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Microstructure and magnetic properties of C/Co-P and Al_2O_3/Co-P composite particles prepared by electroless plating

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The electroless plating is used to synthesize two types of composite powder, such as the activated carbon with pores filled by $Co_{100-X}P_X$ particles and the Al_2O_3 microgranular coated by the shell which consists of $Co_{100-X}P_X$ particles with $4 < X < 18$. The magnetic and structural properties of the composite particles are characterized by scanning electron microscopy, X-ray diffraction, and vibrating sample magnetometer. It is found that the average Co(P) particle size in composite powders decreases from 300 nm to 120 nm with an increase in P- content from 4 to 18 at. %. It causes a reduction in coercivity from 300 to 80 Oe for Al_2O_3/Co(P) powders and from 680 to 150 Oe for C/Co(P) powders. The effects of two methods of immobilization of Co(P) particles on magnetic properties are studied. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4800037]

I. INTRODUCTION

The interest in nanostructured Me-P (Me = Ni, Co, Fe) materials is motivated by their unique properties in the fields of catalysis, microwave absorptive materials, magnetism, and drug delivery.[1,2] But spontaneous aggregation of nanoparticles frequently causes the magnetic and chemical properties deterioration. A promising solution of this problem is to use the various supports preventing particles aggregation. Immobilization of particles on substrate can be performed by several ways, namely, particles can be supported on the surface of various granular[3,4] or embedded into pores of powder matrix.[5–7] In order to investigate the effects of two methods of immobilization of Co(P) particles on magnetic properties, we produce two types of composite particles. The first sample is an activated carbon with pores filled by Co(P) particles, the second one is Al_2O_3 granular coated by the shell which consists of Co(P) particles. Detailed microstructures and magnetic characterizations are presented.

II. EXPERIMENTAL

The activated carbon/Co(P) and Al_2O_3/Co(P) composite particles were prepared by electroless reduction of metals from aqueous solutions of the corresponding salts at 80 °C. Each plating bath was comprised of source metal ion ($CoSO_4$), metal chelator ($Na_3C_6H_5O_7$), *p*H stabilizer (NH_4Cl buffer solution), and reducing agent ($NaPO_2H_2$). The Al_2O_3/Co(P) composite particles consist of core from Al_2O_3 granular surrounded by shell from $Co_{100-X}P_X$ particles with $4 < X < 18$. The Al_2O_3 granules used as substrate were synthesized by an explosive method.[8] The average size of Al_2O_3 granules is about 300 nm. For preparing $Co_{100-X}P_X$ particles embedded into an activated carbon pores we used commercially available activated carbon with powders size varying in the range of 10–100 μm. The morphology and the composition of the powders were analyzed using a scanning electron microscope (Carl Zeiss EVO 60) and an energy-dispersive spectrometer (INCA, Oxford Instruments). The phosphorus content was determined by a chemical analysis and by the wavelength dispersive X-ray fluorescence spectrometry (S4 PIONEER, Bruker). The crystalline structure of the composite powders was determined using a DRON-4 X-ray diffractometer operating with Cu Kα radiation. X-band ferromagnetic resonance spectra were recorded using a standard EPR (electron paramagnetic resonance) spectrometer. The field and low-temperature dependences of magnetization, M(T,H), were measured in the external field range up to 50 kOe and at 4.2–300 K using a vibrating sample magnetometer.

III. RESULTS AND DISCUSSION

The SEM images of composite particles are presented in Fig. 1. We can see that the activated carbon (Fig. 1(a)) contains pores from 5 to 10 μm in diameter and from 1 to 5 μm in wall thickness. For the C/Co(P) sample (Fig. 1(b), it can be seen that there is a set of particles between the planar walls, confirming that Co(P) particles fill the carbon pores. According to the SEM data, the Co(P) particle shape is nearly spherical for C/Co(P) and $Al_2O_3/Co_{100-X}P_X$ composite powders. In electroless plating, the composite particle shape and size of grain depend on phosphorus content. An increase in the phosphorus content causes a reduction of the grain size. It is found that the average Co(P) particle size supported on the surfaces Al_2O_3 granular decreases from 300 nm to 120 nm with an increase in P-content from 4 to 18 at. %.

