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Width of the ferromagnetic resonance line in highly dispersed powders of crystalline and amorphous Co–P alloys

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The resonance characteristics (inhomogeneous FMR linewidth ΔH) in highly dispersed ($d = 0.1–3\ \mu$m) powders of crystalline and amorphous Co–P alloys are investigated as a function of the composition, particle size, and atomic structure. It is established that ΔH for powders of amorphous Co–P alloys is two to three times larger than ΔH for crystalline Co–P powders. According to the investigations performed, this is caused by thermodynamically stimulated segregation of nonmagnetic Co_2P inclusions, apparently an effective relaxation channel, in the amorphous state of Co–P powders. [S1063-7834(99)01903-6]

Ferromagnetic resonance (FMR) is widely used to investigate amorphous ferromagnetic alloys obtained by various methods in the form of thin films, foils, and coatings.[1–4] The magnetic properties of these materials (static, quasistatic, and microwave characteristics) are largely determined by their composition and structure.

In the last few years amorphous alloys have been obtained by different methods (see, for example, Ref. 5) in the form of small particles: ultradispersed ($d = 10–100\ \mu$m), highly dispersed ($d = 0.1–4\ \mu$m), and dispersed ($d > 5\ \mu$m).

Investigations have established that the magnetic properties of small amorphous particles differ substantially from the analogous properties characterizing amorphous films, foils, and coatings having the same composition.[6]

The present paper reports the results of an investigation of the resonance characteristics (inhomogeneous width ΔH of the FMR line) in highly dispersed Co–P powders having different compositions, particle sizes, and structure. The objective is to determine the differences and similarities of the dependences of ΔH in Co–P alloys obtained by the same technological method in different morphological modifications (powders, films). Of special interest in this investigation is to check the assumption advanced in Ref. 2 that the inhomogeneous FMR linewidth ΔH in amorphous alloys is completely determined by the magnitudes H_a of the local anisotropy field in these alloys on microscopic scales.

1. EXPERIMENT

Highly dispersed powders of the alloys Co–P were obtained by chemical deposition from water solutions ($T = 80\,°C$) of Co salts ($CoSO_4$) using sodium hypophosphite (NaH_2PO_2) as the reducing agent. Next, they were washed in distilled water and acetone to passivate the surface of the particles. The phosphorus concentration was determined by chemical analysis (to within ±0.5 at. % P). The particle sizes were found by analyzing electron micrographs obtained in a JEM-100C electron microscope. Prewashed powder was sorted by a sedimentation method into six fractions differing by the average particle diameter (0.1, 0.3, 0.7, 1, 2, and 3 μm). The electron micrographs for each fraction contained of the order of 200 particles, which made it possible to construct a histogram of the particle size distribution, determine the average particle diameter, and the standard deviation.

Diffraction investigations (DRON-3 diffractometer) with Cu $K\alpha$ radiation was used to determine the atomic structure of the powders of the Co–P alloys. The FMR linewidth ΔH was measured on a standard EPA-2M spectrometer (frequency 9.2 GHz). The method developed in Ref. 7 was used to calculate the local anisotropy field in the region where the magnetization approached saturation. The magnetization curve $M(H)$ was measured with a vibrating magnetometer in the range of fields from 0 to 14 kOe.

2. RESULTS

Chemical analysis showed that the phosphorus concentration in the powders of Co–P alloys ranged from 4 to 27 at. %, depending on the technological conditions of the chemical deposition process (hypophosphate concentration, Ph of the solution). The phosphorus concentration (x) in a Co–P solid solution influenced the shape of the particles formed. Morphological analysis of the electron micrographs shows that $Co_{100-x}P_x$ particles with $x \leqslant 9$ at. % are predominantly hexahedral prisms and that for $x \geqslant 12$ at. % the ideal shape of the $Co_{100-x}P_x$ particles is spherical. The results of x-ray diffraction analysis agree with the morphological data. The typical x-ray diffraction patterns of powders with different phosphorus content are presented in Fig. 1. Powders of Co–P alloys with phosphorus content less than 9 at. % P were characterized by x-ray diffraction patterns with a set of reflections attesting to a hexagonal close-packing (hcp) structure of the powder particles. The x-ray diffraction patterns of the powders $Co_{100-x}P_x$ ($x \geqslant 12$ at. %) contained one diffuse

