

UDC 54.03, 538.995, 539.89

DOI: 10.15372/CSD20180507

Modification of the Structure and Magnetic Properties of $\text{Al}_2\text{O}_3/\text{Co(P)}$ Composite Particles during Mechanical Activation

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Abstract

Changing the structure and magnetic properties of composite $\text{Al}_2\text{O}_3/\text{Co(P)}$ particles was investigated in a ball mill. The initial particles were produced by electroless plating of the crystal Co_{95}P_5 shell characterized by the hexagonal dense packed structure into Al_2O_3 granules by chemical reduction. It was determined that the sequences of phase transitions during mechanoactivation was different for Co_{95}P_5 particles and composite $\text{Al}_2\text{O}_3/\text{Co}_{95}\text{P}_5$ species. The use of composite particles allows significantly reducing mechanoactivation time required for producing the optimum phase ratio of α/β cobalt in powders. Grain size reduction during milling causes an increase in the fraction of superparamagnetic particles reaching 12 % upon mechanical activation for 75 min, which causes a decrease in the value of saturation magnetization. Changing the magnetic properties of composite particles during ball milling correlates with structural modification of samples. The amount of the hexagonal dense packed cobalt phase in the sample determines the value of the field of local magnetic anisotropy. The latter is reduced from 8.4 to 3.8 kOe upon an increase in mechanoactivation time to 75 min.

Key words: composite particles, mechanoactivation, magnetic properties

INTRODUCTION

Cermets manufactured by powder metallurgy methods are uniformly distributed ferromagnetic particles in the oxide matrix. The former attract researchers attention due to their unique combination of magnetic and mechanical properties, such as microwave absorption, giant magnetoresistance, catalytic properties with preservation of mechanical properties of oxide ceramics [1–3]. In recent decades, more and more attention is drawn to nanostructured materials, in which it is possible to implement additional opportunities to im-

prove useful properties due to high dispersion (below 100 nm) of phases and crystallites. For example, the required mechanical properties (microhardness and strength) may be reached by introducing cobalt nanoparticles with a certain ratio of α/β phases into the oxide matrix [4, 5].

Cermets are traditionally made by the mixing of metal and oxide particles followed by pressing and high-temperature annealing [6], which limits an opportunity to preserve the nanostructure. Mechanical activation and mechanical alloying in high-energy mills are the most promising methods to produce non-equilibrium structures

in solids, such as amorphous and nanostructured alloys, metastable supersaturated solid solutions, and others [7]. Nevertheless, in order to make cermets by mechanochemical synthesis, processing in a high-energy mill-activator for a long time (16–20 h) is required.

We have earlier proposed a method to accelerate the formation of a supersaturated solid solution in systems with a positive enthalpy of mixing through the use of composite core-shell particles as initial ones for the mechanical alloying process [8]. This research work used a similar approach to reach the optimum α/β ratio of cobalt phases with the minimum processing time in the mill. In other words, unlike the ordinary way of mechanical activation of a mixture of Al_2O_3 and Co(P) powders, we use composite $\text{Al}_2\text{O}_3/\text{Co(P)}$ particles to reduce mechanical activation time.

In the present work, we report on the evolution of structural and magnetic properties of $\text{Al}_2\text{O}_3/\text{Co(P)}$ composite particles during ball milling

geneous Co_{95}P_5 powders were produced from the same solution.

Mechanoactivation was carried out in an AGO-2U planetary ball mill. The diameter of the drums and working space volume were 70 mm and 150 cm^3 , respectively. The drums and the balls were made of stainless steel and the ball-to-powder ratio was 20 : 1. Processing was interrupted in regular intervals and a material sample was removed for analysis.

In order to determine the atomic structure of alloys produced during mechanoactivation of these powders, diffraction research was carried using the DRONE-4 X-ray diffractometer with CuK_α radiation. The morphology of powder particles was investigated by JEM-100C and Hitachi T3000 scanning electron microscopes with an energy-dispersive device. Information about the magnitude of the local magnetic anisotropy field $H_A = 2K/M_S$ (or the constant of anisotropy, K), and also the size of orientation-assigned region of anisotropy $2R_C$ were calculated from magnetization curves till saturation $M(H)$ [8] measured on a vibrating sample magnetometer in the range of fields up to 14 kOe. In order to assess the phase composition of a ferromagnetic alloy, a method based on measurements of magnetization dependences *versus* temperature and external field was used [10].

