

Directional crystallization and self-assembling initiated by mechanical shock or electron beam in nanocrystalline Co–C and Fe–C films

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Abstract

We investigated iron and cobalt films with 20% carbon concentration with nanocrystalline structure. One of the aims of this work is to analyze the physical nature of high-speed structural self-assembling as often happens in explosive crystallization processes in these films. © 2006 Published by Elsevier B.V.

Keywords: Alloys; Iron; Cobalt; Carbon; Surface tension; Crystallization; Transmission electron microscopy (TEM); Surface thermodynamics

1. Introduction

Iron and cobalt films of nanoscale thickness attract great interest in the last years because nanoscale structures exhibit a wide spectrum of unusual properties. These films may be prepared, e.g., sputtering on substrate at high condensation rates. In this case, nanoparticles are formed directly at the substrate surface.

2. Experimental

We realized the high-rate vacuum condensation using the method of pulse plasma sputtering (PPS) with laser heating. Films prepared by this method from a refined iron or cobalt targets have characteristic properties of the nanocrystalline state and contain a large amount of dissolved carbon (up to 20 at.%). This method is characterized by high pulse condensation rates ($>10^5$ Å/s) at a pulse duration of $\sim 10^{-4}$ s, cooling rates of the condensate of about 10^8 K/s, pulse repetition rates of 1–10 Hz, and the working vacuum of 10^{-6} Torr. The physical and engineering features of this process were described in detail in [1].

The required relationship between the metal and carbon concentration were obtained by selecting proper metal and graphite areas at the target. The volume concentrations were determined from the total film thickness measured by the interference technique and the metallic constituent thickness measured by the X-ray fluorescent analysis. The substrate temperature during the film sputtering in all cases was 20 °C. The film thickness varied from 500 to 2000 Å. The microstructure and phase composition of the films were analyzed using a transmission electron microscope PREM-200. The initial films are nanocrystalline, which is corroborated by the diffuse diffraction patterns.

3. Results

The crystallization of the films goes in an explosive way with forming from initial nanocrystalline state structures – similar to single-crystal. We noted that domains with similar to the single-crystal structure arose from the nanocrystalline state under the action of either mechanical shock (see Fig. 1) or electron beam (see Fig. 2) in a short time (~ 0.1 ms). Electron microdiffraction patterns (see Figs. 1b and 2b) obtained from these domains similar to the diffraction pattern from a single crystal. These domains

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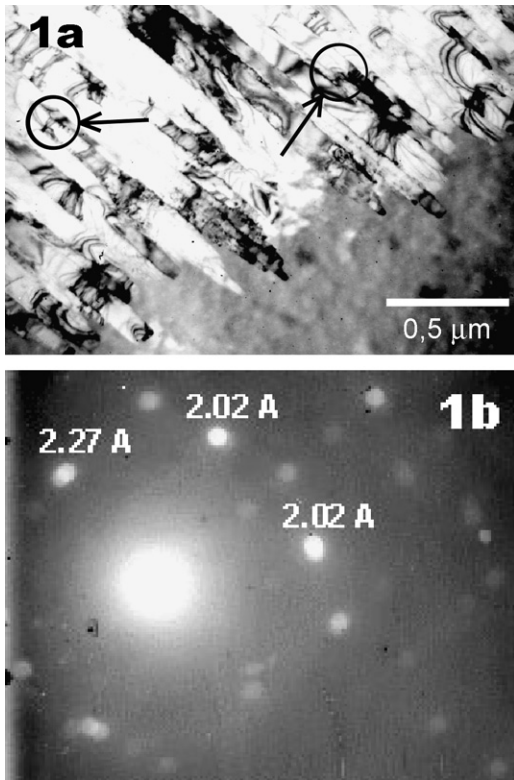


Fig. 1. (a) The electron microscopy image of Fe-C film after shock crystallization; points of bifurcation are indicated by arrows. (b) Electron diffraction picture for “single” crystal.

are self-assembling in regular structure. Since point reflections are strongly dispersed on electron diffraction patterns, interatomic distances vary within a range of 8%. Transmission electron micrograph of the “single crystals” in Fe-C film (see Fig. 1a) exhibit bending contours in the form of dark fringes that testify to strong internal bending of “atomic planes”, which reach $100^\circ/\mu\text{m}$.

4. Discussion

The high internal bends of crystalline lattice were observed in thin solid films with the high concentration of elastic and viscous stresses [2].

For this reason, we think that the excited-atom model can be used to explain of nature of self-assembling in our films. Atoms that can be shifted at a critical distance corresponding to the maximum interatomic attraction are called excited atoms [3,4].

The excited-atom has a position located on critical distance with regard to other atoms. The free volume is not a hole, it is an excited-atom volume.

