Cobalt-Based Bulk Nanostructured Materials Prepared via the Dynamic Compacting of Core−Shell Composite Particles

E. A. Denisova[a, e, *], **L. A. Kuzovnikova**[b], **R. S. Iskhakov**[a], **A. A. Kuzovnikov**[c],
I. V. Nemtsev[d], **and V. K. Mal'tsev**[a]

[a] *Kirensky Institute of Physics, Krasnoyarsk Scientific Center, Siberian Branch, Russian Academy of Sciences,*
Krasnoyarsk, 660036 Russia
[b] *Krasnoyarsk Institute of Railway Engineering, Krasnoyarsk, 660028 Russia*
[c] *ZAO Pulsed Technologies, Krasnoyarsk, 660001 Russia*
[d] *Krasnoyarsk Scientific Center, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, 660036 Russia*
[e] *Siberian Federal University, Krasnoyarsk, 660034 Russia*
***e-mail: len-den@iph.krasn.ru**

Abstract—Bulk nanostructured Co−P/Cu and Al_2O_3/Co−P composites are fabricated via dynamic compaction. The initial core−shell particles are synthesized by means of chemical deposition. Structural and magnetic characteristics of the composites are investigated. It is shown that the use of composite particles allows homogeneous compacts with the structure and magnetic characteristics of initial powders to be obtained.

INTRODUCTION

Materials with nonequilibrium metastable structure, including nanoparticles and nanostructured powders, have recently been objects of intense study in materials science. The size of structural units and their spatial distribution over a composite's volume become factors that determine the chemical and physical properties of nanostructured materials [1−3]. The development of bulk materials that retain a set of specific physical properties of nanoparticles will allow us to broaden considerably the range of composite applications. The techniques most developed are high-vacuum pressing, pressure sintering, hot isostatic pressing, severe plastic deformation, and high-temperature gas extrusion [4−7]. However, the static compaction of powders causes certain problems. Cold pressing does not always yield dense samples. During hot pressing, it is difficult to prevent recrystallization and the formation of large pores upon high-temperature treatment. One effective way of obtaining bulk samples is dynamic compaction. Synthesis under the action of shock waves is of interest in fabricating bulk materials with metastable phases [8, 9]. The mechanical impact of a shock wave creates conditions both for fragmentation of the initial materials and for synthesizing final products. The energy of explosions is widely used to initiate phase transitions. After the shock wave propagates, the material cools rapidly, stabilizing any high-temperature and metastable crystal modifications [10]. The aim of this work was to fabricate bulk nanostructured materials via the dynamic compaction of powder with CoP/Cu and Al_2O_3/Co(P) composite core-shell particles. The use of magnetostructural and magnetophase techniques and nuclear magnetic resonance (NMR) along with traditional diffraction methods provided additional information about the initial nanostructured materials and processes that occur in them during dynamic compaction.

EXPERIMENTAL

The precursors used for dynamic compaction in this work were powders with nanocomposite core−shell particles. In the samples of series I, the core was Al_2O_3 particles about 370 nm in diameter and synthesized using the explosive technique. The $Co_{88}P_{12}$ alloy's shell was formed via chemical deposition, based on the reaction of reducing metals from aqueous solutions of the corresponding salts with sodium hypophosphite used as a reductant. In the samples of series II (($Co_{88}P_{12})_{100−x}$/Cu_x), amorphous Co-P powders with a phosphorous content of 12 at % (Fig. 1a) were prepared and then coated with crystal copper shells of different thicknesses. The chemical solutions for copper coating of the Co-P powders contained the formaldehyde reductant. It was established that the composite particles were spherical at all of the investigated phosphorous and copper concentrations, and the copper layer thicknesses, depending on copper concentration, changed from 0.05 μm in the $(Co−P)_{80}$/Cu_{20} powders to 0.2 μm in $(Co−P)_{10}$/Cu_{90}.
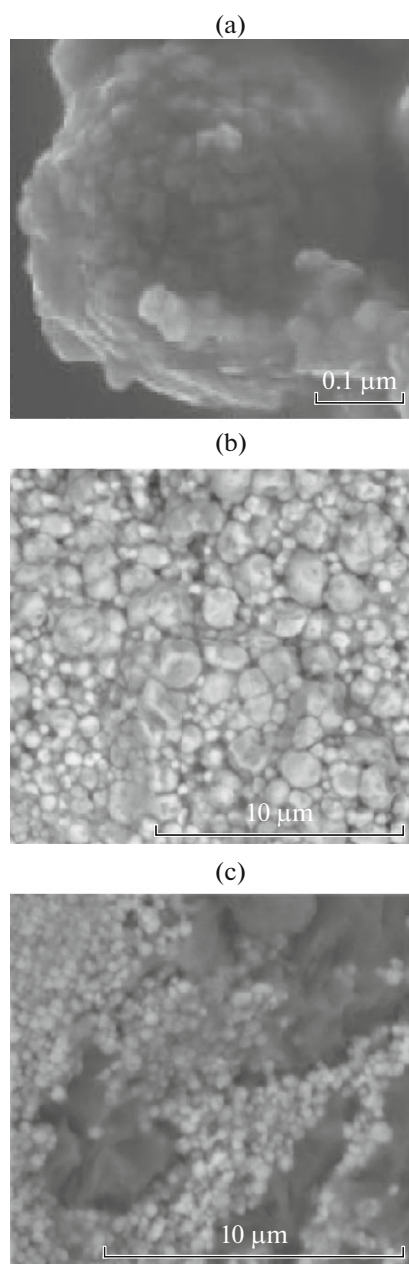
(a)

