

Scale Invariance of the Structure upon Explosive Crystallization of Amorphous Films

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Experimental results that are obtained in the process of the explosive crystallization of x-ray amorphous films Fe₂Tb and CoPd with magnetic anisotropy perpendicular to the film plane are reported. The internal bending of thus obtained “single crystals” reaches 100 deg/μm. An explanation of the mechanism and kinetics of explosive crystallization in the Fe₂Tb and CoPd films is proposed in the framework of the shear transformation zone theory. © 2005 Pleiades Publishing, Inc.

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The problem of the microstructure of amorphous and nanocrystalline materials obtained under nonequilibrium conditions is an important unsolved problem of solid state physics. For this reason, experimental investigations of the structure formation in such materials are of decisive importance for revealing and understanding the general laws governing amorphous and nanocrystalline substances, as well as for determining their nature and new possibilities of using them in engineering. We study Fe–Tb and Co–Pd nanocrystalline films obtained under nonequilibrium conditions. Explosive crystallization initiated by a small thermal action of 0.1–0.2 kT_{melt} or mechanical impact is observed in these films.

This work is devoted to determination of the mechanism of explosive crystallization in amorphous films of alloys based on transition metals. The regular crystal lattice does not necessarily grow in film structures; i.e., the length and arrangement of short-range interatomic bonds do not always coincide with the length and arrangement of bonds in the regular structure, respectively. In this case, local regularity is combined with adaptability necessary for growth. This behavior is observed in twin structures and quasicrystals [1] obtained under ultrafast cooling conditions. If films are magnetically ordered, their saturation magnetization upon explosive crystallization usually decreases [2, 3].

One of the aims of this work is to analyze the physical nature of explosive crystallization and the corresponding features of structure formation (rotation shifts and internal bending of an atomic lattice that are as large as 100 deg/μm or larger) in the framework of the shear transformation zone (STZ) theory [4–6]. This theory is based on the concept that macroscopic deformation in amorphous materials is a result of local rearrangements due to the cooperative motion of molecules in mesoscopic domains [4]. Plastic flow is created due

to the creation and annihilation of the transformation zone whose velocity depends linearly on load. A dynamic model of super-Arrhenius relaxation in glassy materials was recently developed in [5] and is based on a well-known liquid-like model [6]. The authors of [5] 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. Let the string length be equal to Nl , where N is an integer and l is a certain characteristic molecular length, and a domain with radius R arises around the STZ string. The expression for the total free energy of the system has the form

$$\Delta G(N, R) = \Delta G_{\infty} + Ne_0 - TS(N, R) + E_{\text{int}}(N, R), \quad (1)$$

where the first term is the activation energy for high temperatures, which is necessary for formation of a vacancy or a free gap. It is the Arrhenius activation energy. The remaining terms describe the string as a fluctuation in a solid glass: $T_0 \equiv e_0/vk_B$, where e_0 is the energy per step along the string and $v = \ln q$, where q is the number of paths possible for each transition. The number of such transitions is given by the expression

$$W(N, R) \approx \text{const} \times q^N \exp\left(-\frac{R^2}{2N\lambda^2}\right). \quad (2)$$

The entropy that is obtained by calculating the number of free transitions consisting of N steps in the radius R is written as

$$S(N, R) \approx vk_B N - k_B \frac{R^2}{2N\lambda^2}. \quad (3)$$

The repulsion energy is given by the expression

$$E_{\text{int}}(N, R) \approx k_{\text{B}} T_{\text{int}} \frac{N^2 \lambda^d}{R^d}, \quad (4)$$

where $k_{\text{B}} T_{\text{int}}$ is the dimensionless repulsion energy and d is the dimension of space where the string exists.

An irreversible transition occurs between the internal states of an amorphous solid. Adam and Gibbs [7] 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 [5] postulated “that, at temperatures low enough that most of the system is tightly jammed, localized molecular rearrangements might be entropically enabled by strings of small molecular displacements that distribute the disturbance throughout larger parts of the material.”

The Fe_2Tb and CoPd films were obtained by deposition with a rate of 10 nm/s on glass substrates in a vacuum of 2×10^{-4} Pa and at room temperature. The thickness of the films under investigation was equal to about 50 nm. The films were separated from the substrates by etching in a 10% hydrofluoric-acid solution with the subsequent washing in distilled water. The microstructure and phase composition of the films were analyzed using a transmission electron microscope PREM-200.

The initial Fe_2Tb and CoPd films are x-ray amorphous, which is corroborated by the diffuse diffraction patterns. Electron-beam-induced crystallization occurs with a rate of about 1 cm/s with formation of dendrites. We noted that domains with similar structure to the single-crystal structure arose from the x-ray amorphous structure under the action of either an electron beam or mechanical load in a short time (~ 0.1 ms). Electron microdiffraction patterns (see Fig. 1a) obtained from these domains are similar to the diffraction pattern from a single crystal. Point reflections in the electron diffraction patterns are strongly dispersed, and no ring reflections are observed. Microphotographies of the “single crystals” (see Fig. 1b) exhibit bending contours in the form of dark fringes that testify to strong internal bending of “atomic planes,” which reaches 100 deg/ μm [9].