MATERIALS AND METHODS

Composite $\text{Al}_2\text{O}_3/\text{Co(P)}$ particles used as initial ones for mechanoactivation are the core of granules of Al_2O_3 (50 mass %) surrounded by a shell of Co_{95}P_5 alloy particles. The explosive method was used to make Al_2O_3 granules with an average diameter of 370 nm [5]. Co_{95}P_5 particles were immobilized on the surface of the granules by electroless plating based on the reaction of metal reduction from aqueous solutions of the corresponding salts [9]. The plating bath was comprised of source metal ion (25 g/L CoSO_4), metal chelator (90 g/L $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$), pH stabilizer (42 g/L $(\text{NH}_4)_2\text{SO}_4$ buffer solution), and reducing agent (50 g/L NaPO_2H_2). The required pH level was maintained by adding NaOH solution. In order to identify the effect of Al_2O_3 on the mechanical activation process, homo-

RESULTS AND DISCUSSION

As demonstrated by electron microscopic images of the powders, the initial particles are spherical in shape (Fig. 1). It can be seen that mechanically processed $\text{Al}_2\text{O}_3/\text{Co}_{95}\text{P}_5$ powders are comprised of spherical large particles with a diameter of 150–400 nm. Small spherical particles are located on the surface of large species. The average size of Co_{95}P_5 particles immobilized on the surface of Al_2O_3 of granules is 50 nm.

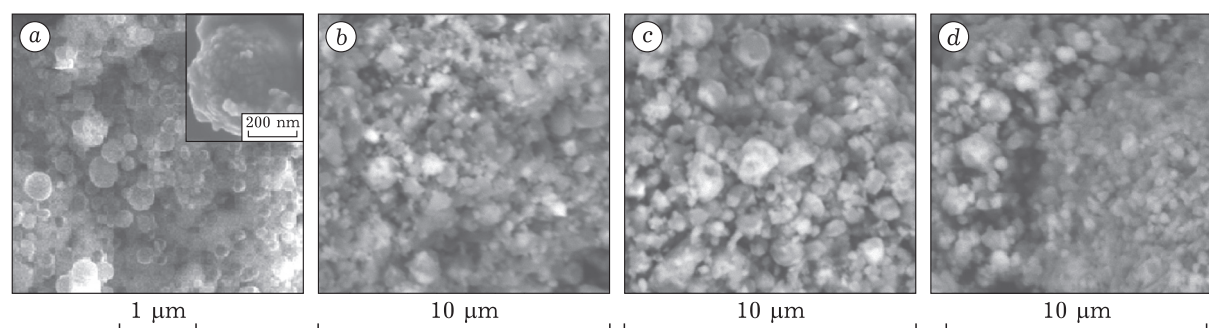


Fig. 1. SEM of initial composite $\text{Al}_2\text{O}_3/\text{Co}_{95}\text{P}_5$ particles (a) and those after MA for 15 (b), 45 (c) and 75 min (d): a – the inset shows a separate Al_2O_3 granule with Co_{95}P_5 particles immobilized on its surface.