0.1 μm

(b)

10 μm

(c)

10 μm

Fig. 1. (a) SEM images of composite particles of Al_2O_3/$Co_{88}P_{12}$ powder, (b) compacts prepared via dynamic compaction of Al_2O_3/$Co_{88}P_{12}$ composite particles, and (c) our Al_2O_3 and $Co_{88}P_{12}$ powder mixture. Dark areas correspond to Al_2O_3 regions.

Bulk samples were fabricated via dynamic compaction using a flat pressing scheme. The structure, morphology, and phase composition of the compacts were studied using electron microscopy, X-ray diffraction, and NMR. Nuclear magnetic resonance spectra were obtained using the spin echo technique. The low-temperature and field dependences of magnetization were measured on a vibrating sample magnetometer in the

field range of 0 to 14 kOe at temperatures of 77–300 K. The resonance characteristics were investigated on a standard EPA-2M spectrometer at a frequency of 9.2 GHz. The main (saturation magnetization M_0 and local anisotropy field H_a) and integral (coercivity H_c and ferromagnetic resonance (FMR) linewidth ΔH) magnetic characteristics of the obtained samples were studied.

RESULTS AND DISCUSSION

The samples subjected to dynamic compaction were continuous metal plates $12 \times 7 \times 2$ mm in size without visible cracks and pores. To perform a more detailed analysis, we investigated fracture of the compacted samples. Figure 1 shows scanning electron microscopy (SEM) images of the samples of series I. After the Co–P particles were immobilized on the surfaces of Al_2O_3 dielectric grains, the SEM images revealed (Fig. 1a) large spherical particles from 150 to 400 nm in size and small nanoparticles from 20 to 50 nm in size on their surfaces. According to the EDX data, the use of composite particles in dynamic compaction allows us to obtain products with uniform component distribution over the volume (Fig. 1b). For comparison, Fig. 1c shows a compact prepared from a mixture of Al_2O_3 and $Co_{88}P_{12}$ powders. It can be seen that this bulk material is characterized by a nonuniform component distribution.

Comparative analysis of diffraction patterns of the initial composite particles of both series and compacts fabricated at $P < 3.2$ GPa revealed no significant changes in the sample structure upon dynamic compaction. The $Co_{88}P_{12}$ alloy remained X-ray amorphous in the samples of series I. The region of coherent scattering estimated using the Scherrer formula is 40 nm. Note that X-ray diffraction patterns of composite particles and $(Co_{88}P_{12})_{100-x}$/Cu_x compacts nearly coincide with the pattern of pure copper.

