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Effect of Crystal Size on the Crystalline Structure and Magnetic Properties of Cobalt Films Obtained via Chemical Deposition

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Abstract—A study is performed of the relationship between the sizes of cobalt crystallites and the coercive and anisotropic properties of Co–P films obtained via chemical deposition. The emergence of induced anisotropy in films obtained at low pH (7.2–8.7) is due to size effects that transform the cobalt's crystal lattice from face-centered cubic to hexagonal close-packed as the film grows in a magnetic field.

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INTRODUCTION

Technologies that help discover new properties of different materials for practical use due to the manifestation of size effects are of particular interest [1–3]. Of undoubted interest in this field is the chemical technology for obtaining magnetic films, which is based on reducing metals from aqueous solutions without using an external source of electric current [4]. Chemical deposition can be used to grow nanostructures or nanosized films (including ones with multiple layers) on surfaces of complex shape [5] and powders. This technology allows us to change the crystal structure of films relatively easily by altering the composition of solutions from which metal ions are reduced. This is especially seen in Co–P films obtained via chemical deposition, where changing the pH of solutions results in a qualitative change in the magnetic characteristics of samples [6].

In addition to interesting magnetic characteristics, cobalt–phosphorus films have properties that make them promising electrocatalytic coatings for electrodes when generating hydrogen via electrolysis [7–9], a process now becoming essential in developing green energy. Cobalt films are also considered an effective alternative to chromium coatings, due to the simpler organization of the technological process [10].

The aim of this work was to determine the relationship between the size of Co crystallites and the anisotropic properties of Co–P films in the 7.2 to 8.7 range of pH, in which a face-centered close-packed (HCP) cobalt phase emerges.

EXPERIMENTAL

Samples of thin films ~300 nm thick, were obtained via the chemical reduction of cobalt from aqueous solutions based on cobalt sulfate that contained sodium citrate as a complexing agent, sodium hypophosphite as a reducing agent, and sodium carbonate as an alkaline reagent [11]. The pH value of the working solution was determined at room temperature using a pH-150МИ meter. Co–P films were deposited on coverslip substrates that were sensitized and activated in aqueous solutions of tin chloride and palladium chloride, respectively. The working solution was heated to ~100°C in a water bath and deposited in a constant magnetic field applied in the vertical plane of the film. A magnetic field of H ~ 2.5 kOe in the substrate area was created by a pair of permanent magnets connected by a magnetic circuit made of transformer iron. The composition and thickness of the films were determined using an S4 Pioneer X-ray fluorescence spectrometer.

The diffraction patterns were recorded with a BrukerDUO diffractometer, according to the procedure described in [12]. Constant K_U of induced magnetic anisotropy was determined by analyzing the torque curves obtained at room temperature with a