The typical powder XRD patterns of the $C/Co_{100-X}P_X$ and $Al_2O_3/Co_{100-X}P_X$ materials are shown in Figure 2. The $Al_2O_3/Co_{100-X}P_X$ powder XRD pattern corresponds to the hcp Co phase. The lack of Al_2O_3 peaks is due to the fact that the Co(P) particles form continues layer on the Al_2O_3 core. In samples $C/Co_{90}P_{10}$, XRD peaks corresponding to the Co hcp phase are presented together with the Co fcc phase. No characteristic peaks of cobalt oxides or hydroxides are

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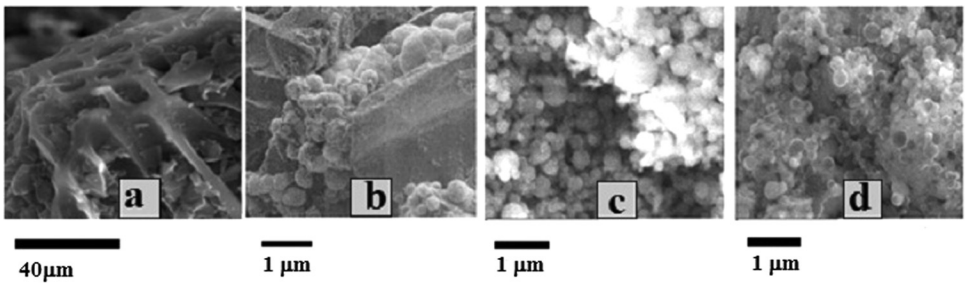

FIG. 1. SEM imagine of activated carbon (a), composite materials C/Co(P) (b), starting Al_2O_3 particles (c), and composite particles $Al_2O_3/Co_{100-X}P_X$ (d).

detected. The X-ray powder diffraction analysis shows that Co(P) particles with P-content less than 8% have hcp structure, whereas Co(P) particles with 8 to 11 at. % P are partly amorphous, and Co(P) with greater than 11 at. % P is totally amorphous.

The hysteresis loops of the Al_2O_3/Co(P) and C/Co(P) composite powders are shown in Fig. 3. The coercivity values of the composite powders depend on microstructure of particles. The composite powders of both types with amorphous $Co_{100-X}P_X$ particles ($X > 14$) have minimal coercivity equal to 80 Oe for Al_2O_3/Co(P) powders and 150 Oe for C/Co(P) powders, its squareness, M_r/M_s, is about 0.3. Such low values of the coercive force and residual magnetization allow us to easily manipulate composites by applying an external field. Therefore, in conjunction with the absorption properties that makes them attractive for use as catalysts and adsorbents. The maximum value of coercivity is 680 Oe for C/Co(P) powders and 300 Oe for Al_2O_3/Co(P) powders. It is achieved when the phosphorus content varies in the range of 10−12 at. %. In this case, the structure of Co(P) alloy is a mixture of both fcc-Co and amorphous phase. We observe that the coercivity for the Co(P) particles embedded into an activated carbon pores exceeds the corresponding values of the Co(P) particles supported on the Al_2O_3 granular and of the ultrafine Co(P) particles with same composition prepared by chemical reduction.[9] Therefore, it is possible to tune the magnetic properties of the particles by their structural architecture. Both composites possess high saturation magnetization: $M = 54$ emu/g for $Al_2O_3/Co_{86}P_{14}$ particles and $M = 40$ emu/g for $C/Co_{86}P_{14}$ particles. The low-temperature dependence of magnetization for C/Co(P) composite powders at $80 < T < 300$ K obeys the Bloch's $T^{3/2}$ law with Bloch constant being close to the ultrafine powders value.[9] The inset of Fig. 4 shows the temperature dependence of magnetization for the $Al_2O_3/Co_{86}P_{14}$ and $Al_2O_3/Co_{95}P_5$ composites. We fit the M(T) curve with the following equation:

$$M(T) = A(1 - BT^{3/2}) + CL\left(\frac{D}{T}\right), \quad (1)$$

where $M(T)$ is magnetization of Al_2O_3/Co(P) particles at temperature T, B is the Bloch constant, $L(x)$ is the Langevin function, $A = M_f V_f$ and $C = M_{sp} V_{sp}$, D are fitting constants. Here, M_f is the average magnetization of the ferromagnetic phase, V_f is the volume fraction of this phase, M_{sp} is the average magnetization of the superparamagnetic phase, V_{sp} is the volume fraction of this phase. The first term corresponds to the contribution of the ferromagnetic phase. The second term represents the contribution of the superparamagnetic ultra-

