Gente, M. Oehring, R. Bormann, Phys. Rev. B **48**, 13244 (1993).
- [4] M. A. Uimin, A. Ye. Yermakov, V. V. Serikov, *et al.*, Phys. Status Solidi A **165**, 337 (1998).
- [5] J. Y. Huang, Y. K. Wu, A. Q. He, *et al.*, Nanostruct. Mater. **4**, 293 (1994).
- [6] Y. Ueda, S. Ikeda, and S. Chikazawa, Jpn. J. Appl. Phys. **35**, 3414 (1996).
- [7] R. S. Iskhakov, L. A. Kuzovnikova, S. V. Komogortsev, E. A. Denisova, A. D. Balaev, V. K. Mal'tsev, G. N. Bondarenko, Technical Physics Letters, **30**, 60 (2004).
- [8] R. S. Iskhakov, L. A. Kuzovnikova, S. V. Komogortsev, E. A. Denisova, A. D. Balaev, G. N. Bondarenko, The Physics of Metals and Metallography, **102** S66 (2006).
- [9] R. S. Iskhakov, E. A. Denisova, L. A. Chekanova, IEEE Trans. Magn, **33** 3730 (1997).
- [10] R. S. Iskhakov, L. A. Chekanova, E. A. Denisova, Phys. Solid State, **41**, 416 (1999).
- [11] R. S. Iskhakov, L. A. Kuzovnikova, S. V. Komogortsev, E. A. Denisova, V. K. Mal'tsev, G. N. Bondarenko, Chemistry for Sustainable Development **2**, 209 (2005).
- [12] R. S. Iskhakov, G. V. Popov, M. M. Karpenko, Fiz. Met. Metalloved. **56** (1), 85 (1983).

*Corresponding author: rauf@iph.krasn.ru

References

- [1] J. R. Childress, C. L. Chien, Phys. Rev. B **43**, 8089 (1991).
- [2] P. Panissod, M. Malinowska, E. Jedryka, *et al.*, Phys.