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Phase Formation and Controlled Nanostructuring in Amorphous $Fe_{80}B_{20}$ Alloy

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Abstract—The temperature dependence of the volume fraction of the crystalline phase in $Fe_{80}B_{20}$ amorphous alloy is calculated using equations from the homogeneous nucleation theory of binary systems. It is shown that the crystallization of $Fe_{80}B_{20}$ alloy is two-stage, as is confirmed by the experimental data obtained by means of highly sensitive dilatometry and X-ray diffractometry. On the basis of results of calculations performed within the theory of the high-temperature stability of amorphous alloys, two areas of its practical application are proposed: (i) enhancing the thermal stability of amorphous alloys by isothermal annealing in the range of temperatures where crystalline nuclei can transition to the amorphous phase; (ii) controlled nanostructuring of the amorphous state with different modes of treatment. Methods are proposed for obtaining the nanostructured state from the initial amorphous state. Alloys in the nanocrystalline state are obtained, as is confirmed by the results from electron microscope investigations.

Keywords: amorphous alloys, crystallization, high-temperature stability, nanocrystals

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INTRODUCTION

Iron-based amorphous alloys are materials that find wide practical application; new nanocrystalline or amorphous nanocrystalline materials can be obtained on their basis via partial crystallization from the amorphous state [1, 2]. In addition, binary amorphous alloys are convenient model objects for studying the properties of disordered systems in the condensed state. We selected $Fe_{80}B_{20}$ binary alloy as our object of investigation, since the Fe–B system serves as the basis for creating multicomponent alloys that find broad application in technology. Processes of phase formation are investigated for the $Fe_{80}B_{20}$ binary alloy upon continuous heating by means of highly sensitive dilatometry and X-ray diffractometry, and theoretical calculations are performed for the process of crystallization. Metastable amorphous alloys obtained by ultrafast quenching do not always suited for practical use, due mainly to insufficient temperature stability over time. One area of current interest in studying amorphous alloys is developing methods for controlled nanostructuring via their partial crystallization as a result of external effects [3, 4]. A nanocrystalline structure can be formed in amorphous alloy through its partial crystallization. The aims of such investigations are determined according to the conclusions of the thermodynamic theory of amorphous alloys' high-temperature stability of [5], according to which external effects can substantially shift the phase equilibrium in the heterogeneous system of an amorphous matrix and frozen-in crystallization centers.

THEORETICAL AND EXPERIMENTAL INVESTIGATIONS OF THE CRYSTALLIZATION OF AMORPHOUS $Fe_{80}B_{20}$ ALLOY

The volume fraction of the crystalline phase at a given instant is an important characteristic of the crystallization of amorphous phases. For binary alloys, the temporal dependence of the fraction of the crystalline phase is described by the equations [6, 7]

$$\frac{dX(t)}{dt} = \left(1 - \sum_{i=1}^{k} X_i(t)\right)\frac{4}{3}\pi\langle J_{0i}U_i^3\rangle(t - t_{0i})^3,$$
$$\left\langle J_{0i}, U_i^3\right\rangle = \int_0^1 J'_{0i}(c_2)U_i^3(c_2)dc_2, \tag{1}$$

where k is the number of crystalline phases; U_i is the linear rate of growth for crystals of the ith phase; J_{0i} is the initial frequency of nucleation, which corresponds to $\sum_{i=1}^{k} X_i = 0$; and t_{0i} is the time required for the onset of ith phase crystallization.