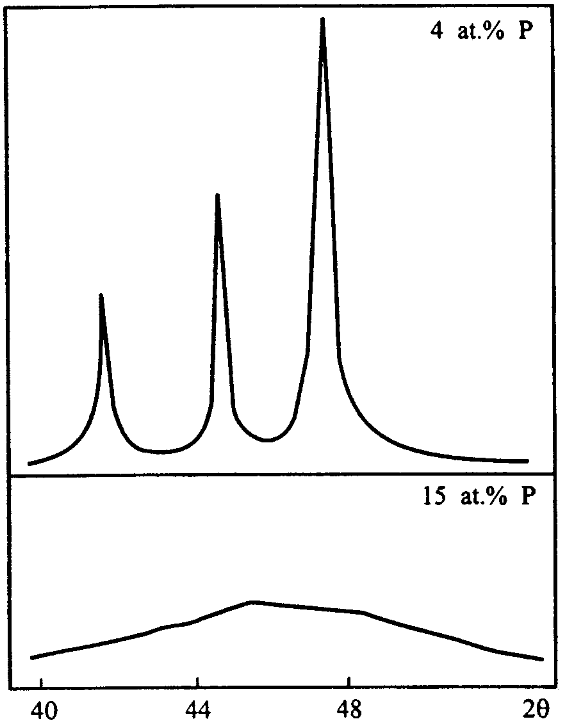

FIG. 1. Diffraction curves for powders of crystalline and amorphous alloys Co–P with phosphorus concentrations of 4 at. % and 15 at. %.

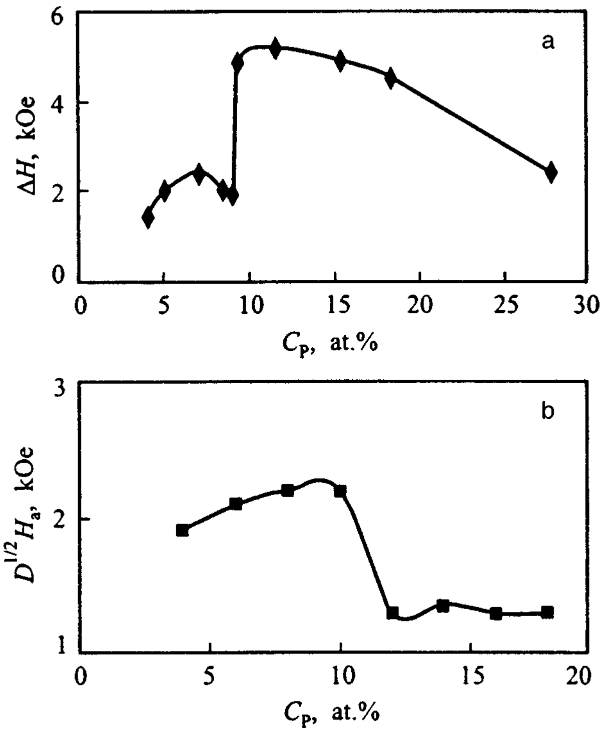

FIG. 2. a — Concentration dependence of the linewidth ΔH for powders of Co–P alloys, b — concentration dependence of the local anisotropy field H_a for powders of the alloys Co–P.

peak, centered near $d_{hkl}=2.01$ Å with width $\sim 10^0$ (2θ). Such diffraction curves attest to an amorphous structure of the particles of these powders. (According to the x-ray diffraction analysis, powders of Co–P alloys in the range from 9 to 11 at. % P consisted of a mixture of crystalline (hcp) and amorphous phases.) Co–P powders obtained with phosphorus concentration $x > 20$ at. % (eutectic region of the melting diagram of Co–P) were also characterized by a crystalline impurity. The x-ray diffraction data attest to the formation, in this case, of the crystalline phosphide Co_2P — for 27 at. % P the diffraction curve is mainly formed by reflections of this chemical compound.

