Ostwald step rule in films of metastable nanocrystalline alloys Fe–C prepared by pulsed plasma vaporization

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Ferromagnetic nanocrystalline Fe(C) films were prepared by pulsed plasma vaporization. A comprehensive investigation of the structure and magnetic properties made it possible to identify the type of short-range order here and to establish the sequence of structural states occurring in these films in the process of thermal relaxation: fcc-Fe(C)→hcp-Fe(C)→bcc-Fe+C. On the basis of an analysis of the metastable phase diagrams using Ostwald's rule, it is shown that the observed scenario of the structural transformations in these metastable nanocrystalline alloys Fe(C) is a natural phenomenon. © *1999 American Institute of Physics.* [S0021-3640(99)00523-X]

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It is well-known that crystalline iron exists in three polymorphic modifications, bcc-Fe (α-Fe, δ-Fe), thermodynamically stable in the temperature range 1183–1667 K Fe (γ-Fe), and thermodynamically stable at high pressures ($\sim$130 kbar) hcp-Fe (ϵ-Fe). The latter two modifications of the close-packed structure of Fe in the form of metastable phases can also be obtained at low temperatures and atmospheric pressure. These metastable phases are ordinarily prepared in the form of ultrathin (several molecular layers) films on appropriate substrates[1,2] or small coherent inclusions (precipitates) in the appropriate materials,[3] and in the form of thin films and microwires by fast cooling of the melt.[4,5]

A new technological method, called here pulsed plasma vaporization (PPV) in vacuum, has been developed at the Institute of Physics of the Siberian Branch of the ran.[6–8] In this technology condensation occurs at a high rate (estimated to be $\sim 10^4$ Å/s in a pulse), and solidification of the condensate occurs according to the scheme vapor $\rightarrow$ liquid $\rightarrow$ crystal. This technology makes it possible to obtain films of a transition metal with a high carbon content ($\sim$20 at.%) in a metastable nanocrystalline state.[9]

The purpose of the present work is to identify the initial and investigate the sequence of structural states of films of a nanocrystalline alloy Fe (synthesized under ultrafast condensation conditions), which appear in the process of thermal relaxation.

EXPERIMENTAL PROCEDURE

The experimental methods used in our work are based on a study of the static and dynamic magnetic properties of nanocrystalline Fe films, as well as the atomic and chemical structure of this material. Fe films, 200–2000 Å thick, were obtained on dielectric substrates (cover glass, pyrex glass, NaCl, MgO) by PPV in vacuum with residual-gas pressure $P_0 \approx 5.5 \cdot 10^{-6}$ mm Hg. The atomic structure of the nanocrystalline Fe films prepared by the PPV method was determined by x-ray diffraction of synchrotron radiation (SR) (Institute of Nuclear Physics, Siberian Branch of the Russian Academy of Sciences, Siberian International Center for SR). The SR wavelength was 1.49 Å. The electronic structure and chemical composition of these films were determined from investigations of photoelectron and Auger spectra on a RIBER photoelectron spectrometer (a source with an Mg anode and energy of the Mg K line $h\nu = 1253.6$ eV was used) at the Institute of Semiconductor Physics of the Siberian Branch of the Russian Academy of Sciences.

The dynamical magnetic properties of nanocrystalline Fe films, determining the ferromagnetic resonance (FMR) parameters, was studied in a standard ÉPA-2M spectrometer with frequency $f = 9.2$ GHz. The FMR resonance fields were measured in the entire range of angles between the external field and the film plane in order to calculate the effective magnetization M_{eff} from the equation

$$H_{\perp}^r - 4\pi M_{\text{eff}} = \sqrt{H_{\parallel}^r(H_{\parallel}^r + 4\pi M_{\text{eff}})}, \tag{1}$$

where $H_{\perp}^r$ and $H_{\parallel}^r$ are the FMR fields with the corresponding experimental geometry. The measurements were performed at room temperature.

The static magnetic measurements were performed with an automated vibrating magnetometer with fields up to 20 kOe and temperatures ranging from 4.2 to 250 K. The temperature dependence of the saturation magnetization $M_s(T)$ of nanocrystalline Fe films, measured with external field $H = 20$ kOe in the temperature range 70–210 K is described well by the law

$$M_s(T) = M_{s0}(1 - BT^{3/2}), \tag{2}$$

which made it possible to determine the saturation magnetization and the numerical value of the constant B and to calculate the exchange interaction constant A:

$$A = \frac{k}{8\pi}\left(\frac{g\mu_B}{M_{s0}}\right)^{1/3}\left(\frac{2.612}{B}\right)^{2/3}. \tag{3}$$

The high-temperature dependences of the saturation magnetization $M_s(T)$ were measured on a torsional anisometer in the temperature range from 273 to 750 K with constant field $H = 5.7$ kOe. The Curie temperatures T_c of nanocrystalline Fe were determined by extrapolating the temperature dependence $M_s(T)$ to zero magnetization using the linear dependence of M_s^2 on T near T_c, observed for these materials.