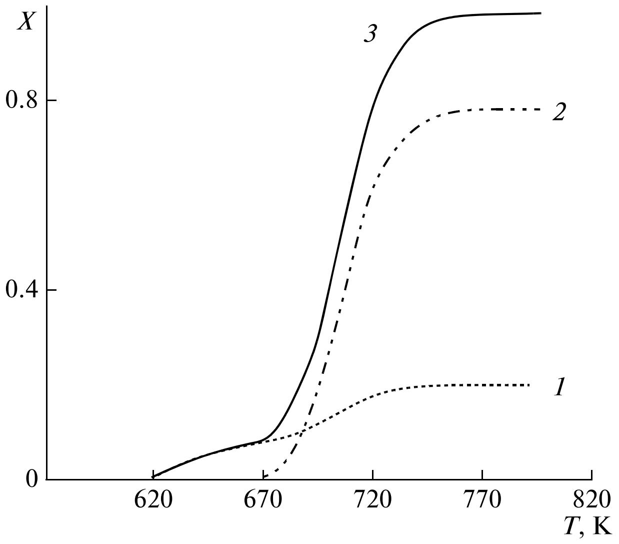

Fig. 1. Results from theoretical calculations of the kinetics of low-temperature crystallization in $Fe_{80}B_{20}$ amorphous alloy: (*1*) $X_\beta(T)$, (*2*) $X_\gamma(T)$, and (*3*) $X(T)$.

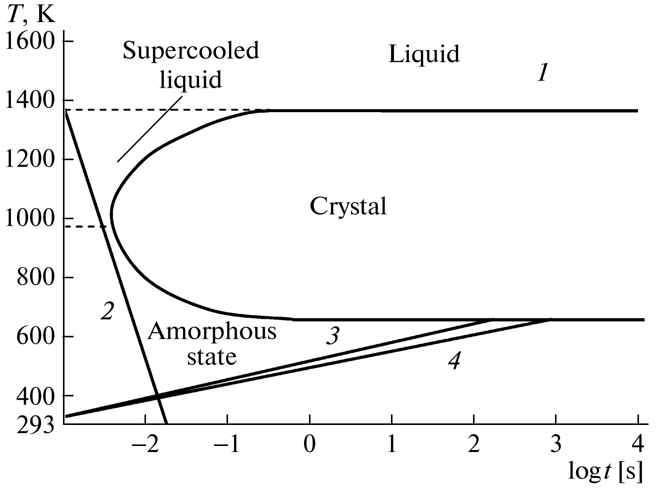

Fig. 2. (*1*) TTT diagram for $Fe_{80}B_{20}$ binary alloy; (*2*) quenching at rate $dT/dt = 10^5$ K/s with the formation of an amorphous state; (*3*) heating at rate $dT/dt = 0.17$ K/s; and (*4*) heating at rate $dT/dt = 0.03$ K/s.

The frequency of nucleation for binary systems is defined as the distribution function of the emerging crystalline nuclei according to certain values of concentration, i.e.,

$$J_i'(c_2) = dJ_i/dc_2 = N\frac{D}{a^2}$$
$$\times \exp\left[-\frac{16\pi\sigma^3V^2}{3kT(\Delta G^{\alpha-i}(c_2) - 2|\Delta G^{\alpha-\alpha}(c_2)|)^2}\right], \quad (2)$$
$$\Delta G^{\alpha-i}(c_2) = \Delta G^{\alpha}(c_2) - \Delta G^{i}(c_2),$$
$$\Delta G^{\alpha-\alpha}(c_2) = \Delta G^{\alpha}(c_2) - \Delta G^{\alpha}(c_{20}),$$

where $\Delta G^{\alpha}(c_2)$ and $\Delta G^{i}(c_2)$ are the concentration dependences of the Gibbs relative integral free energy in amorphous (α) and crystalline (i) phases; c_{20} in the initial concentration of the second component in the α phase; c_2 is an arbitrary concentration of the second component in the α and i phases; σ is the surface tension at the interface of two phases; V is the molar volume; N is the number of atoms in the volume unit; a is the atomic diameter; and D is diffusivity.

The linear growth rate of crystals for binary alloys is described by the equation

$$U_i = \frac{D}{a}\left(1 - \exp\left(-\frac{\Delta G^{\alpha-i} - |\Delta G^{\alpha-\alpha}|}{RT}\right)\right). \quad (3)$$

Note that Eq. (1) is solved by means of numerical integration, with which all $X_i(t)$ for the system are determined. It is evident that $X(t) = \sum_{i=1}^{k} X_i(t)$.