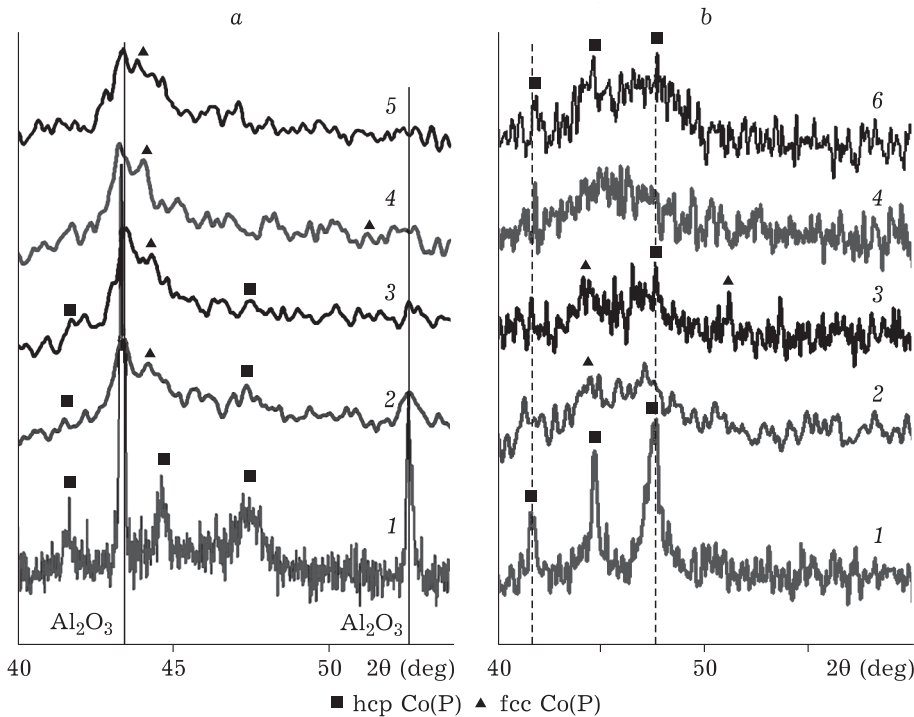


Fig. 2. XRD spectra of Al₂O₃/Co₉₅P₅ (a) and Co₉₅P₅ (b) powders: 1 – initial, 2–6 – after MA within 15 (2), 30 (3), 60 (4), 75 (5), and 90 min (6).

Spherical powder particles are plastically deformed during mechanical alloying. They acquire the irregular shape, while larger particles break up. Mechanical processing within 45 min leads to an increase in the average particle size from 0.2 to 0.4 μm with a wider particle size distribution. When the mechanical processing time is further increased, the fraction of particles with sizes below 100 nm is scaled up. According to energy-dispersive analysis data, regardless of size, each particle contains both Al₂O₃ and Co(P).

Figure 2 presents X-ray diffraction spectra of the initial Co₉₅P₅ and Al₂O₃/Co₉₅P₅ powders and samples after different mechanical activation times. X-ray diffraction patterns of composite Al₂O₃/Co(P) powders and homogeneous Co₉₅P₅ ones are characterized by a set of reflexes, indicating the hexagonal close-packed hcp Co(P) structure of powder particles. A broadening of reflexes with an increase in mechanical activation time is caused by reduced grain size and enhanced microdeformation level. As demonstrated by X-ray structural analysis data, during mechanical processing, Co₉₅P₅ powders undergo the following transformations: hcp Co(P) \rightarrow fcc Co(P) \rightarrow amorphous state \rightarrow hcp Co(P) after 30, 60, and 90 min of milling, respectively. The milling of composite powders also results in transformation of hcp \rightarrow fcc Co phases (other authors have repeat-

edly observed this transformation [11, 12]). There is no step of complete amorphization of Co(P) alloy in all phase transformations during mechanical activation. Hard Al₂O₃ particles are likely to inhibit amorphous state formation.

Figure 3 gives field and temperature dependences of saturation magnetization. The course of the temperature dependence is well described by the equation:

$$M(T) = A(1 - BT^{3/2}) + CL(D/T)$$

where $M(T)$ is the magnetization of Al₂O₃/Co(P) particles at temperature T ; B is the Bloch constant and $L(x)$ is the Langevin function; $A = M_f V_f$, $C = M_{sp} V_{sp}$ and D are fitting parameters. The first term describes the contribution of the ferromagnetic phase, the second – from the superparamagnetic (SPM) phase consisting of Co(P) clusters not coupled by the exchange interaction. According to the fitting results, an increase in mechanical activation time from 15 to 75 min leads to an increase in the volume fraction of the SPM phase from 2 to 12 %, in other words, the number of particles with a size less than critical is increased. Apparently, this is what a decrease in saturation magnetization of Co(P) alloy with mechanical activation time for composite Al₂O₃/Co_{100-x}P_x powders is related to.