The measurements of the FMR linewidth for the initial Co–P powders (not separated into size fractions) with different phosphorus concentration are presented in Fig. 2a. The characteristic linewidth ΔH is 1.5–2 kOe for crystalline powders and 4–5 kOe for amorphous powders. We note that the FMR linewidth of amorphous ferromagnetic alloys prepared in the form of films, foils, and coatings, as a rule, does not exceed several hundreds of oersteds (see, for example, Refs. 2 and 3). Another difference of the concentration dependence $\Delta H(x)$ in Co–P powders from the analogous concentration dependences $\Delta H(x)$ in Co–P films is the following. The concentration phase transition ''crystalline solid solution — amorphous state of the alloy'' detected by x-ray diffraction analysis does not appear in the curve $\Delta H(\text{at. \% P})$ in Co–P films;[2] this transition does appear in the concentration dependence $\Delta H(\text{at. \% P})$ in Co–P powders in the form of an abrupt increase in ΔH by a factor of two or three near the critical concentration $x_c = 10$ at. % P.

Measurements of the magnetization curve $M(H)$ for Co–P powders showed that in the region where the magnetization approaches saturation the high-field part of this curve is described by the function $M(H) = M_0(1 - DH_a^2/H^2)$. This latter property made it possible to determine the concentration dependence $M_0(x)$ of the saturation magnetization and to calculate the local anisotropy field H_a characterizing the powder particles. (According to Ref. 7, here $D = 2/105$ for cubic symmetry and 1/15 for hexagonal symmetry; for the crystalline phase $H_a = 2K/M_0$, where K is the magnetocrystallographic anisotropy constant.) It was found that the values of M_0 decrease monotonically with increasing phosphorus concentration in Co–P powders. However, here, in contrast to the linear functions $M_0(x)$ found in Refs. 7–9 for films and coatings of Co–P alloys, a change in the gradient $\partial M_0/\partial x$ from ≈ 37 G/at. % P to 45 G/at. % P is observed near $x = x_c$. The concentration dependence of the computed values of the local anisotropy field H_a for powders is presented in Fig. 2b. The local anisotropy field H_a obviously is sensitive to the concentration phase transition of the crystalline solid solution Co–P into an amorphous state: A jump-like decrease of H_a by a factor of two is recorded near $x = x_c$. This latter behavior distinguishes the concentration variation of $H_a(x)$ in Co–P powders from the analogous dependence measured previously for Co–P coatings.[7]

Measurement of the static and resonance characteristics of Co–P powder fractions sorted according to the average particle size d made it possible to study the effect of the sizes of the particles on their magnetic characteristics. It was found that the functional dependence of the measured characteristics on d depends on the type of atomic structure of the particles — crystalline or amorphous. Thus, the saturation

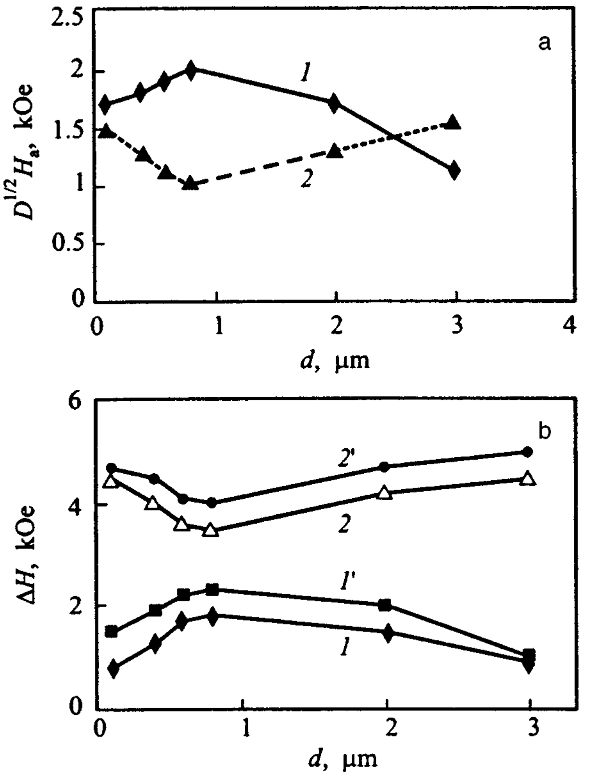

FIG. 3. a — Dependence of the local anisotropy field H_a on the average diameter of particles of Co–P powder: 1 — 4 at. % P, *1'* — 6 at. % P, 2 — 15 at. % P, *2'* — 18 at. % P. b — Linewidth ΔH versus the average diameter of particles of Co–P powder: 1 — 4 at. % P, 2 — 15 at. % P.