The static magnetic measurements also included measurements of the magnetization curve $M(H)$. The local anisotropy H_a (related with the magnetocrystalline anisotropy constant by the relation $K = H_a \cdot M_s/2$) was calculated from the magnetization curves up to saturation, measured in the film plane at $T = 250$ K.

TABLE I.

	Initial state	$T_{an}=200\,°C$	$T_{an}=400\,°C$	bcc-Fe
M_{s0}, G	1540	1180	1150	1740
M_{eff} (FMR), G	1180	1030	–	1740
T_c, °C	400	300	300	770
A, 10^{-7} ergs/cm	5.5	3.2	3.7	20
H_a, kOe	2.0	5.9	6.1	0.5

In the course of the investigations the initial nanocrystalline Fe films were subjected to thermal annealing. The annealing was performed in a high-vacuum chamber for 1 h at temperatures 200 and 400 °C.

RESULTS AND DISCUSSION

The results of the analysis of the photoelectron spectra showed that the surface of the films of nanocrystalline Fe is oxidized — the line O1S (530.4 eV) due to oxygen and a component attesting to the hydroxyl group (OH^-) are observed in the electronic spectra. The shape of the Fe $2P_{3/2}$ line qualitatively indicates two types of nearest-neighbor environment of the Fe atom. The profile of elements contained in nanocrystalline Fe over the film depth was reconstructed by Auger-electron spectroscopy. The composition of the experimental films was as follows: Fe (~75 at.%) and C (~20 at.%) with a uniform distribution of the elements (x_{Fe}/x_C) over the film depth.

The results of the magnetic measurements are presented in Table I. It is evident that the initial metastable state (which we call X_1), realized in films of the alloy Fe(C), is characterized by the following basic magnetic parameters: $A=0.56\cdot10^{-6}$ ergs/cm, $M_0=1540$ G, $H_a=2$ kOe, $T_c=400\,°C$. As a result of thermal relaxation, the initial state transforms into a different metastable state (which we call X_2) with the magnetic parameters $A=0.3\cdot10^{-6}$ ergs/cm, $M_0=1200$ G, $H_a=6.1$ kOe, and $T_c=300\,°C$.

The large difference in the measured magnetic parameters A, M_0, T_c, and H_a attests to structural differences between the observed metastable states. A transition into the thermodynamically equilibrium bcc-Fe phase occurs after a 1-h anneal at $T=600\,°C$.

The results of x-ray crystallographic analysis performed on the initial Fe films (~1000 Å thick) and on the annealed Fe films ($T_{an}=200\,°C$) are presented in Fig. 1. The diffraction curve of the initial films, measured in SR (curve *1* in Fig. 1), contained one broadened peak centered near $d=2.04$ Å and $\Delta(2\theta)\approx3°$ wide. Such a diffraction curve indicates a nanocrystalline structure of the initial material with a grain size of the order of 40 Å. However, it is impossible to draw a conclusion about the type of atomic lattice in these nanocrystalline grains on the basis of a single reflection. The annealed films of nanocrystalline Fe were characterized by a diffraction curve (curve *2* in Fig. 1) containing a set of reflections. Five of the reflections with the highest intensities, marked in Fig. 1, attest to a hexagonal close-packed structure (hcp) for these Fe films. (The fact that a complete set of reflections characterizing a polycrystalline hcp structure is lacking attests, in our view, to a certain degree of texture in these films.) Analysis of these reflections gives the following values for the lattice parameters of Fe: $a=2.63$ Å, $c=4.46$ Å, c/a
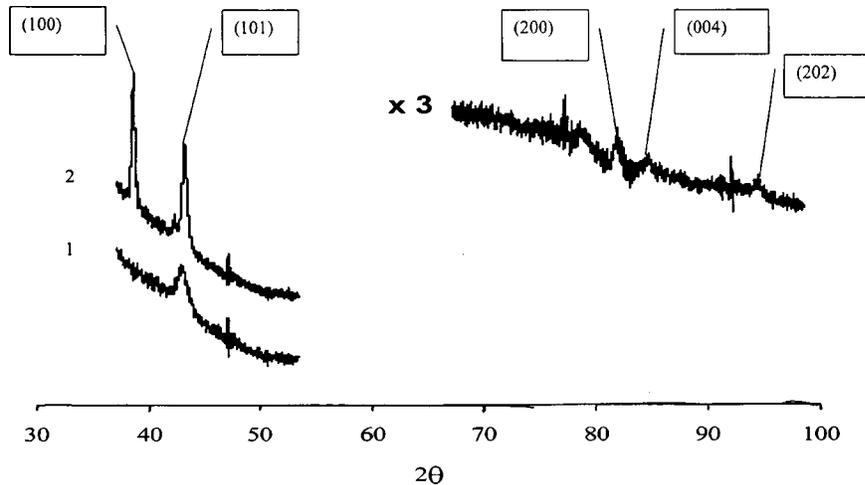
FIG. 1. X-Ray diffraction patterns of the initial nanocrystalline Fe film (1) and a film (2) annealed at T_{an} = 200 °C.