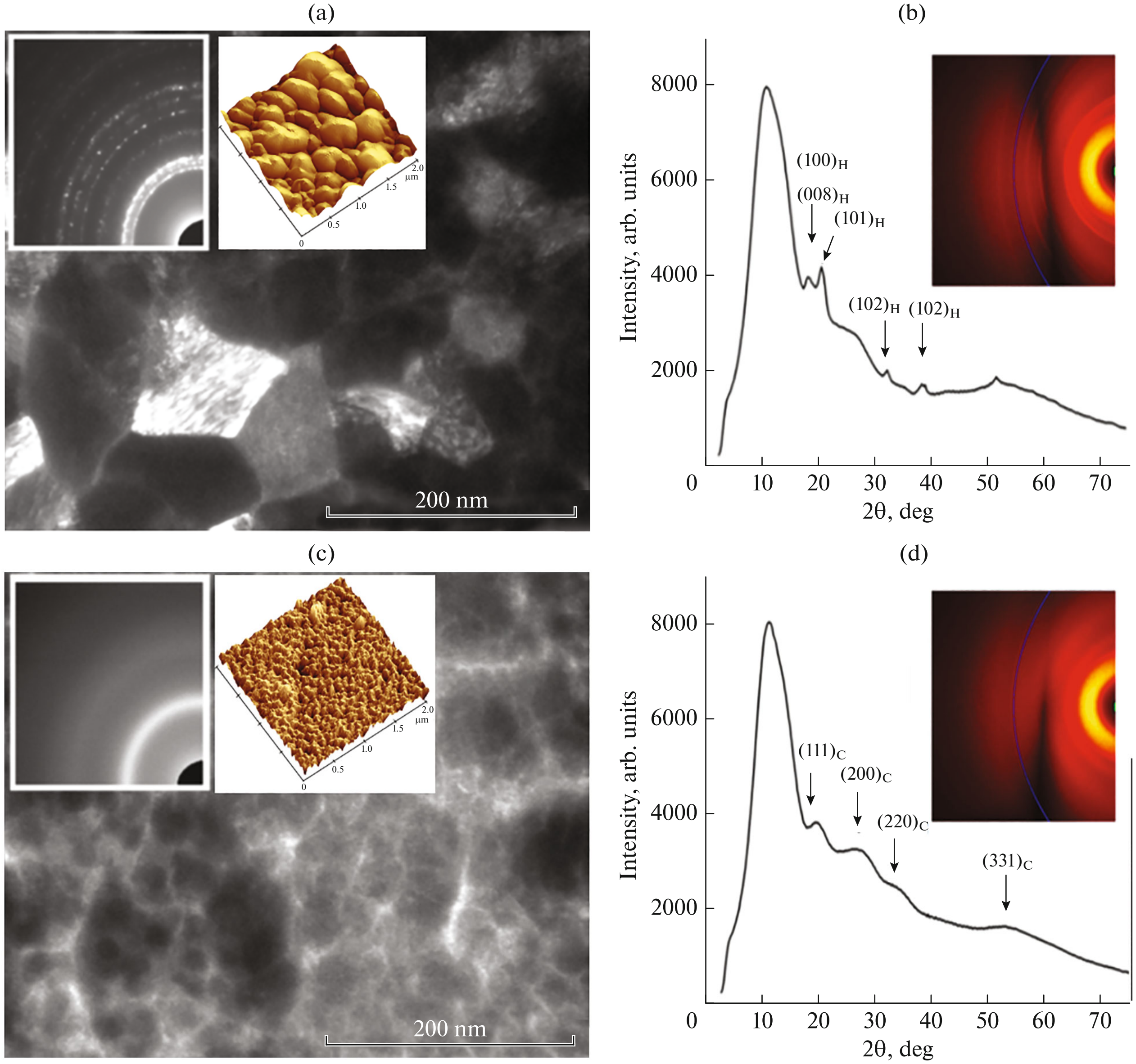

Fig. 1. (a, c) Images of electron diffraction, atomic force microscopy, and electron microscopy and diffraction patterns of (b) high anisotropic and (d) low anisotropic Co–P films obtained at pH (a, b) < 8.5 and (c, d) ≥ 9.

rotational anisometer in a magnetic field of H ~ 10 kOe, applied in the plane of the film.

RESULTS AND DISCUSSION

Co–P films obtained at different acidities of the working solution can differ greatly in the size of cobalt crystallites, as is reflected in a film's surface morphology. The average grain size shrinks monotonically as the pH of the solution grows [13].

A typical surface view and electron microscope images of the structure of Co–P films obtained at pH < 8.5 are presented in Fig. 1a. Their electron diffraction pattern (Fig. 1a, inset) shows the HCP structure of such samples.

Figure 1c shows a typical view of the surfaces of films obtained at high pH ≥ 9; the electron diffraction pattern of such samples reflects an amorphous structure.

More detailed information about the structure of the studied samples can be obtained by analyzing their diffraction patterns. The interpretation of the diffraction patterns of high-coercivity samples obtained at low pH also indicates the presence of HCP cobalt (Fig. 1b), while the diffraction patterns of samples obtained at high pH (Fig. 1d) reflect the existence of a face-centered cubic (FCC) cobalt crystal lattice.

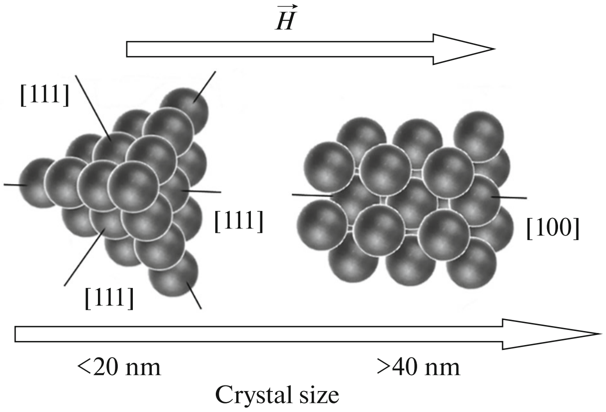

Fig. 2. Orientation of the base plane of HCP cobalt as a film grows in a magnetic field.

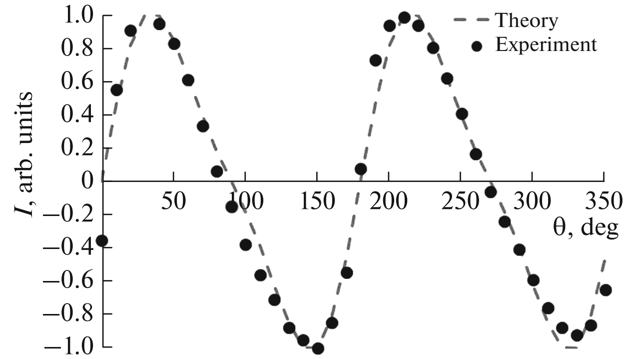

Fig. 3. Angular dependence of the torque moment of a highly anisotropic Co–P film.