Since point reflections are strongly dispersed on electron diffraction patterns, interatomic distances vary within a range of 8%. For this reason, we think that the excited-atom model on which the STZ theory is based is applicable to such films. Atoms that can be shifted at a critical distance corresponding to the maximum interatomic attraction are called excited atoms [10].

Comparison of data obtained by x-ray and electron diffractometry indicates that single crystals without long-range order grow in the Fe_2Tb and CoPd films. Nanocrystallites with the [110] zone axis are oriented with respect to each other as blocks of a mosaic and imitate a single crystal. Investigations of the atomic structure of nonequilibrium phases arising after explosive crystallization in the Fe_2Tb and CoPd nanocrystal-

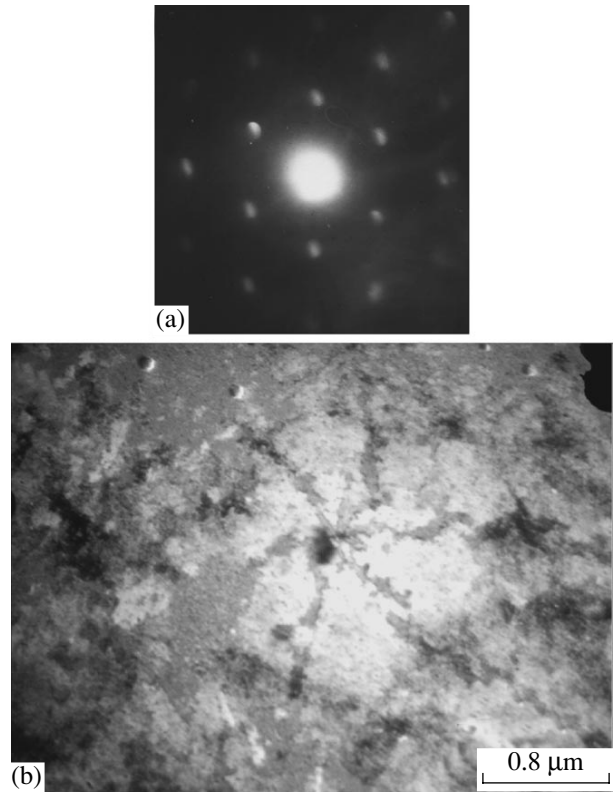


Fig. 1. (a) Electron microdiffraction pattern from a film section crystallized under the action of an electron beam at an accelerating voltage of 100 kV. (b) Microphotograph of the Fe_2Tb x-ray amorphous film with perpendicular magnetic anisotropy; diffuse dark points correspond to poles from which bending extinction contours diverge that testify to the strong internal bending of “atomic planes of the single crystal.”

line films show that these films have the Frank–Kasper tetrahedral close packed structure (Laves cubic phase). Such a structure [11] is characteristic of the equilibrium state of Fe_2Tb films, but it is surprising for CoPd films. An important feature of such a structure is the possibility of compression–tension of its elementary volume by 30% [12].

Crystallization may also begin in the process of sharp pressure on the sample edge in the Fe_2Tb films. Figure 2a shows an optical photograph of the Fe_2Tb x-ray amorphous film situated between crossed polarizers. The dark domain corresponds to the initial x-ray amorphous state with magnetization perpendicular to the film plane. Motley droplet-like regions are formed after crystallization initiated by the pressure of a glass cutter on the sample edge. Magnetic anisotropy in the Fe_2Tb films subjected to pressure is reoriented [13]. We attempted to find a correlation between the structural self-organization processes observed in the Fe_2Tb films and changes in their magnetic structure. Spontaneous deformation arising in nonequilibrium materials can lead to the redistribution of magnetization in local

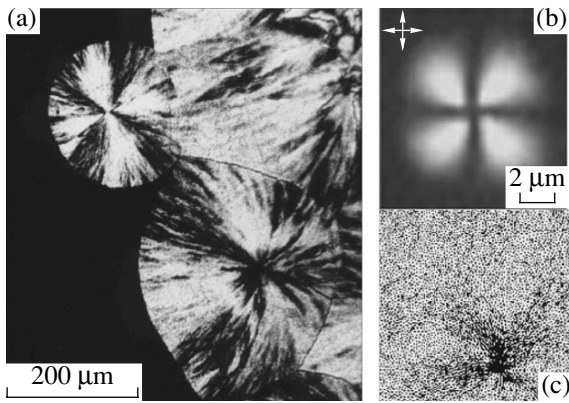


Fig. 2. (a) Optical photograph of the Fe_2Tb x-ray amorphous film situated between crossed polarizers; the dark domain corresponds to the magnetization perpendicular to the film plane. (b) Photograph of the spherical nematic droplet that was made in polarized light with crossed polarizers for the radial configuration of the director [14]. (c) Distribution of the force field for 4938 particles that is obtained by the molecular dynamics method [8].