Figure 1 shows the theoretical dependences for the volume fraction of crystalline phase $X_i(t)$ and the total fraction of crystalline phase $X(T)$ for $Fe_{80}B_{20}$ alloy, calculated using Eqs. (1)–(3). Calculations on the kinetics of low-temperature crystallization showed that the crystallization of $Fe_{80}B_{20}$ alloy proceeds in several stages according to the phase diagram of the Fe–B binary system. The β phase (a solution of boron in iron) initially crystallizes, accompanied by a rise in the concentration of boron in the amorphous matrix. After a certain amount of time, the γ phase (Fe_3B) starts to crystallize. Theoretical curves of the temperature dependence for the volume fraction of the crystalline phase $X(T)$ are characterized by the presence of a shelf, testifying to the two-stage character of the process.

A quantitative analysis of the bulk effects of phase transformations was performed via dilatometry [13]. The molar volume of most alloys in the amorphous and crystalline states differs by 1–3%. We may thus investigate the crystallization of an amorphous alloy by determining the variation in sample length and recalculating it into changes in volume. When an amorphous alloy is heated at a constant rate, its volume increases monotonically; when the temperature reaches a certain value (that of the onset of intense crystallization), the amorphous alloy is transformed into the crystalline state, accompanied by an abrupt decrease in volume. The temperature of intense crystallization onset is determined from the temperature dependence of the relative variation in volume $\Delta V/V(T)$ upon heating the amorphous alloy.

Figure 2 presents the temperature–time–transformation (TTT) diagram for $Fe_{80}B_{20}$ binary alloy. It shows that the temperature of intense crystallization onset is independent of the rate at which the amorphous alloy is heated, as is indicated by the shelf in one part of the diagram.

It follows from Fig. 2 that the temperature of intense crystallization onset is invariable whether the amorphous alloy is heated at $dT/dt = 0.17$ or 0.03 K/s. The volume part of the crystalline phase is calculated from the data of dilatometric investigations:

$$X(T) = \frac{(\Delta V/V)_k}{(\Delta V/V)_m}, \tag{4}$$

where $(\Delta V/V)_k$ is the relative variation in the volume of the amorphous alloy upon crystallization under continuous heating at a fixed temperature, while $(\Delta V/V)_m$ is the relative variation in the volume of the amorphous alloy upon full crystallization at this temperature.

Figure 3 presents the results from computing temperature dependence $X(T)$ of the crystalline phase volume fraction using the results from dilatometric measurements for $Fe_{80}B_{20}$ alloy. A shelf similar to the one in the computed curve (Fig. 1) can be seen in the plot of temperature dependence $X(T)$ (Fig. 3), testifying to the two-stage nature of crystallization. A comparison of Figs. 3 and 1 shows that in general, the theory satisfactorily describes the experimentally determined temperature dependences for the volume fraction of the crystalline phase. In addition, it allows us to trace the emergence and growth of individual phases, depending on variations in temperature.

We obtained X-ray diffraction patterns for $Fe_{80}B_{20}$ alloy before and after isothermal annealing at different temperatures. During the initial stage of crystallization, the curve of the angular intensity distribution of the scattered X-ray radiation differs slightly from the similar curve for the initial amorphous state after annealing at 630 K and a very low content of the crystalline phase in the amorphous matrix. The lines of mainly two phases are seen in the X-ray diffraction pattern after isothermal annealing at $T = 700$ K: intense reflections from the α-iron lattice (β phase) and the weak diffraction reflections of metastable boride Fe_3B (γ-phase). The experimental data obtained by means of X-ray diffractometry confirm the results from theoretical calculations of crystallization in $Fe_{80}B_{20}$. binary alloy.

Binary alloys of the Fe–B system have very low thermal stability. Let us consider ways of broadening the range of thermal stability for these alloys, along with possible ways of attaining the nanostructured state from the initial amorphous state.

