High-Pressure Phases in Nanocrystalline Co(C) Films Obtained by Pulsed Plasma Vaporization

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Received August 14, 2000

The phase composition of nanocrystalline Co(C) films obtained by a new pulsed plasma vaporization technique was found by studying their atomic structure and magnetic properties. The films deposited at the substrate temperature $T = 50°C$ were of heterophase structure and consisted of a supersaturated solid Co(C) solution and the metastable Co_3C carbide. The films obtained at $T = 150°C$ represented a mechanical mixture of the metastable Co_3C and Co_2C carbides. The metastable Co_3C and Co_2C carbides obtained in a nanocrystalline state were high-pressure phases (~100 kbar). The thermal stability ranges of these metastable phases were determined. © 2000 MAIK "Nauka/Interperiodica".

PACS numbers: 75.70.-i; 76.50.+g; 81.30.Bx

It is known that nanocrystalline alloys possess a high defect density, an excess volume per atom, and hence an excess Gibbs free energy. This leads to the formation of new metastable phases in the nanostructured state. A new pulsed plasma vaporization technique was developed at the Institute of Physics, Siberian Division, Russian Academy of Sciences (Krasnoyarsk). Nanocrystalline Fe, Co, and Ni films containing from 20 to 30 at. % C can be obtained by this technique [1]. Nanocrystalline Fe(C) alloy films were studied in [2]. It was found that a chain of structural transformations, fcc Fe(C) $\longrightarrow$ hcp Fe(C) $\longrightarrow$ bcc Fe + C, was carried out in these films as a result of thermal relaxation. It is known that a closely packed modification, hcp Fe, is a high-pressure phase and is stabilized at $P \sim 50$ kbar. The work presented here is devoted to studying nanocrystalline Co(C) films obtained by the pulsed plasma vaporization technique. The aim of this work is to investigate the phase composition of Co(C) films and to determine the thermal stability ranges of the metastable structural states found in this work.

Co(C) alloy films 1000 Å thick were obtained by the pulsed plasma vaporization technique in a vacuum with the residual gas pressure $P_0 = 10^{-6}$ mm Hg. Glass and glass ceramic were used as substrates. The films were synthesized at the following substrate temperatures T_i: $T_1 = 50°C$, $T_2 = 100°C$, $T_3 = 150°C$, and $T_4 = 250°C$. Stepped annealing of the Co(C) films was performed for an hour in a vacuum chamber with the residual gas pressure $P_0 = 10^{-6}$ mm Hg. The atomic structure of the initial and annealed nanocrystalline Co(C) films was studied by transmission electron microscopy and synchrotron radiation X-ray diffraction (Institute of Nuclear Physics, Siberian Division, Russian Academy of Sciences, Siberian International Center of Synchrotron Radiation). The synchrotron radiation wavelength was $\lambda = 1.748$ Å.

The dynamic magnetic properties of nanocrystalline Co(C) films were studied on a standard x-band spectrometer. The resonant fields of ferromagnetic resonance were measured at room temperature throughout the entire range of angles between the external field and the film plane with the aim of determining the effective magnetization M_{eff} by the equation

$$H_\perp^r - 4\pi M_{eff} = \sqrt{H_\parallel^r(H_\parallel^r + 4\pi M_{eff})},$$

where $H_\perp^r$ and $H_\parallel^r$ are the fields of ferromagnetic resonance for the corresponding experimental geometry.