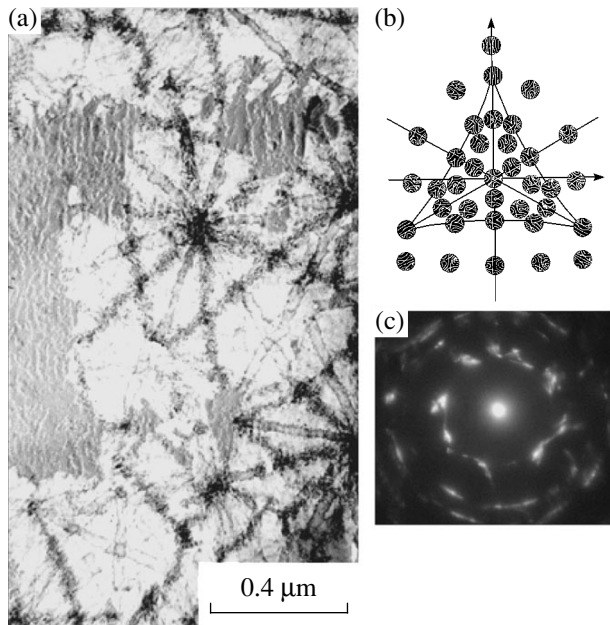


Fig. 3. (a) Microphotograph of the Co-Pd film after the electron-beam irradiation of the initial x-ray amorphous film. (b) Electron diffraction pattern from the Co-Pd sample. (c) Streamlines of a viscous liquid in the central zone of a six-roller mill [18].

domains [14]. Figure 2a shows the redistribution of magnetization in crystallized droplet-like domains.

The classification given in [15] for topologically stable defects in droplets of nematic liquid crystals indicates the radial ordering of the director with a point

defect (hedgehog) in the droplet center. This property corresponds to a similar experimental observation of birefringence in crossed polarizers with a fourth order symmetry axis, which are shown in Fig. 2b.

The effective biaxiality arises in load-induced crystallization processes in the Fe_2Tb film that is deposited on a substrate and is subjected to compression–tension load. In this case, the repetition of structural units of the same type satisfies the same rules as in a liquid crystal. The initial state of the film consists of nanocrystallites with the second-order symmetry axis (the 110 orientation of the Laves cubic phase, as follows from the analysis of electron microdiffraction patterns). Owing to long-range forces acting in thin films [16], the dark and light sections on the pattern in different parts of the film are parallel to each other.

Figure 2c shows a similar distribution of stress fields that is obtained in the molecular dynamics simulation of the behavior of particles in a glass subjected to shear stress when investigating the plastic deformation of atomically disordered media [8]. Simulation was based on the STZ theory and yielded the distribution of the stress field in the figure plane. Comparison of experimental and theoretical results (see Fig. 2) shows that the distributions of stress fields at micro- and mesoscopic levels are scale-invariant.

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 [17]. The symmetry of the single crystal with the sixth-order axis arises in the process of its growth under compression–tension load in the case where the film is separated from the substrate and is irradiated by an electron beam (see Fig. 1a). In this case, the initial state of the film consists of the same nanocrystallites with a second-order symmetry axis (the 110 orientation of the Laves cubic phase, as follows from analysis of the electron diffraction pattern). The direction of explosive crystallization is determined by the temperature gradient; i.e., it is directed from the center to the periphery of the circle. In this case, there is no orienting action of stresses from the substrate. However, conditions arise for the appearance of a third-order symmetry axis by analogy with the appearance of such symmetry in viscous liquid deformation geometry. Figure 3c [18] shows the streamlines of a viscous liquid in the central zone of a six-roller mill immersed in this liquid. The authors suppose the possibility of using such a model to study intermolecular interactions. In our opinion, the STZ theory provides the possibility of describing nonequilibrium processes in a disordered solid containing numerous excited atoms.

Structural elements (nanocrystallites with the second-order symmetry axis) are adaptable due to their mobility. As a result, symmetry with the sixth-order axis is efficiently generated and observed in experiment

(see Figs. 1 and 3). Such a structure is capable of reproducing itself and is an example of a dissipative structure relaxing to the equilibrium state.

In our opinion, there are sufficient reasons to conclude that the features of explosive crystallization processes in metal films with a nonequilibrium structure can be described in the framework of the modern STZ theory based on the excited-atom model.

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