magnetization M_0 of amorphous powders (11 at. % P $<x \leqslant 20$ at. % P) as a function of the particle size d in Co–P powder remains constant within the experimental accuracy of the measurements. For crystalline Co–P powders, however, M_0 decreases by 15% as d increases from 0.1 to 3 μm. The local anisotropy field H_a (Fig. 3a) increases linearly up to $d=1\,\mu$m (H_a changes by 35%) with increasing average particle size in Co–P powder for crystalline particles and then decreases by 40% as d increases to 3 μm. For Co–P powder particles with amorphous structure, the dependence $H_a(d)$ (Fig. 3a) is as follows: As the average particle size increases to $d=0.7\,\mu$m, H_a decreases linearly (by 30–20% depending on the P content in the powders) and as d increases further, H_a increases (by 15–25%).

The measurements of the FMR linewidths $\Delta H(d)$ for amorphous and crystalline Co–P powders are displayed in Fig. 3b. One can see that the particle-size dependence of ΔH is determined mainly by the structural state of the particles: For crystalline powders $\Delta H(d)$ is a convex curve with a maximum at $d=1\,\mu$m, while for amorphous powders $\Delta H(d)$ is a concave curve with a minimum also at $d=1\,\mu$m. We note that the relative deviation of ΔH on the curves $\Delta H(d)$ for crystalline particles is more pronounced than for amorphous particles.

3. DISCUSSION

The experimental curves $\Delta H(x)$, $H_a(x)$, and $\Delta H(d)$, $H_a(d)$ presented in Figs. 2 and 3 are of interest for two reasons. One is the qualitative similarity of the dependences $\Delta H(d)$ and $H_a(d)$ in both crystalline and amorphous states and the other is the substantially different — by the direction of the jump in ΔH and H_a near $x \approx x_c$ — concentration dependences $\Delta H(x)$ and $H_a(x)$. The correlation of the curves $\Delta H(d)$ and $H_a(d)$ agrees with the supposition advanced in Ref. 2 on the basis of the results of an experimental study of the dependences $\Delta H(x)$ and $H_a(x)$ in films and coatings of Co–P alloys. Therefore, in powders of Co–P alloys the FMR linewidth can be represented as a sum of two contributions: $\Delta H(x,d)=\Delta H_u(x,d)+\Delta H_{1,a}(x,d)$, where $\Delta H_{1,a}$ is the contribution of the local anisotropy to the linewidth and ΔH_u is the contribution of some source that creates ''relaxation'' channels, which is reflected in the increase of the FMR linewidth and which predominates in the amorphous state of the powders. (See, for example, Ref. 10 for a detailed analysis of the possible sources of relaxation.) The origin of this source is to be determined by analyzing the experimental results presented. First, we shall study the phase diagram of Co–P powders and compare it with the phase diagram of films and coatings of Co–P alloys, which, apparently, are characterized by the inequality $\Delta H_u \ll \Delta H_{1,a}$.