Additional information about the variations in the immediate environment of a Co atom that occur during compaction of the powders of series II was provided by NMR studies. Figure 2 presents NMR spectra for the initial $(Co_{88}P_{12})_{60}$/Cu_{40} sample and bulk sample. As is well known, the room-temperature NMR spectrum of pure cobalt is characterized by two fundamental frequencies: 213.3 MHz for fcc Co and 221 MHz for hcp Co. Substituting nonmagnetic copper or phosphorous for the magnetic Co atoms in the immediate environment of 12 neighbors leads to the emergence of equidistant satellites. The observed NMR spectrum of the $(Co_{88}P_{12})_{60}$/Cu_{40} composite powder is indicative of a large number of variants of the immediate environment of the magnetically active atoms and topologic inhomogeneities in the alloy, which is consistent with the X-ray diffraction data. Decomposition of the NMR spectrum of the initial powder shows that the immediate environment of Co
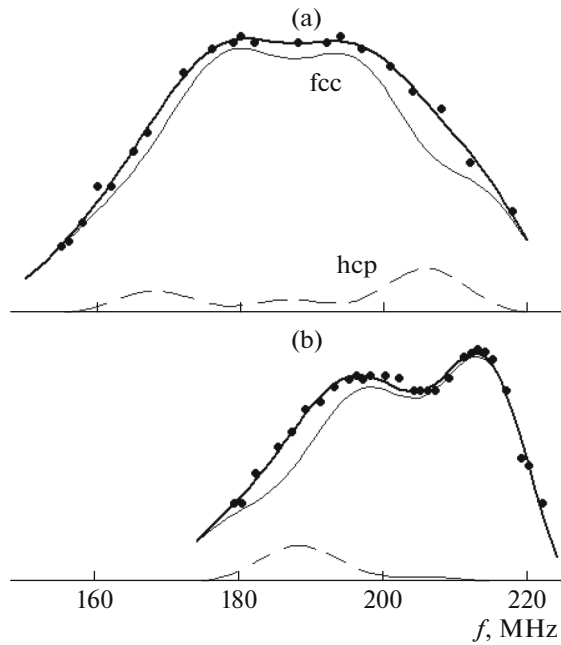
Fig. 2. (a) NMR spectra of the initial $Co_{88}P_{12}$/Cu composite powder and (b) $Co_{88}P_{12}$/Cu compacts prepared via dynamic compaction.

Fig. 3. Hysteresis loops of (*1*) the initial Al_2O_3/$Co_{88}P_{12}$ composite powder and (*2*) the bulk sample prepared via dynamic compaction.

atoms is mainly fcc with one or two nonmagnetic neighbors (Fig. 2a). After the propagation of a shock wave, the NMR spectrum changes: the resonance peaks shift toward higher frequencies and now the spectrum is described by a sum of lines, one of which corresponds to pure fcc cobalt. It should be noted that in the bulk sample, the structure of short-range order in the ferromagnetic phase was most similar to the fcc type.

Study of the NMR spectra of the Al_2O_3/$Co_{100-x}P_x$ samples showed that the $Co_{100-x}P_x$ alloy in the nanocomposite was heterophase for all of the investigated phosphorous concentrations (the NMR spectrum indicates mixed fcc and hcp Co surroundings). It was established that the ratios between the numbers of atoms with the hcp and fcc symmetries of the immediate environment for powders and compacts differ somewhat, but most cobalt atoms are characterized by the fcc symmetry of the immediate environment in both cases.