Co(C) films obtained at $T_i = 50°C$. Figure 1 displays X-ray spectra ($\lambda = 1.748$ Å) of Co(C) films obtained at $T_i = 50°C$. Curve a in Fig. 1 (initial sample) is characterized by two peaks: $d = 2.07$ Å (the region of coherent scattering estimated from the width of this peak equals 40 Å) and $d = 2.20$ Å. The reflection at $d = 2.07$ Å is considerably shifted towards small angles with reference to the reflection from the (111) plane of the fcc Co lattice, which points to an increased value of the lattice constant a. The C content of the fcc Co solid solution can be estimated from this shift. This estimation gives ~$Co_{90}C_{10}$. (Note that the equilibrium solubility of C in Co at $T = 1310°C$ is only $X_0 \sim 3$ at. %). The peak at $d = 2.20$ Å is due to the reflection from the (120) plane of the metastable Co_3C carbide with an orthorhombic lattice. Annealing at $T = 200°C$ leads to the for-
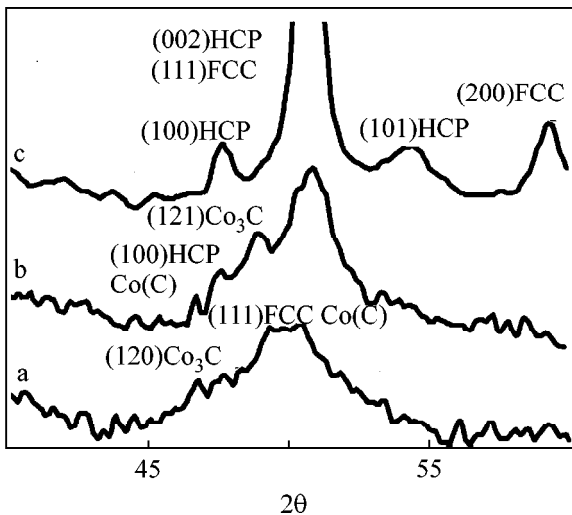
Fig. 1. X-ray diffraction patterns of (a) the initial Co(C) film obtained at $T = 50°C$, (b) an annealed film at $T = 200°C$, and (c) a film annealed at $T = 400°C$.
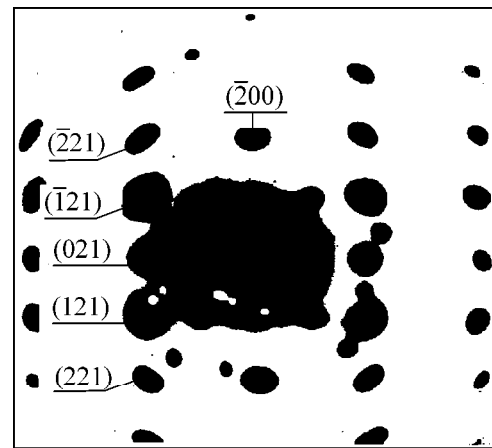
Fig. 2. Microdiffraction pattern obtained from the metastable Co_3C carbide. The axis of the reflection zone is $[01\bar{2}]$.

mation of the carbide (additional reflections appear) and to the appearance of reflections from a solid solution of hcp Co(C). Annealing at $T = 400°C$ leads to the dissolution of Co_3C (reflections from the carbide disappear in curve c, Fig. 1) and to the formation of a heterophase system (hcp + fcc) Co with lattice constants typical of the phases of pure cobalt.
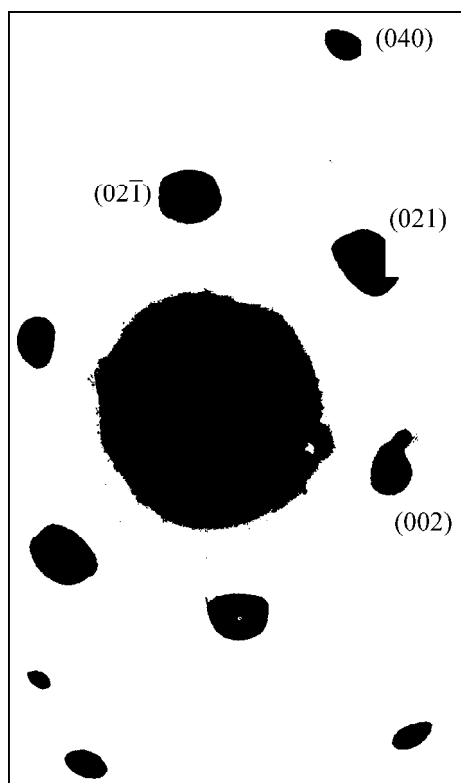
Electron-diffraction patterns obtained for the initial samples were characterized by three diffuse rings, which indicated that the atomic structure of the Co(C) films was disordered [1]. After annealing for one hour ($T = 140°C$), discrete-point diffraction patterns were observed. Figure 2 shows this microdiffraction pattern and its interpretation, indicating that a Co_3C phase with an orthorhombic lattice was observed. The lattice parameters of the metastable Co_3C carbide determined from the diffraction pattern ($a = 4.5$ Å, $b = 5.14$ Å, $c = 6.72$ Å) are in agreement with the results of structural investigations performed for metastable carbides by other authors [3].

