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Magnetostructural Investigations of Bulk Nanostructured $(Co–P)_{100-x}Cu_x$ Alloys

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Abstract—Magnetostructural investigations of bulk nanostructured Co–P/Cu composites prepared by dynamic compacting are performed. The magnetic microstructure of the obtained materials is characterized. It is shown that the use of composite particles allows us to create bulk materials with the structures and main magnetic properties of the initial powders.

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INTRODUCTION

In recent years, the development of bulk nanostructured metal materials has become a priority field of modern materials science. The most developed techniques for their fabrication are high-vacuum pressing, pressure sintering, hot isostatic pressing, high-intensity plastic deformation, and high-temperature gas extrusion [1–3]. One of the most effective ways of forming bulk samples is dynamic compacting, which allows us to prepare bulk materials with metastable phases [4]. In this work, we fabricate bulk nanostructured materials via the dynamic compacting of powders with core–shell Co(P)/Cu composite particles. As was shown in [5], the magnetic properties of nanostructured ferromagnets are due to features of their micromagnetic structure. To optimize the magnetic properties of nanostructured alloys, we must establish the correlation between the macro- and microscopic parameters of a material. In nanostructured ferromagnets, this correlation is described by the random magnetic anisotropy model, in which the spin system of a ferromagnet and thus the characteristics of it most important for application (e.g., coercivity and magnetic susceptibility) are determined by microscopic parameters that include exchange coupling constant A, magnetization M_s, local magnetic anisotropy constant K, and grain (cluster) size $2R_c$ [6, 7]. The aim of this work was to investigate the magnetic properties and magnetic microstructures of bulk nanostructured Co(P)/Cu alloys.

EXPERIMENTAL

Our dynamic compacting precursors were powders consisting of core–shell composite particles.

At the first stage, we prepared powders of the amorphous $Co_{88}P_{12}$ alloy via chemical deposition with sodium hypophosphite as the reductant. At the second stage, Co(P) particles were coated with crystal copper shells of different thicknesses. The reductant used in the chemical coppering solution was formaldehyde. Bulk samples were formed via dynamic compacting using a flat pressing scheme. The structures, morphologies, and phase compositions of the samples were studied via electron microscopy (TM 3000), X-ray diffraction (DRON-3), and nuclear magnetic resonance (NMR). Nuclear magnetic resonance spectra were recorded using the spin echo technique. The low-temperature and field dependences of magnetization were measured on a vibrating sample magnetometer in fields of 0 to 14 kOe in the temperature range of 77–300 K. The resonance characteristics were measured on a standard EPA-2M spectrometer at a frequency of 9.2 GHz. Parameters of the magnetic structure, including the size of magnetic correlation regions (the so-called stochastic magnetic domains), the effective anisotropy in them, and the spatial dimensionality of the spin system, were calculated using a correlation magnetometry technique based on the random anisotropy model and the law of approaching saturation magnetization [8].

RESULTS AND DISCUSSION

Figures 1a and 1b show SEM images of $Co_{88}P_{12}$/Cu particles and element distribution maps for them based on energy-dispersive X-ray spectroscopy (EDX) data. It was established that the composite particles were spherical for all the investigated phosphorous and