Films and coatings of Co–P alloys, obtained by chemical deposition, in the concentration range from 1 to 20 at. % P are metastable solid solutions (substitution type), as is indicated by the linearity of $M_0(x)$ observed in Refs. 7–9. The gradient of $M_0(x)$ in this case is due to electronic mechanisms of transport of the p electrons of P into the d band of Co and does not depend on the type of structural ordering of the solid solution.[11] Indeed, films and coatings of Co–P alloys are characterized by a hexagonal close-packed structure (hcp) in the concentration range 1–4 at. % P, face-centered cubic structure (fcc) in the range 5–8 at. % P, and an amorphous structure in the range 9–20 at. % P, but the critical concentrations $x_{i,c}$ of these concentration phase transitions were not manifested in the linear dependence $M_0(x)$. We note also the results obtained in Ref. 12, where the NMR method was used to show that short-range order in films of amorphous Co–P alloys is characterized by fcc symmetry. The latter fact served as a reason (as shown in Refs. 2 and 7) why the transition fcc Co–P → amorphous state in films, in contrast to the transition hcp Co–P → fcc Co–P, was not manifested in the curves $\Delta H(x)$ and $H_a(x)$.

The form of the phase diagram of powders of Co–P alloys is qualitatively different — here there is no region of fcc crystalline states. The powders of Co–P alloys have hcp structure in the region 1–8 at. % P and amorphous structure in the region 10–20 at. % P. Comparing the curve $H_a(x)$ with the analogous curve for films,[7] due to the jump-like decrease of H_a near concentrations $x \approx x_c$, suggests that short-range order in powders of amorphous Co–P alloys (just as in films) is characterized by fcc symmetry. This supposition corresponds to the form of the diffraction curve of amorphous powders (Fig. 1), which can be obtained by broadening of the [111] line of the fcc lattice according to the Debye–Scherrer equation. We note that according to this equation the broadening of the reflections of an hcp lattice will lead to an asymmetric diffraction curve, which is at variance with the experimental curve presented in Fig. 1.

Therefore the concentration transition ‘‘hcp Co–P → amorphous state’’ is accompanied by a decrease of the contribution $\Delta H_{1,a}$ to the total FMR linewidth near x_c. The latter signifies that the relaxation source due to which the contribution of ΔH_u to $\Delta H(x)$ predominates is activated near the concentration transition x_c.

The indication of the origin of this relaxation source contains the above-discussed dependence $M_0(x)$ for Co–P powders, which is characterized by a change in the gradient of $M_0(x)$ near x_c. Since the electron transport mechanism does not depend on the type of structural ordering of the solid solution,[11] the increase at $x \approx x_c$ of the rate of decrease of M_0 with increasing x is initiated by an additional factor which is realized in amorphous powders. Such a factor is the thermodynamically stimulated stratification of the supersaturated solid solution Co–P into a less concentrated Co–P solution and Co_2P inclusions (precipitates). This supposition does not contradict the x-ray diffraction data which show that the Co_2P inclusions first appear in the diffraction curves (for $x > 20$ at. % P) only if the inclusions are sufficiently large. Just like nonmagnetic pores, Co_2P inclusions strongly influence the formation of the linewidth ΔH_u from the moment of formation, while nonmagnetic pores have a negligible effect on the local anisotropy H_a. We note that in the Ref. 2, where a radical difference was observed between the temperature dependences $\Delta H(T)$ and $H_a(T)$ for films of the amorphous alloy $Co_{87}P_{13}$ in the temperature range $T > 300\,^\circ C$ was observed, stratification of Co–P into Co and Co_2P was also invoked to explain the shape of these curves. In amorphous powders of Co–P alloys with an anomalously high vacancy density (which is indicated indirectly by a change in the morphology of the particles at x_c, indicating a change in the growth mechanism of the particles), stratification effects in the solid solution Co–P can occur at lower temperatures (preparation temperature $80\,^\circ C$) and P concentrations ($x \approx 10$ at. %).

In summary, our investigations established the following. The resonance characteristics (inhomogeneous FMR linewidth ΔH) of Co–P powders obtained by chemical deposition are more than an order of magnitude larger than the analogous characteristics of films and coatings of Co–P alloys (prepared by the same method). The linewidth ΔH of powders of the alloys Co–P with amorphous particles is two to three times larger than ΔH for Co–P powders of crystalline particles. This is a result of stratification processes with the precipitation of nonmagnetic Co_2P formations in the amorphous powders. For a constant concentration of nonmagetic precipitates in the powder particles, the dependence of the linewidth ΔH on the average particle size correlates with the analogous dependence of the local anisotropy field H_a.

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