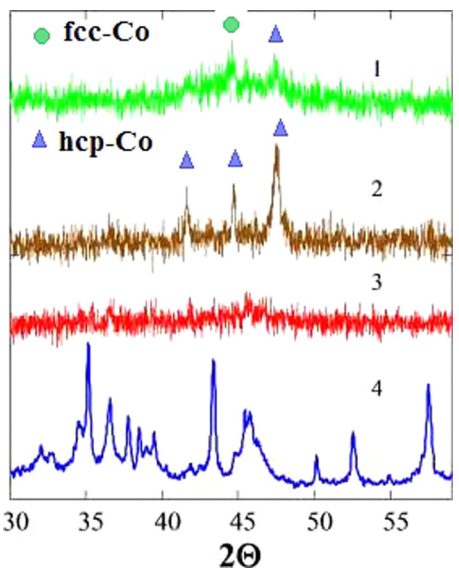

FIG. 2. XRD pattern of composite particles $C/Co_{90}P_{10}$ (1) and $Al_2O_3/Co_{100-X}P_X$: 2 – X = 5; 3 – X = 14; starting powder Al_2O_3 (4).

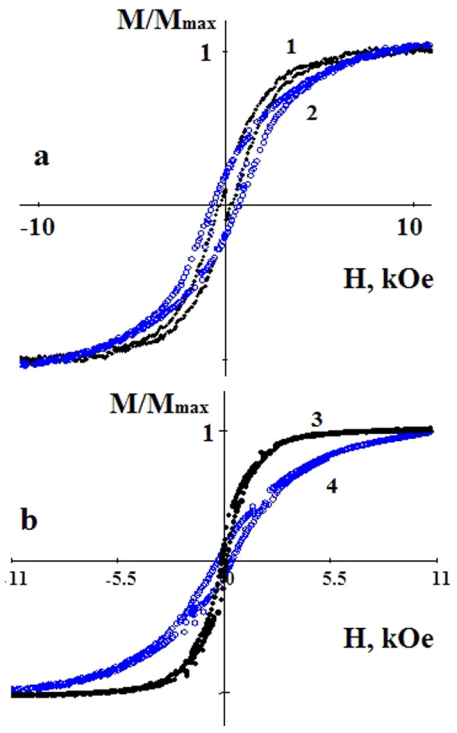

FIG. 3. The hysteresis loops measured at room temperature for (a) $C/Co_{86}P_{14}$ (1), $C/Co_{90}P_{10}$ (2); (b) $Al_2O_3/Co_{86}P_{14}$ (4), $Al_2O_3/Co_{90}P_{10}$ (3).

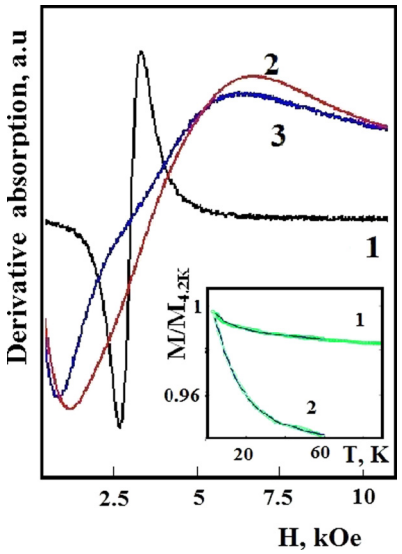

FIG. 4. FMR spectra of $C/Co_{100-X}P_X$ particles: 1−X = 14, 2−X = 5, 3−X = 10. Inset shows the temperature dependence of magnetization for the $Al_2O_3/Co_{95}P_5$ (1) and $Al_2O_3/Co_{86}P_{14}$ (2) composites.

thin ferromagnetic clusters not coupled by exchange. The fitting results indicate that more than $V_f \sim 98\%$ for $Al_2O_3/Co_{95}P_5$ particles and $V_f \sim 95\%$ for $Al_2O_3/Co_{86}P_{14}$ particles.