One ferromagnetic resonance line was observed for the film under study when it was aligned parallel to the magnetic field. We measured the angular dependence of this line throughout the entire range of angles. Using Eq. (1), we determined the effective magnetization of a supersaturated solid Co(C) solution (metastable Co_3C carbide was found to be paramagnetic at room temperature). For the films under study, Table 1 presents M_{eff} of the Co(C) solid solution, the annealing temperatures, and the phase states found by structural methods. An increase in magnetization after annealing at $T = 250°C$ is associated with the fact that the decomposition of the metastable Co_3C carbide results not only in an increase in the volume fraction of the Co(C) solid solution, but also in a decrease in the concentration of C in this solid solution down to X_0.

Nanocrystalline Co(C) films obtained at $T_i = 100–150°C$. As well as the samples obtained at $T_i = 50°C$, these films were found to be two-phase systems. However, the metastable Co_3C carbide was the major matrix phase in this case. Another metastable carbide, Co_2C, was present as inclusions dispersed in this matrix. Figure 3 shows a photograph of a Co_2C carbide microdiffraction pattern and its interpretation. The orthorhombic lattice constants of the stoichiometric Co_2C carbide calculated in this work ($a = 2.9$ Å, $b = 4.47$ Å, $c = 4.43$ Å) are in agreement with the results obtained by other authors [3]. The Co_2C carbide has higher thermal stability than the Co_3C phase. It was observed even in Co(C) films annealed at $T = 500°C$. It was possible to determine the decomposition temperature of metastable carbides by ferromagnetic resonance measurements carried out for the given sets of samples after their thermal annealing. Note that these films in the initial state exhibit no resonance absorption of microwave radiation energy, because the Co_2C carbide, as well as the Co_3C carbide, is paramagnetic at room temperature. After annealing these films for one hour at $T = 250°C$ (the decomposition temperature of Co_3C), a ferromagnetic resonance signal appears. From measurements of the angular dependence of the resonant fields, it was found that a supersaturated Co(C) solid solution was the ferromagnetic matrix in these

Table 1. Co(C) at $T = 50°C$

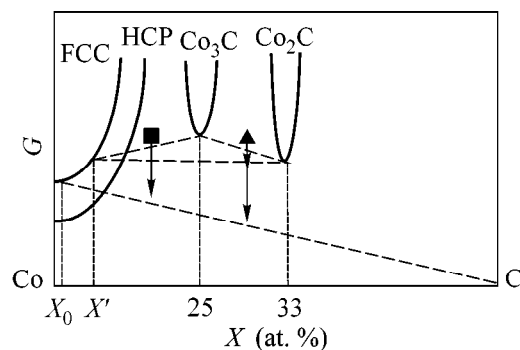| T_{anneal}, °C	M_{eff}, Hz	Composition
Initial	990	$-Co_3C + Co_{90}C_{10}$
150	1000	$-Co_3C + Co_{90}C_{10}$
250	1280	$-Co(C)$

Fig. 3. Microdiffraction pattern obtained from the metastable Co_2C carbide. The axis of the reflection zone is [100]. The film was obtained at $T = 500°C$, and annealing was carried out at a temperature of $300°C$.

annealed films. Table 2 gives the values of effective magnetization M_{eff} calculated from the ferromagnetic resonance curves and the annealing temperatures for this series of films. From the data presented in Table 2, it is evident that the metastable Co_2C carbide is decomposed after annealing for one hour at $T = 520°C$.