As demonstrated by analysis of curves of magnetization approximation to saturation, in high fields (greater than 5 kOe) for the initial powders

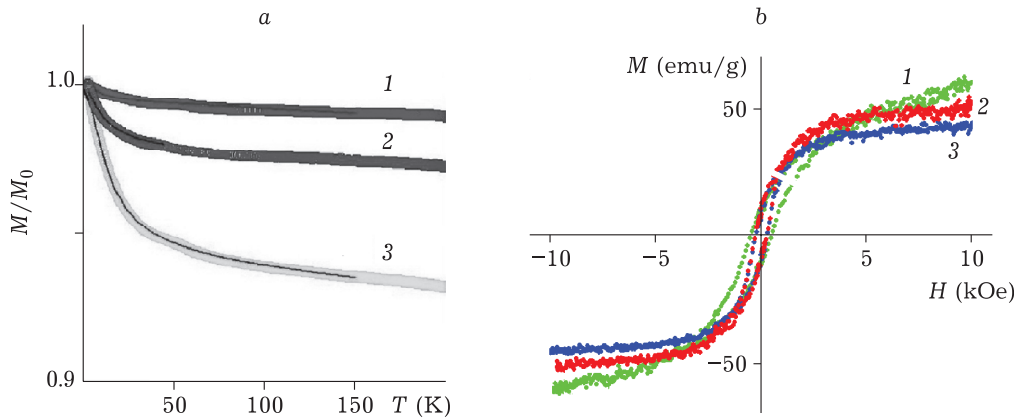


Fig. 3. Temperature (a) and field (b) dependences of saturation magnetization for initial composite particles (1) and after MA within 15 (2) and 75 min (3).

and samples exposed to different milling duration, magnetization curves follow well the law of Akulov ($\Delta M \sim H^{-2}$), and experience crossover ($\Delta M \sim H^{-0.5}$) in lesser fields. This allowed determining the value of the local magnetic anisotropy field, H_a and area size (radius) of its space correlation, R_C .

It was found that H_a was reduced from 8.4 to 3.8 kOe with an increase in mechanical activation time to 75 min. One may affirm that the dependence course of local anisotropy field *versus* milling time is determined by the phase transformation of the highly anisotropic hcp Co phase into the fcc one. The coercive force in the mechanical activation process is slightly decreased.

All the investigated samples are ferromagnetic. Therefore the use of magneto-structural and magneto-phase methods alongside with traditional diffraction techniques would allow gaining additional information regarding both the initial powders and processes occurring with the material during mechanoactivation.

Single-phase Co-P (hcp, fcc, and amorphous) alloys are characterized by the determined Bloch

constants (B_i) and local anisotropy field ($a_i H_{a_i}$ where a_i is symmetry coefficient), almost independent on composition. Therefore for powders of heterophase alloys, there may be recorded the following system of equations:

$$\begin{cases} x_{\text{hcp}} + x_{\text{fcc}} + x_A = 1 \\ B_1 x_{\text{hcp}} + B_2 x_{\text{fcc}} + B_3 x_A = B_{\text{eff}} \\ (a_1 H_{a1})^2 x_{\text{hcp}} + (a_2 H_{a2})^2 x_{\text{fcc}} + (a_3 H_{a3})^2 x_A = (a H_{a,\text{eff}})^2 \end{cases}$$

Solving it, one may determine the fractions of hcp, fcc, and amorphous phases for the investigated powders based on Co(P) alloy [10]. Figure 4, c presents the evolution of mixture phase composition computed based on equations data during mechanical activation. The initial Co(P) alloy both in case of composite particles and homogeneous powders is almost completely characterised by the hcp structure; fcc phase content is not higher than 0.5%.

All samples after mechanical activation (even for 15 min) are heterophasic, which is in agreement with XRD data. The proportion of the hcp