Information on local anisotropy field and the grain size in the systems of exchange coupled grains can be obtained from investigation of approach magnetization to saturation law.[10–12] Approach to magnetic saturation curves in the applied fields up to $7 \div 20$ kOe for the all nanocomposites follows Akulov's law,

$$M(H) = M_0(1 - aH_a^2/H^2), \quad (2)$$

where $H_a = 2K/M_s$ is local magnetic anisotropy field, a is the symmetry coefficient. This allowed us to calculate the local magnetic anisotropy field H_a. In the field range from 1 to $3 \div 6$ kOe magnetization approaches saturation as $M \sim H^{-1}$ for $Al_2O_3/Co(P)$ composite particles. It was shown[13] that the two-dimensional spatial packing of the grain leads to the transformation of dependence $M \sim H^{-2}$ to $M \sim H^{-1}$ as the field decreases. It makes it possible to conclude that there is two-dimension spatial packing of the Co(P) grain in the shell of the composite particles.[13] This is consistent with X-ray data.

The FMR spectrum for $C/Co_{100-X}P_X$ particles consists of a single absorption line for $X < 8$ and $X > 12$. At the $8 < X < 12$ where the Co(P) alloy is a mixture of both fcc-Co and amorphous phase, an additional resonance line appears. Typical FMR spectra of $C/Co_{100-X}P_X$ particles are shown in Fig. 4. The FMR spectrum for $Al_2O_3/Co_{100-X}P_X$ particles consists of a single absorption line for all samples. If the particles were spherical, the resonance field would be given by $\boldsymbol{H_r} = \frac{\omega}{\gamma}$, where $\boldsymbol{\omega = 2\pi f}$ is microwave frequency and γ gyromagnetic ratio. For our studies $f = 9.2$ GHz and Hr ≈ 2.9 kOe. It is observed that $\boldsymbol{H_r}$ values for $Al_2O_3/Co_{100-X}P_X$ particles are lower approximately 1–2 kOe. Such discrepancy may be explained by the anisotropy field of non-spherical particles.[14] We determine the random magnetic anisotropy field H_a from approach magnetization to saturation curves for investigated composite powders. It turns out that the FMR linewidth of $Al_2O_3/Co(P)$ powders is proportional to the local magnetic anisotropy field (Fig. 5). Consequently, the FMR linewidth is mainly determined by the local anisotropy field.

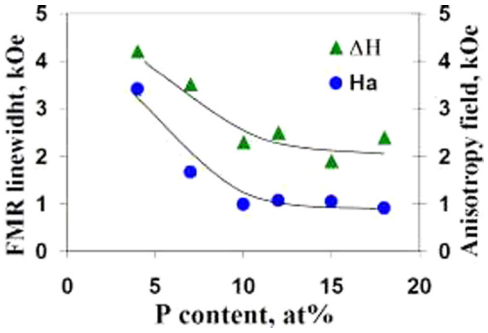

FIG. 5. The FMR linewidth and the local magnetic anisotropy field of $Al_2O_3/Co(P)$ particles as a function of P content.

IV. CONCLUSIONS

In summary, we demonstrate fabrication of composite powders with Co(P) particles supported on the surfaces Al_2O_3 granular or embedded into activated carbon pores through an electroless reduction. It is found that by varying the phosphorous content and applying different immobilization methods, we can control the magnetic properties of composite particles. Using magnetostructural techniques, we show that the CoP particles form a continuous layer on the Al_2O_3 core. The FMR linewidth of $Al_2O_3/Co(P)$ particles is mainly determined by the local anisotropy field. It is found that the coercivity magnitude for the Co(P) particles embedded into an activated carbon pores significantly exceeds the corresponding values of the Co(P) particles supported on the Al_2O_3 granular and of the ultrafine Co(P) particles with the same composition prepared by chemical reduction.

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