One of the aims of this work is to analyze the physical nature of structural self-assembling in explosive crystallization processes. The presence of gradients of temperature and pressure create the gradients of velocity during the movement groups of nanoparticles relatively to each other. As a result, it is provided aligning action on individual

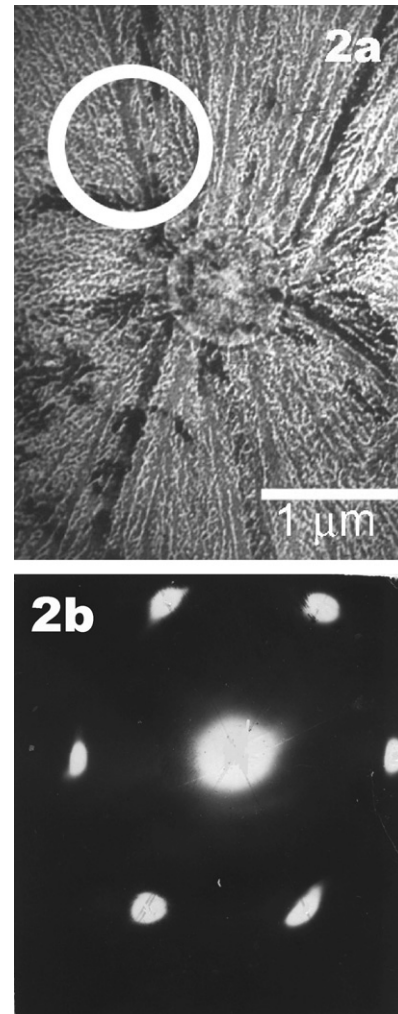


Fig. 2. Electron-microscopy images of Co-C films: (a) micrograph of “single” crystal, initiated by electron beam; (b) electron diffraction picture, indicated by circle area on (a).

nanoparticles. The phenomenon of explosive crystallization with the formation of pseudomonocrystals, both periodic and quasiperiodic can be observed. In our opinion, there are sufficient reasons to consider that the features of explosive crystallization processes in metal films with a self-assembling structure can be described in the framework of the modern theory shear transformation zone (STZ) based on the excited-atom model [3,4]. This theory is based on the concept that macroscopic deformation in nonequilibrium materials is a result of local rearrangements due to the cooperative motion of molecules in mesoscopic domains.

Plastic flow appears due to the creation and annihilation of the transformation zone which velocity depends linearly on strain. A dynamic model of super-Arrhenius relaxation in glassy materials was recently developed in [4] and is based on a well-known liquid-like model [3]. Adam and Gibbs [5] divided the free energy of viscous-flow activation into two components: the energy of interatomic-bond changeover and the energy necessary for the rearrangement

of a large group of atoms. The authors of [4] proposed a hypothetical mechanism that “might be visualized as a kinetic fluctuation that allows molecules to undergo small displacements along a force chain” – a string. Investigations of the atomic structure of self-assembling phases arising after explosive crystallization in the Co–C and Fe–C nanocrystalline films show that these films have the Frank–Kasper tetrahedral close packed structure (the [1 1 0] orientation of the Laves cubic phase, as follows from the analysis of electron microdiffraction patterns). Nanocrystallites with [1 1 0] zone axis are oriented to each other as a mosaic owing to long-range forces acting in thin films. It is the imitation of single crystal with tetrahedrally close-packed structure. Such a kind of atomic structures is usual for Tb–Fe alloys but was unknown for Co–C, Fe–C alloys. An important feature of such structure is the possibility of compress–tension of its elementary volume by 30% [6]. It is necessary to take into account, that due to a difference in temperature factors of linear expansion with a substrate the film can feel pressure about 1–6 GPa. The hydrodynamic and thermal effects competition create the structures involved periodic, quasiperiodic and chaotic structures, which are observed in our experiments. Crystallization – the complex process including mass- and heat-transmission, chemical reactions and phase transitions. Such chaotic behaviour induces casual changes of temperature, concentration that results in occurrence of local pressures and defects of crystal structure.

It is known [7], that the maximum of elastic energy loss at plastic deformation is connected to formation of grafted bends with corners of 36° and 45°. Such corners appear after disproportional deformation of low-symmetric periodic structures. From such positions it is possible to explain formation of high-symmetric quasicrystalline structures which have been found out experimentally in our previous works [8].

5. Conclusion

The originality of this work is holding in possibility to explain the physical nature of high-speed structural self-assembling.

We investigated iron and cobalt films with 20% carbon concentration with nanocrystalline structure. One of the aims of this work is to show the directional crystallization and self-assembling initiated by mechanical shock or electron beam in nanocrystalline Co–C and Fe–C films. The other aim of this work is to analyze the physical nature of structural self-organisation in explosive crystallization processes in these films. The originality of this work is holding in possibility to explain the physical nature of high-speed structural self-organisation and the corresponding features of structure formation (rotational shifts, internal bending of atomic lattice that is as large as 100°/1000 nm or larger) in the framework of the modern super-Arrhenius relaxation theory [3–5]. For explosive crystallization with strong bending of the crystal lattice or plastic deformation with rotation effects, the model of super-Arrhenius relaxation is consistent with the model of the bifurcation of the atomic lattice that was proposed in catastrophe theory [9,10].

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