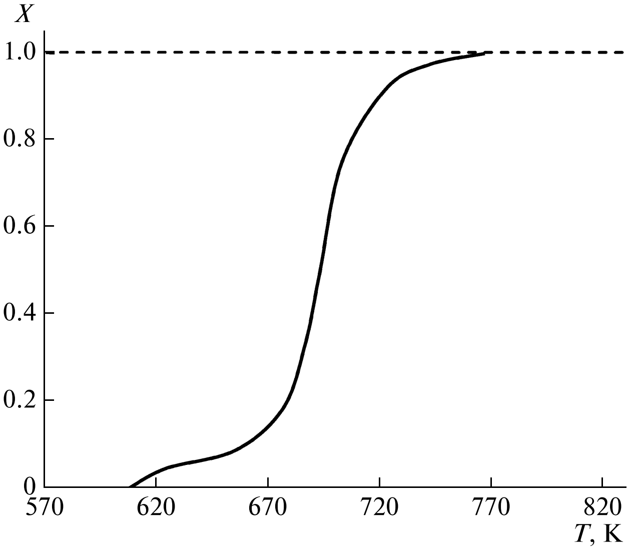

Fig. 3. Temperature dependence of the fraction of crystalline phase $X(T)$ for $Fe_{80}B_{20}$ alloy.

ANALYZING THE THEORY OF THE HIGH-TEMPERATURE STABILITY OF AMORPHOUS ALLOYS AND WAYS OF APPLYING IT IN PRACTICE

The high-temperature thermal stability of amorphous alloys is often associated with the total absence of crystalline phase nuclei. However, numerous electron microscopy investigations confirm that even after ultrafast quenching from the liquid phase at quenching rates of around 10^4–10^6 K/s, crystallization centers frozen into the amorphous matrix occur in amorphous alloys. The authors of [5] determined the thermodynamic conditions for the emergence of frozen-in crystallization centers in an amorphous matrix. for the *i*th component in a heterogeneous system of amorphous phase and frozen-in crystallization centers is described by the expression

$$\begin{aligned}\Delta\mu_i(T) = &-\frac{\chi_T^\alpha V_\beta + \chi_T^\beta V_\alpha}{\chi_\alpha + \chi_\beta}\frac{2\sigma}{r_{02}} \\ &-\frac{(V_\beta - V_\alpha)(\bar{V}_\beta^i - \bar{V}_\alpha^i)}{(\chi_\alpha + \chi_\beta)\bar{V}}\left[1 - \left[\frac{r_{01}}{r_{02}}\right]^3\right] + \Delta\mu_{0i}(T),\end{aligned} \tag{5}$$

where $\Delta\mu_i(T) = \mu_i^\alpha - \mu_i^\beta$ is the difference between the chemical potentials of the *i*th component in the α and β phases allowing for the pressure at the crystalline nucleus–amorphous phase interface due to surface tension (where σ is the surface tension coefficient) and elastic stresses; V_α, V_β and χ_T^α, χ_T^β are the molar volumes and isothermal compressibility coefficients of the α and β phases, respectively; r_{01} and r_{02} are the radii of crystalline nuclei for pressure and no pressure at the crystalline nucleus–amorphous phase interface; and $\Delta\mu_i = \mu_{0i}^\alpha - \mu_{0i}^\beta$ is the difference between the chemical potentials of pure components, represented by the following expression (as the standard state, we