$= 1.696$. The volume per Fe atom calculated from these parameters is $V_{at} = 13$ Å^3. We note that the computed volume V_{at} per Fe atom in these Fe films is more than 10% greater than the analogous quantity in thermodynamically equilibrium hcp-Fe and is close to the value $V_{at} \approx 13$ Å^3 observed in rapidly quenched metastable alloys hcp-Fe-C.[5]

The results of x-ray diffraction on SR made it possible to identify the atomic structure of the metastable state X_2 and to assert with adequate substantiation that this is hcp-Fe. Structural investigations using a TEM turned out to be most informative for identifying the initial metastable state X_1. The point is that the transition $X_1 \rightarrow X_2$ can be obtained not only by isothermal annealing at $T = 200$ °C, $t = 1$ h, but also by irradiation with a beam of electrons in an electron microscope (voltage 150 kV). Under such actions the initial ''x-ray amorphous'' state in the nanocrystalline films transforms into the hcp solid solution Fe(C). This process is virtually instantaneous (several seconds). Careful analysis of the observed transformations in nanocrystalline films of the alloy Fe(C) established that the hcp-Fe reflections arising in the electron diffraction pattern under the action of an electron beam are secondary. Initially, ordering of the initial ''x-ray amorphous'' (nanocrystalline) state occurs. This is indicated by the appearance of reflections against the background of the initial halo. In the course of the further action of the electron beam on the experimental film, reflections of the hcp phase of Fe appear, and reflections of the initial metastable state vanish. We were able to identify the initial metastable phase. This was found to be a state with face-centered cubic packing fcc-Fe. The lattice parameter of this fcc state is $a = 3.72$ Å and the volume per Fe atom is V_{at} $= 13.05$ Å. Figure 2 shows the diffraction pattern of the initial nanocrystalline state (Fig. 2a) and its transformation under the action of the electron beam. Figure 2b shows the interpretation of the metastable structures that arise. Using the well-known relation $\Delta a \sim f$ (at. %C), we determined the chemical composition of the fcc solid solution of a microsection from which the diffraction pattern presented in Fig. 2b — $Fe_{82}C_{18}$ was obtained.
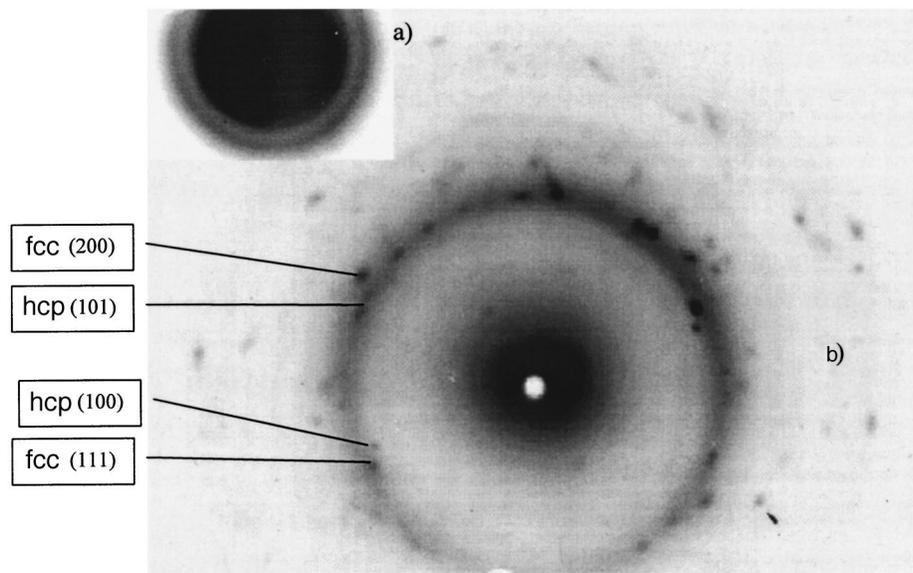
FIG. 2. Electron diffraction patterns of nanocrystalline films Fe(C): a) initial state; b) annealed by an electron beam.