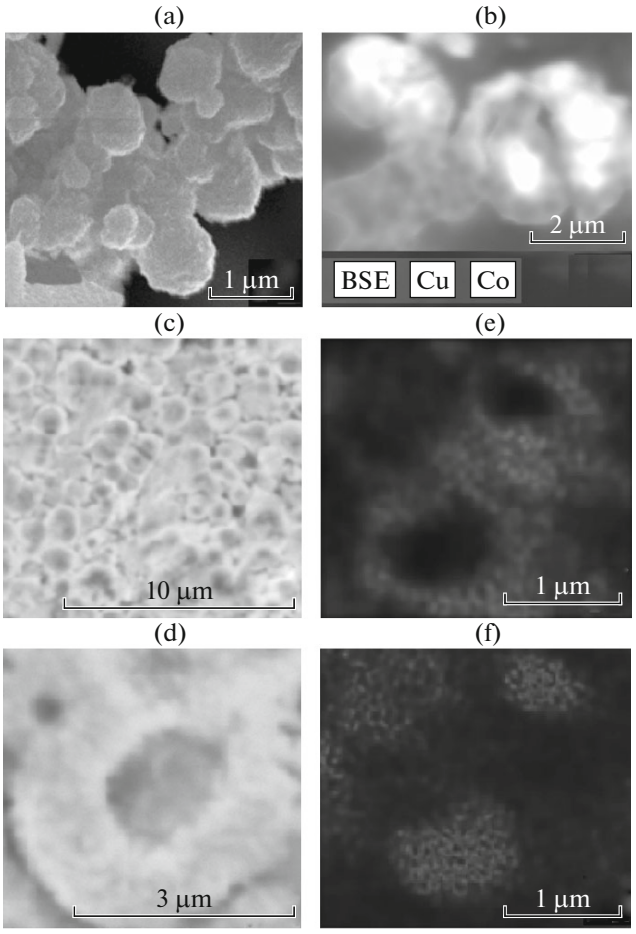

Fig. 1. (a, b) SEM images of $Co_{88}P_{12}/Cu$ composite powder particles, EDX element distribution map in powder particles, sections of the bulk, (c) $(Co_{88}P_{12})_{80}/Cu_{20}$ and (d) $(Co_{88}P_{12})_{30}/Cu_{70}$ samples formed by dynamic compacting of $Co_{88}P_{12}/Cu$ particles, and EDX maps of (e) copper and (f) cobalt distributions in the samples.

copper concentrations. Depending on the copper concentration, the copper layer thickness varied from 0.1 μm for $(Co–P)_{80}/Cu_{20}$ powders to 0.8 μm for $(Co–P)_{10}/Cu_{90}$ ones. The samples prepared via dynamic compacting were solid metal plates 15 × 8 × 2 mm in size with no visible cracks or pores. For more detailed analysis, we studied fractures in and sections of the compacted samples. Figures 1c–1f show SEM images of longitudinal sections of $(Co_{88}P_{12})_{80}/Cu_{20}$ and $(Co_{88}P_{12})_{30}/Cu_{70}$ samples and the EDX element distribution maps for them. It can be seen that the Co(P) core of the composite particles remained almost spherical after a shock wave passed through at compacting pressures of $P < 3.2$ GPa. The solidity of the samples was ensured by the greater plasticity of the copper shell (the brighter areas in the SEM images correspond to copper). Note that the diffraction patterns of the $(Co_{88}P_{12})_{100-x}/Cu_x$ composite particles and samples virtually coincide with those of pure copper; i.e., no appreciable structural changes were

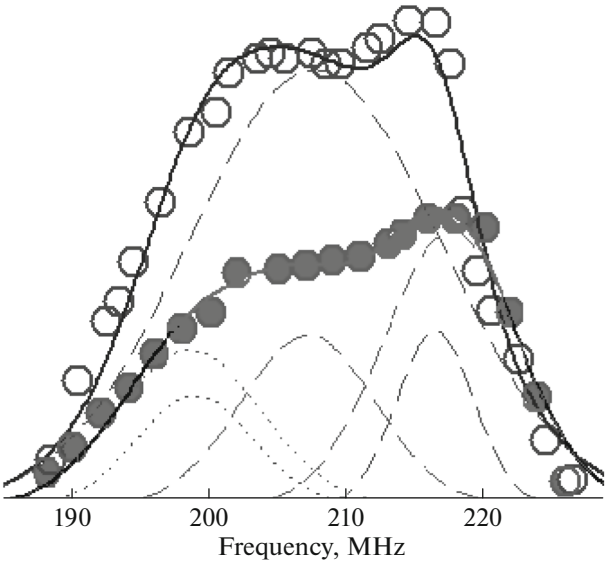

Fig. 2. NMR spectra of $(Co_{88}P_{12})_{100-x}/Cu_x$ samples with different copper contents. White dots correspond to x = 20%, black dots, to x = 40%.

observed in the samples during dynamic compacting under the chosen conditions.

We used a set of magnetostructural investigations to obtain more information about changes in the immediate environment of Co atoms and the magnetic microstructure of composite particles during the compacting of the Co(P)/Cu powders. NMR was used to establish that most of the cobalt atoms in the particles of the initial powders had the fcc immediate environment with a small number of hcp positions. Shock-wave loading led to the formation of more homogeneous Co(P) alloy with a higher number of cobalt atoms with the hcp immediate environment. Figure 2 shows the NMR spectra recorded at $T = 77$ K for samples with different copper shell thicknesses. The shape of NMR spectra observed for bulk samples of all the compositions is indicative of the heterophase structure of the Co(P) ferromagnetic phase; more specifically, the coexistence of cobalt atoms with the hcp and fcc immediate environments. The ratios between the numbers of atoms with hcp and fcc symmetries of the immediate environment differ somewhat for samples with different copper shell thicknesses. The fraction of cobalt atoms with the fcc symmetry of the immediate environment grows along with the copper content.