The formation of one phase modification or another in cobalt particles can result from size effects (i.e., the difference between the free energy of a particle in FCC or HCP, depending on the particle size). The free energy of a particle can be presented as the sum of the volume and surface components:

$$W = W_v + W_s. \quad (1)$$

Experimental data and theoretical estimates of the free energy for cobalt particles of different phases [14, 15] suggest that in fine cobalt particles with linear dimensions smaller than 20 nm, the free energy is lower in the FCC phase than in the HCP phase, resulting in predominance of the cubic phase. In contrast, the relative contribution from the surface energy in large particles (over 40 nm) becomes smaller in the HCP phase, resulting in the predominance of this phase. A mixture of these phases is observed in the intermediate region (from 20 to 40 nm).

Such features of cobalt particles explain the transformation of the crystal structure of Co–P films upon a change in the pH of solutions. The typical sizes of crystallites in the studied films obtained at low pH were ~70 nm and higher. The hexagonal phase is stable for such cobalt particles, as is observed experimentally from the high values of the coercive force [11]. Raising the pH reduces the size of cobalt particles, making the hexagonal phase unstable with cobalt atoms fitting into FCC structures in the immediate environment.

Competing factors in the formation of different modifications of the cobalt phases are apparently also observed in film growth at the low acidity of the solutions. A Co–P film forms by an island mechanism during chemical deposition [16], and the smallness of individual crystallites causes the FCC phase to predominate at the initial stage of deposition. However, as the film grows thicker with an increase in film continuity as a result of the growth and coalescence of cobalt crystallites, conditions are created for the emergence of the HCP phase.

The packing of atoms in the basic HCP plane defined by axis *c* corresponds to the packing of FCC atoms with crystallographic direction [111] [17]. When there is no external magnetic field, the axes of easy magnetization of individual HCP cobalt crystallites fit into the plane of the film because of the demagnetizing factor. Due to the randomness of the orientations of the FCC planes, axis *c* of HCP cobalt in the plane of the film is then oriented in all directions with equal probability, resulting in magnetic isotropy of the films. However, applying a magnetic field in the plane of the film creates favorable conditions for the growth of crystallites whose axes of easy magnetization are directed close to the direction of the field, leading to induced magnetic anisotropy. Such rearrangement of the cobalt structure from FCC to HCP as a film grows in a magnetic field is shown schematically in Fig. 2.

Using the calculations given in [18] for polycrystalline cobalt, the energy of induced magnetic anisotropy for a thin film when an external magnetic field is applied in its plane can be determined as

$$W_{\mathrm{in}} = (0.434K_1 + 0.299K_2)\cos^2\theta + 0.293\cos^4\theta, \quad (2)$$

where θ is the angle between the axis of easy magnetization and the direction of the magnetic field. K_1 and K_2 are the first and second constants of anisotropy of the HCP cobalt phase.

Mechanical moment $L(\theta)$ acting on the film from the side of the magnetic field, defined as

$$L(\theta) = -\frac{dW_{\mathrm{in}}}{d\theta}, \quad (3)$$

is

$$L(\theta) = (0.434K_1 + 0.592K_2)\sin 2\theta + 0.147\sin 4\theta. \quad (4)$$

Figure 3 shows theoretical curve $L(\theta)$ (dashed curve) obtained at known K_1 and K_2 of HCP cobalt, which is in good agreement with experimental data (dots). This confirms the above mechanism of induced anisotropy in the considered films that is associated with the formation of an HCP cobalt phase from the FCC phase as a film grows in a magnetic field.

CONCLUSIONS

Our results suggest that the formation of Co–P films with different crystal structures during chemical deposition is determined by size effects (i.e., the difference between the free energy of cobalt particles of the HCP and FCC phases). The size effects in the studied films are observed during growth at low acidities of the solution. The FCC phase predominates according to an island mechanism at the initial stage of film deposition, due to the smallness of the cobalt crystallites. Conditions for the emergence of the HCP phase and an increase in film continuity resulting from the growth and coalescence of cobalt crystallites are created as the film grows thicker. This conclusion is confirmed by the angular dependence of the torque moment and the induced anisotropy of Co–P films obtained in a magnetic field at low acidities of the solution.

CONFLICT OF INTEREST

The authors declare they have no conflicts of interest.

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