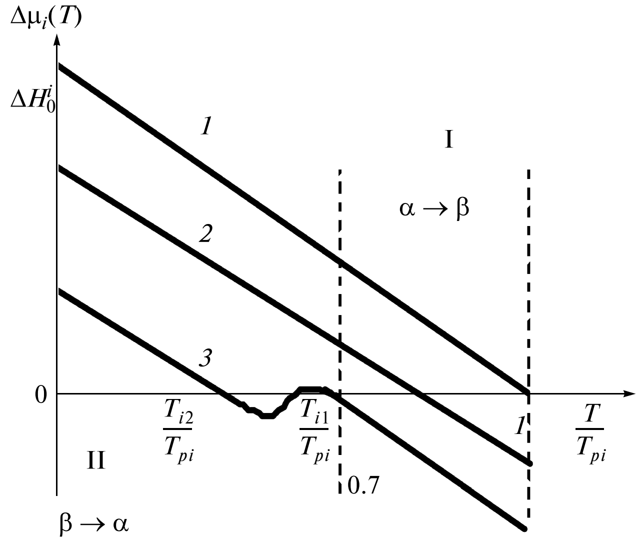

Fig. 4. Temperature dependence of $\Delta\mu_i$ for alloys (*1*) upon slow cooling of the melt $V_\alpha = V_\beta$, $a_1^\alpha = a_1^\beta$, and $r_{02} \to \infty$; (*2*) upon rapid cooling of the melt $V_\alpha \approx V_\beta$, $a_1^\alpha < a_1^\beta$, and $r_{02} = \text{const}$; (*3*) upon ultrafast cooling of the melt $V_\alpha \neq V_\beta$, $a_1^\alpha < a_1^\beta$, $r_{02} = \text{const}$; I is the region of viscous liquid, and II is the region in which the pressure caused by elastic stresses due to $V_\alpha \neq V_\beta$ is considered.

selected the chemical potential of the *i*th components in pure crystalline metal of type *i*):

$$\Delta\mu_0 = \frac{\Delta H_0^{(i)}(T_{pi} - T)}{T_{pi}} + RT\ln a_i^\alpha(C_i^\alpha, T) - RT\ln a_i^\beta(C_i^\beta, T), \qquad (6)$$

where $\Delta H_o^{(i)}$ is the enthalpy of melting for the *i*th component; T_{pi} is the melting point of the *i*th component; and a_i^α and a_i^β are the activities of the *i*th component in the α and β phases.

Figure 4 shows the plot of dependences $\Delta\mu_i(T)$, calculated by formula (5) with allowance for (6) under different conditions of crystallization in a melt. According to the homogeneous nucleation theory, crystalline phase nuclei are formed during the ultrafast quenching of a melt in the range $T \sim 0.7T_p$ (where T_p is the melting point), with the supercooled liquid transforming into a solid amorphous phase. A heterogeneous system of frozen-in crystallization centers and an amorphous matrix is thus formed in which elastic stresses emerge. Calculations showed that allowing for additional pressure at the crystalline nucleus–amorphous phase interface reduces $\Delta\mu_i$ relative to $\Delta\mu_i$ in the region where there are no elastic stresses. The transition of crystalline nuclei into the amorphous phase is thus possible in the temperature range of T_{i1} to T_{i2} (i.e., in the region where $\Delta\mu_i < 0$). It should be noted that the probability of new crystalline nuclei emerging below temperature T_{i1} is zero, since the frequency of nucleation tends to zero in this region, according to the homogeneous crystallization theory. Only the slow growth of already existing crystallization centers is possible in this region.

An analysis of the results from calculations performed within the theory of the high-temperature stability of amorphous alloys yields two areas for its practical application. The first is enhancing the thermal stability of amorphous alloys via thermal treatment in the range T_{i1}–T_{i2}, where crystalline nuclei can transition to the amorphous phase (dissolve in the amorphous phase). The second is the controlled nanostructuring of amorphous alloy via prolonged low-temperature isothermal annealing at temperatures $T_{\text{ann}} < T_{i1}$, i.e., in the temperature region where frozen-in crystallization centers can grow. To reproduce these processes, temperatures T_{i1}, T_{i2}, and T_{ann} must be determined experimentally.

As an example of applying the conclusions from the above theory, we performed experiments on the thermal treatment of the $Fe_{80}B_{20}$ amorphous alloy with the aim of enhancing the thermal stability of alloys and developing ways to obtain alloys in the nanostructured state. We determined the temperature of intense crystallization onset for the initial alloy before and after thermal treatment using the dilatometric procedure [3]. The temperature of intense crystallization onset for $Fe_{80}B_{20}$ alloy was 650 K. We performed three types of thermal treatment: thermal cycling (three sequential cycles of heating to $T = 630$ K with subsequent cooling to room temperature), isothermal annealing (at $T = 600$ K for 1 h); and cryogenic treatment (heating to $T = 600$ K, annealing at this temperature, and then abruptly cooling to the liquid nitrogen temperature of 77 K to stabilize the final nanostructured state). A nonisothermal regime (thermal cycling) at high temperature (20 K lower than that of intense crystallization onset) was used to avoid sample crystallization due to possible overheating. Dilatometric investigations showed that the temperature of intense crystallization onset for $Fe_{80}B_{20}$ amorphous alloy after thermal cycling rose by 80 K, since thermal treatment leads to the dissolution of frozen-in crystallization centers.