At temperatures of 77–300 K, the $M(T)$ dependence for the initial composite powders of both series and compacts is characteristic of ferromagnets; i.e., it obeys the Bloch law $M(T) = M_0(1 - BT^{3/2})$, where B is the Bloch constant. In the samples of series I, the saturation magnetization did not change during compaction and was determined by the ratio between Al_2O_3 and $Co_{88}P_{12}$ in the initial powders. In the samples of series II, the saturation magnetization fell monotonically from 800 to 240 G with an increase in the copper concentration from 0 to 70 at % in the initial particles
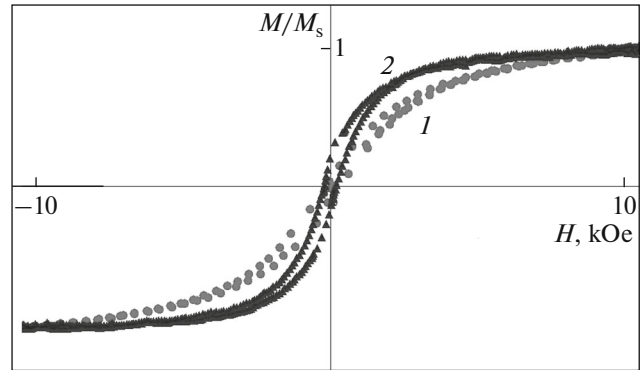
and remained almost invariable upon shock-wave loading. Figure 3 shows hysteresis loops for the initial Al_2O_3/$Co_{88}P_{12}$ sample and bulk sample obtained via dynamic compaction. It can be seen that the coercivity remained virtually the same during compaction ($H_c \sim$ 200 Oe); however, the compact is saturated in lower fields due to weakening of the dipole–dipole interaction. In the samples of series II, the initial powders and compacts are saturated in the same field, since the copper shell weakens the dipole–dipole interaction between powder particles [11]. It was found that shock-wave loading narrows the FMR line and the coercivity falls slightly at all copper concentrations. Magnetization curves $M(H)$ measured for the investigated samples showed that the magnetization approaches saturation in the range of 1 to 3 kOe according to the law $M \sim H^{-\alpha}$, where $\alpha \approx 0.75$. This dependence indicates that the Co-P alloy is nanocrystal [12]. The high-field part of these curves ($H > 5$ kOe) satisfies the dependence $M(H) = M_0(1 - DH_a^2/H^2)$. The latter allowed us to calculate the local anisotropy field H_a for the Co(P) alloy. It was found that in the samples of series I, the propagation of a shock wave through the sample reduces the local anisotropy field from 3.8 to 3 kOe, due possibly to the relaxation of internal stresses and the growth in the number of cobalt atoms with the fcc nearest surroundings. In the samples of series II, the local anisotropy field was reduced slightly at all copper concentrations.

CONCLUSIONS

Bulk nanostructured Co–P/Cu and Al_2O_3/Co–P composites with saturation magnetization analogous to that of the initial sample were prepared using the dynamic compaction technique. Like the initial samples of both compositions, the $Co_{88}P_{12}$ alloy in the compacts was a heterophase system consisting of a mixture of phases with the fcc and hcp short-range order. The shock-wave loading during sample compaction

changes the ratio between the numbers of atoms with the hcp and fcc symmetries of the immediate environment. It was established that using core–shell composite particles as the initial powder in dynamic compaction allows us to obtain samples with uniform component distribution over the sample volume.

ACKNOWLEDGMENTS

REFERENCES

1. Gusev, A.I., *Nanomaterialy, nanostruktury, nanotekhnologii* (Nanomaterials, Nanostructures, and Nanotechnology), Moscow: Fizmatlit, 2005.

2. Fan, X., Mashimo, T., Huang, X., et al., *Phys. Rev. B*, 2004, vol. 69, p. 094432.

3. Gleiter, H., *Acta Mater.*, 2000, vol. 48, p. 1.

4. Lyakishev, N.P., Kalin, B.A., and Solonin, M.I., *Byull. Mezhdunar. O-va. Metalloved.*, 2000, no. 1, p. 22.

5. Andrievskii, R.A., Ragulya, A.V., *Nanostrukturnye materialy* (Nanostructured Materials), Moscow: Tsentr "Akademiya," 2005.

6. Rong, C., Zhang, Y., Poudyal, N., et al., *Appl. Phys. Lett.*, 2010, vol. 99, p. 102513.

7. Valiev, R.Z. and Aleksandrov, I.V., *Nanostrukturnye materialy, poluchennye intensivnoi plasticheskoi deformatsiei* (Nanostructured Materials Produced under Severe Plastic Deformation), Moscow: Logos, 2000.

8. Chen, K.H., Jin, Z.Q., Li, J., et al., *Appl. Phys.*, 2004, vol. 96, p. 1276.

9. Jin, Z.Q., Li, J., Thadhani, N.N., et al., *AIP Conf. Proc.*, 2006, vol. 845, no. 1, p. 1157.

10. Rempel, A.A., *Russ. Chem. Rev.*, 2007, vol. 76, p. 435.

11. Yaroslavtsev, R., Komogortsev, S., Chekanova, L., et al., *Solid State Phenom.*, 2015, vols. 233–234, p. 629.

12. Iskhakov, R.S., Komogortsev, S.V., Balaev, A.D., and Chekanova, L.A., *JETP Lett.*, 2000, vol. 72, no. 6, p. 304.

Translated by E. Bondareva