The magnetic order of metastable close-packed phases of iron, fcc and hcp, is determined by the volume per Fe atom. The volume per Fe atom $V_{at}=11.5-12$ Å^3 in this material is critical. When this volume is reached the atoms of the close-packed structures transform from a low- into a high-spin state.[1] Nanocrystalline films of the alloy Fe(C) obtained by PPV are supersaturated solid solutions. The volumes per atom in these structures are $V_{at} \approx 13$ Å^3, which is more than 10% greater than the corresponding volumes per Fe atom in thermodynamically stable close–packed fcc and hcp structures ($V_{at} \approx 11$ Å^3). For this reason, the ferromagnetic (high-spin) state of the metastable Fe phases which we investigated is a natural state.

Thus, the initial metastable fcc phase Fe(C) is characterized by the following magnetic parameters: $A=0.56 \cdot 10^{-6}$ ergs/cm, $M_0=1540$ G, $H_a=2$ kOe, and $T_c=400\,°C$. The basic magnetic characteristics of the metastable phase of hcp-Fe(C) — $A=0.3 \cdot 10^{-6}$ ergs/cm, $M_0=1200$ G, $H_a=6$ kOe, and $T_c=300\,°C$ — are close to the corresponding values for cubic tight packing. An exception here is the magnetocrystallographic anisotropy field, which is three times greater than H_a in the fcc phase of Fe.

We have shown above, by structural investigations and measurement of the magnetic characteristics, that in a nanocrystalline iron alloy with the carbon structural transformations fcc-Fe(C) $\rightarrow$ hcp-Fe(C) occur as a result of thermal relaxation. A clear understanding of the sequence of the observed states can be obtained using Ostwald's rule. According to this rule, at a transition from a nonequilibrium into an equilibrium state, the system passes through all possible intermediate metastable states. Figure 3 shows the qualitative room-temperature (G,x) phase diagram of iron, where the Gibbs energy is $G=H-TS$ (H is the enthalpy and S is the entropy) and x is the carbon concentration. Here the order of magnitudes of the transition enthalpies are $\Delta H^{\gamma \rightarrow \epsilon} \approx 0.11$ kcal/mole and
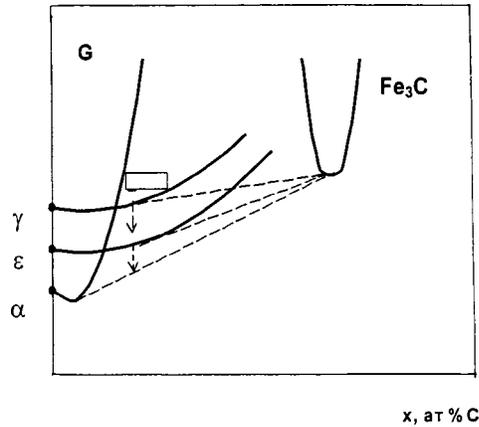
FIG. 3. Qualitative (G, X) phase diagram of iron.

$\Delta H^{\gamma \to \alpha} = 0.22$ kcal/mole, the stoichiometric compound Fe_3C (cementite) is characterized by a positive formation energy $\Delta H = 5.4$ kcal/mole.[10]

This phase diagram gives an idea of the possible scenarios realized in the metastable system Fe(C). The realization of a particular metastable state will be determined by the initial coordinates (G_0, x_0) in the phase plane or, in other words, the stored excess energy ΔG relative to the stable equilibrium of the mechanical mixture bcc-Fe + graphite. The degree of nonequilibrium ΔG of the Fe(C) condensates obtained is dictated by the technological processes of PPV. In the first place, this method makes it possible to obtain supersaturated solid solutions Fe(C), which increases the elastic energy due to an increase in the interatomic distances; in the second place, the nanocrystalline alloy Fe(C) is characterized by a small grain size (40 Å) and therefore a large energy contribution due to the specific surface area S_n. The contributions enumerated above to the thermodynamic Gibbs potential can be represented as $\Delta G = P \Delta V + \sigma_n S_n$, where P is the internal pressure, ΔV is the change in the molar volume, and σ_n is the surface energy density. According to the experimental results presented above, the initial state of the nanocrystalline alloy Fe(C), obtained by the PPV method, occupies in the (G, x) phase diagram a location indicated by the dashed rectangle. It is evident that under relaxation of the initial state Fe(C), in this case, the following structural transformations should be observed:

fcc-Fe(C) $\to$ hcp-Fe(C) $\to$ bcc-Fe+C.

The fcc and hcp solid solutions Fe(C) in the (G, x) phase diagram are shown to be in equilibrium with the stoichiometric carbide Fe_3C. Structural investigations (TEM) of separate sections of nanocrystalline Fe(C) films indicate a negligible presence of cementite. However, the high-temperature investigations of the saturation magnetization $M_s(T)$ of nanocrystalline Fe(C) films did not show the presence of an F_3C phase, characterized by the temperature $T_c = 210\,°C$. Therefore the volume fraction of iron carbide Fe_3C in the experimental Fe(C) metastable films, in all probability, does not exceed 10%.

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