Figure 5 shows the results from electron diffraction and electron microscopy studies for $Fe_{80}B_{20}$ alloy before and after thermal treatment.

The initial amorphous state (Fig. 5a) is characterized by frozen-in crystallization centers with average sizes of up to 20 nm. After thermal cycling at $T = 630$ K, the size of crystalline nuclei falls to 5–10 nm on average (Fig. 5b). In this temperature region, $\Delta\mu_i < 0$, and the crystalline nuclei thus shrink and can dissolve in the amorphous phase. After isothermal annealing at $T = 600$ K (Fig. 5c), the samples were

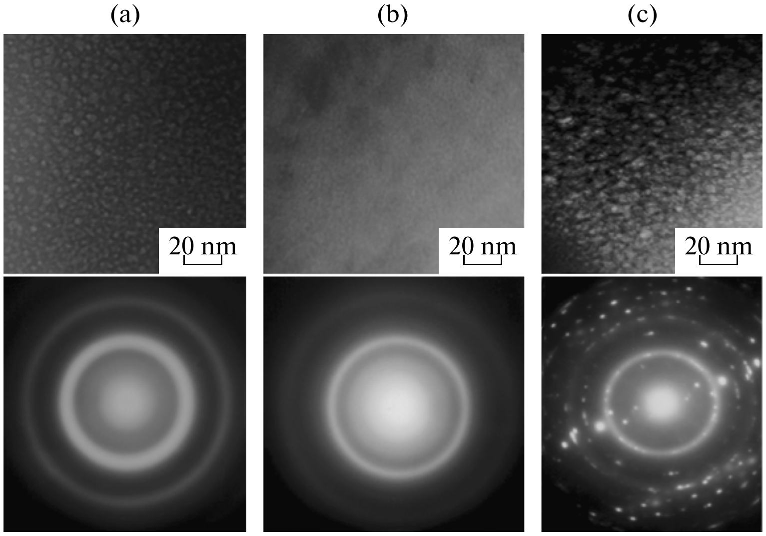

Fig. 5. Electron diffraction patterns and dark-field images for $Fe_{80}B_{20}$ alloy (a) in the initial state; (b) after thermal cycling at T = 630 K; and (c) after isothermal annealing at T = 600 K.

characterized by a structure with average nanocrystal sizes of up to 50 nm (i.e., the crystalline nuclei grew in this region).

CONCLUSIONS

It was confirmed experimentally that external effects which reduce the difference between the chemical potentials of the ith component in an amorphous matrix and in frozen-in crystallization centers (in the temperature region where $\Delta\mu_i < 0$) result in the dissolution of frozen-in centers and thus to an increase in the thermal stability of amorphous alloy. Prolonged low-temperature isothermal annealing allows us to form nanostructured states and fix them with subsequent cryogenic treatment.

The temperature dependence of the volume fraction of the crystalline phase for $Fe_{80}B_{20}$ alloy was calculated with equations of the homogeneous nucleation theory of binary systems. It was shown that the crystallization of this alloy is two-stage, in accordance with the phase diagram of the Fe–B binary system: initially, the β phase crystallizes (a solution of boron in iron), and the γ phase (chemical compound Fe_3B) starts to crystallize some time later.

Based on our analysis of results from calculations within the theory of high-temperature stability of amorphous alloys, two areas of its practical application were proposed: (i) enhancing the thermal stability of amorphous alloys by isothermal annealing in the range of temperatures where crystalline nuclei can transform into the amorphous phase; (ii) transforming the amorphous state into a nanocrystalline state via prolonged low-temperature isothermal annealing.

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