It was established that the saturation magnetization fell monotonically from 800 to 240 G when the copper content in the initial particles was raised from 0 to 90 at %, and remained virtually the same upon shock-wave loading. Specimens for detecting magnetization curves were cut from the samples in the form of plane-parallel plates 3 × 7 × 1 mm in size. It was found that the magnetization curves detected in mutually perpendicular directions of the external field relative to the plate virtually coincided, as in the ferromagnetic

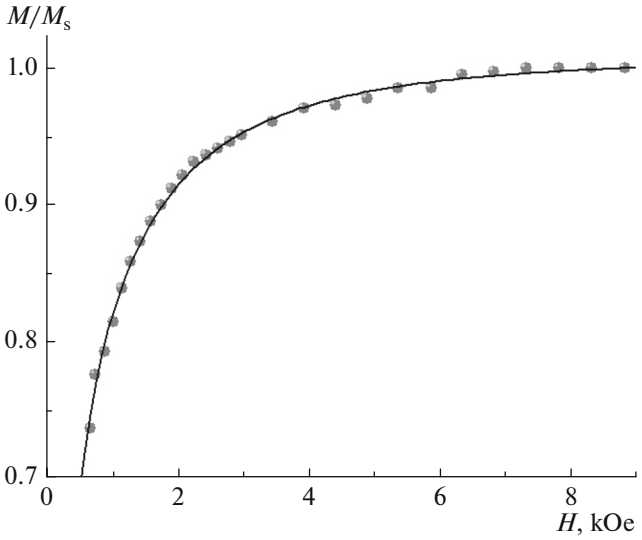

Fig. 3. Magnetization curve for the bulk $(Co_{88}P_{12})_{80}/Cu_{20}$ sample. The solid line shows our fitting using formula (1).

resonance spectra recorded at different sample orientations relative to the external field. Dipole–dipole interaction thus did not determine the shape of the magnetization curve for the investigated x values in the bulk $(Co_{88}P_{12})_{100-x}/Cu_x$ composite objects. In the Co(P)/Cu samples, the main contribution came from by the shape of Co(P) particles. After cosidering the demagnetizing field of grains ($4\pi M_s/3$), the composite alloys were studied by means of correlation magnetometry. The best fitting of the curves of approaching the saturation magnetization for these materials was achieved with

$$M(H) = M_s\left(1 - 1/15\, H_a^2 H^{-1/2}\left(H^{3/2} + H_R^{3/2}\right)^{-1}\right), \quad (1)$$

where $H_a = 2K/M_s$ is the local field of anisotropy, a is the symmetry coefficient, and $H_R = 2A/M_s R_c^2$ is the exchange correlation field above which Akulov's law applies and below which power dependence H^{-n} with an exponent that depends on the dimensionality of anisotropy inhomogeneity is observed [9]. The dependence we observed for the Co(P)/Cu samples in the random anisotropy model corresponds to the three-dimensional packing of exchange-coupled grains. Figure 3 shows the magnetization curve for the bulk $(Co_{88}P_{12})_{80}/Cu_{20}$ sample formed by dynamic compacting; the solid line corresponds to the fitting according to formula (1). Local anisotropy field aH_a, correlation field H_R, anisotropy field $\langle aH_a\rangle$ of a stochastic domain, and its size R_f are given in the table. The consolidated materials were characterized by a weaker local anisotropy field than that of the initial powders. It was found that shock-wave loading reduced the FMR linewidth and coercivity at all copper concentrations.

Characteristics of the $(Co_{88}P_{12})_{100-x}/Cu_x$ compact magnetic microstructure

Weight fraction of copper, %	aH_a, kOe	H_R, kOe	$\langle aH_a\rangle$, Oe	R_f, nm
0	2.1	6.2	82	55
20	0.9	2.3	60	70
40	1.4	3.1	130	45
50	0.8	1.4	140	47
70	0,8	1,5	120	45

CONCLUSIONS

Using dynamic compacting, we fabricated bulk nanostructured Co–P/Cu composites with the saturation magnetization of the initial powders. In both the initial powders and compacted samples, $Co_{88}P_{12}$ alloy was a heteorophase system consisting of the fcc and hcp short-range order phases. The local anisotropy field and the anisotropy field and size of the stochastic domain were determined via correlation magnetometry. It was established that shock-wave loading during sample compacting reduced the local anisotropy field, coercivity, and FMR linewidth.

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