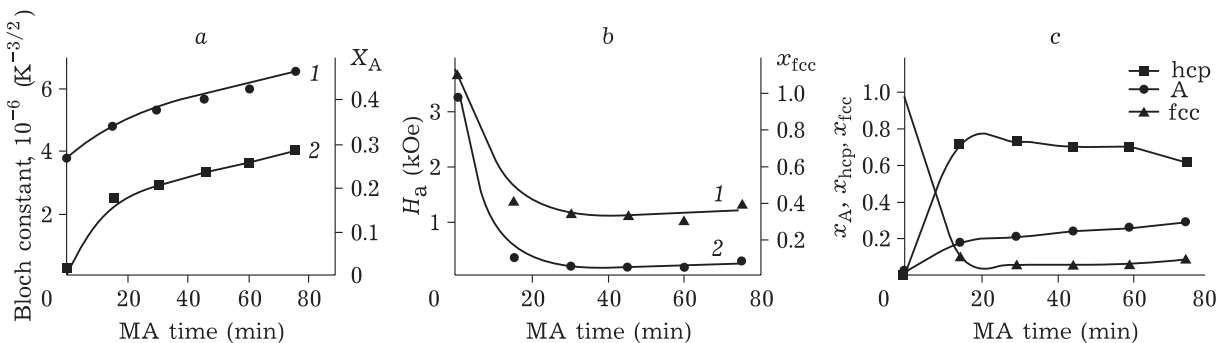


Fig. 4. Magnetic parameters *versus* mechanical activation time: a – Bloch constants and the volume fraction of the amorphous phase (x_A); b – local magnetic anisotropy field (H_a) and volume fraction of the hcp Co phase (x_{hcp}); c – Co(P) phase composition (x_A , x_{hcp} , and x_{fcc} are volume fractions of amorphous, hcp, and fcc phases, respectively).

fraction falls dramatically to 14 % and further, remaining almost constant upon an increase in grinding time after 15 min of mechanical activation. Amorphous phase content is increased to 60 % upon mechanical activation of composite particles.

Figure 4 *a, b* gives Bloch constant and amorphous phase content (x_A), and also the local anisotropy field and the Co hcp phase fraction (x_{hcp}) versus mechanical activation time. It can be seen that changing amorphous phase fraction in the composite powder determines the nature of this dependence. This is in agreement with the fact that the value of the Bloch constant of the amorphous phase is several times higher than B values for crystal phases. The hcp phase of Co(P) alloy is characterised by the maximum H_a value. Qualitative matching of $H_a(t)$ and x_{hcp} dependencies testifies that precisely the H_a value of the composite powder determines the hcp phase fraction in the Co(P) shell.

CONCLUSION

Modifying the structure and magnetic properties of composite Al₂O₃/Co₉₅P₅ particles was investigated during mechanical activation. The alloy passes into heterophase state when exposed to plastic deformation. The former is comprised of hexagonal close-packed, face-centered cubic, and amorphous Co(P) phases. The fraction of superparamagnetic particles is significantly increased

during mechanoactivation, which results in reduced saturation magnetization of samples. The phase transformation of the highly anisotropic hcp phase of cobalt into the fcc phase during mechanical activation of composite particles causes a significant decrease in the local magnetic anisotropy field of Co(P) alloy.

REFERENCES

- 1 Fujieda, S. Ikeda, S. Suzuki, T. Abe, *J. Jpn. Inst. Met.* 2002. Vol. 166 (3). P. 135.
- 2 Xiao J. Q., Jiang J. S., Chien C. L., *Phys. Rev. Lett.* 1992. Vol. 68. P. 3749.
- 3 Andreev A. S., Tikhov S. F., Salanov A. N., Cherepanova S. V., Lapina O. B., Bolotov V. A., Yuriy Y., Sadykov V. A., d'Espinose de Lacaillerie J.-B., *Adv. Mater. Res.* 2013. Vol. 702. P. 79.
- 4 Cha S. I., Hong S. H., Ha G. H., Kim B. K., *Int. J. Refractory Metals & Hard Mater.* 2001. Vol. 19. P. 397.
- 5 Tai W., Watanabe T., *J. Mater. Sci.* 1998. Vol. 33. P. 5795.
- 6 USA Pat. No. 5462903, 1955.
- 7 Suryanarayana C., *Progr. Mater. Sci.* 2001. Vol. 46, No. 1. P. 1.
- 8 Iskhakov R. S., Denisova E. A., Kuzovnikova L., Komogortsev S., Balaev A., Bondarenko G., *J. Optoelectr. Adv. Mater.* 2008. Vol. 10. P. 1043.
- 9 Denisova E. A., Chekanova L. A., Iskhakov R. S., Bondarenko G. N., *J. Appl. Phys.* 2013. Vol. 113. P. 17A340.
- 10 Chekanova L. A., Denisova E. A., Komogortsev S. V., Iskhakov R. S., Goncharova O. A., *The Physics of Metals and Metallography.* 2013. Vol. 114, No. 2. P. 122–128.
- 11 Ignatchenko V. A., Iskhakov R. S., Popov G. V., *Sov. Phys. JETP.* 1982. Vol. 55. P. 878.
- 12 Kuzovnikova L., Denisova E., Kuzovnikov A., Iskhakov R., Lepeshev A., *Solid State Phenomena.* 2012. Vol. 190. P. 192.