Co films obtained at $T_i = 250°C$ are characterized by (hcp + fcc) Co reflections. The lattice constants calculated from these reflections are typical of the phases of pure cobalt. The measured magnetic characteristics exhibit the same property.

The structural states occurring in metastable Co(C) films were analyzed with the use of a metastable Co–C phase diagram shown in Fig. 4 in the coordinates (G, C), where $G = H - TS$ (H is enthalpy and S is

Table 2. Co(C) at $T = 100–150°C$

T_{anneal}, °C	M_{eff}, Hz	Composition
Initial	–	$-Co_3C + Co_2C$
250	820	$-Co_2C + Co(C)$
350	850	$-Co_2C + Co(C)$
520	1250	Co(C)

Fig. 4. Qualitative phase diagram of a Co–C system on the (G, X) coordinates.

entropy) is the Gibbs energy. Here, the transition enthalpy $\Delta H^{fcc \to hcp} = 0.22$ kcal/mol [4], and the positive formation enthalpies of the Co_3C and Co_2C carbides are ~6 kcal/mol and ~4 kcal/mol, respectively [4]. Co(C) solid solutions that are in equilibrium with metastable carbides are supersaturated. The highest concentration of carbon in an equilibrium solid solution is $X_0 \sim 3$ at. %, which is considerably lower than the concentration of carbon in the metastable alloy $X' \sim 10$ at. %. In accordance with the results of studying the structure and magnetic properties, the initial state of the metastable Co–C films obtained by pulsed plasma vaporization at $T_i = 50°C$ is shown by a square in Fig. 4. An increase in the substrate temperature during deposition to $T_i = 100–150°C$ results in the formation of a mechanical mixture of the metastable Co_3C and Co_2C carbides in the initial state. This state is shown by a triangle in Fig. 4. The metastable Co_3C and Co_2C carbides are high-pressure phases and are stabilized in the Co–C alloy at the pressure $P \sim 100$ kbar [5]. The occurrence of the metastable phases in the nanocrystalline films under study was possible for the following reasons. Because of the small grain size (~40 Å), the specific area S_n of the nanocrystalline Co(C) alloy is very large. The surface energy density σ_n in the metastable Co(C) films obtained by the pulsed plasma vaporization technique turned out to be so high that the contribution of the surface energy $S_n \times \sigma_n$ to the thermodynamic Gibbs potential ΔG was comparable to the formation enthalpy of the metastable carbides $\Delta G \sim \sigma_n S_n \geq \Delta H^{carbide \to Co + C}$. Heating a metastable Co(C) film results in an increase in the grain size of the nanocrystalline alloy; therefore, the relationship between ΔG and $\Delta H^{carbide \to Co + C}$ reverses its sign: $\Delta G < \Delta H^{carbide \to Co + C}$. Thus, the decomposition of metastable phases occurs.

It may be concluded that high-pressure phases occur in nanocrystalline Co(C) films obtained by the pulsed plasma vaporization technique at certain substrate temperatures. Films synthesized at $T_i = 50°C$ are heterophase systems and consist of a supersaturated Co(C)

solid solution and the stoichiometric Co_3C carbide. The following chain of structural transformations is observed upon thermal relaxation in the given systems (see the square in Fig. 4): $Co(C) + Co_3C \longrightarrow Co + C$. In the case of nanocrystalline Co(C) films obtained by the pulsed plasma vaporization technique at $T_i = 100-150°C$, the initial phase composition and the sequence of structural transformations appear to be different (see Fig. 4, triangle): $Co_3C + Co_2C \longrightarrow Co(C) + Co_2C \longrightarrow Co(C) + C$. The decomposition of the metastable Co_3C and Co_2C carbides proceeds at temperatures of 250°C and 520°C, respectively.

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Translated by A. Bagatur'yants