

The Influence of Intensive Plastic Deformation on the Phase Formation Processes in Amorphous Alloys

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(Received 03 March 2016; published online 21 June 2016)

The influence of intensive plastic deformation on the properties and structure of amorphous alloys was investigated experimentally. Using highly sensitive dilatometric techniques, it is shown that intensive plastic deformation of amorphous alloys leads to an increase in thermal stability interval that can be explained by a shift of the phase equilibrium in a heterogeneous system: amorphous matrix – frozen crystallization centers. In this case, there is dissolution of frozen crystallization centers presented in the original sample that is confirmed by the results of electron microscopic study.

Keywords: Amorphous alloy, Phase formation processes, Frozen crystallization centers, Intensive plastic deformation, Electron microscope study.

DOI: [10.21272/jnep.8\(2\).02032](https://doi.org/10.21272/jnep.8(2).02032)

PACS numbers: 64.70.pe, 61.43.Dq, 71.23.Cq

1. INTRODUCTION

Modern materials with an amorphous structure are characterized by a complex of unique physical and chemical properties, however, when heated to a certain temperature, amorphous metal alloys pass into a more stable crystalline state losing their characteristic features. The high-temperature stability of amorphous alloys is often associated with a complete absence of nuclei of the crystalline phase, but numerous electron microscopic studies show that amorphous alloys are heterogeneous systems amorphous matrix – frozen crystallization centers. Amorphous alloys are in a metastable state; therefore, their properties significantly depend on the influence of external conditions, such as temperature, pressure, and isothermal exposure time, especially in the phase transformation zone. The physical and chemical properties of amorphous alloys depend on the conditions of their production and further treatment that makes it necessary to predict in advance the temperature-time stability of alloys in an amorphous state. Since the questions on the mechanisms of influence of external factors on the properties and structure of amorphous alloys remain open, it is interesting to study the behavior of amorphous alloys under the action of intensive plastic deformation.

2. STATEMENT OF THE PROBLEM AND EXPERIMENTAL TECHNIQUE

The statement of the problem follows from the thermodynamic theory of high-temperature stability of amorphous alloys [1-2]. According to the theory of thermodynamic stability of amorphous alloys, external actions (isothermal annealing, prolonged exposure at room temperature or intensive plastic deformation) can lead to a significant shift of the phase equilibrium in a heterogeneous system: amorphous matrix – frozen crystallization centers. The equilibrium in such a system is determined by the difference in chemical potentials of the alloy components in the amorphous and crystalline phases. The process of nucleation of crystallization centers is influenced by the difference in chemical potentials between the amorphous and crystalline phases $\Delta\mu_i$ at that a decrease in $\Delta\mu_i$ promotes an increase in the thermal stability of

the alloys. The influence of intensive plastic deformation on the properties and structure of amorphous alloys was experimentally studied in this work. The investigations were carried out with the samples of amorphous alloys obtained by melt spinning method in G.V. Kurdyumov Institute for Metal Physics of the National Academy of Sciences of Ukraine. Multicomponent amorphous alloys were produced by adding the modifying impurities to the base binary alloys.

The intensive plastic deformation of the samples of amorphous alloys was caused by 5 GPa quasi-hydrostatic pressure treatment. The sample of an amorphous alloy (with the known area S) was placed between the metal plates, and compression was performed. The magnitude of the force F , which acted in compression, was calculated in such a way that the resulting pressure on this sample was equal to the required value P .

The main characteristic of the thermal stability of amorphous alloys is the temperature of the beginning of intensive crystallization, which is determined using a highly sensitive dilatometric technique, the essence of which is as follows [3]. The molar volume of most alloys in the amorphous and crystalline states differs by 1-3 %. The crystallization process of an amorphous alloy can be studied by fixing a change in the sample length during heating and recalculating it to the volumetric changes. In heating of an amorphous alloy with a constant rate, its volume increases monotonically, when the temperature reaches a certain value (the temperature of the beginning of intensive crystallization), the transition of an amorphous alloy to the crystalline state occurs. This process is accompanied by a sharp decrease in volume. The temperature of the beginning of intensive crystallization is determined from the temperature dependence of the relative volume change $\Delta V/V$ when an amorphous alloy is heated. The heating rate was equal to 10 K/min and the systematic relative error did not exceed 5 %.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Using highly sensitive dilatometric technique for the determination of the influence of intensive plastic deformation on the thermal stability, the temperature dependences of the relative volume change $\Delta V/V$ were obtained

for the initial samples and after treatment with quasi-hydrostatic pressure of $P = 5$ GPa for a number of binary and multi-component amorphous alloys.

In Fig. 1, Fig. 2 we present the temperature dependences of the relative volume change $\Delta V/V$ of amorphous alloys with continuous heating and cooling for the initial samples and for the samples subjected to pressure.

As seen from Fig. 1, the temperature of the beginning of intensive crystallization of $\text{Fe}_{83}\text{B}_{17}$ amorphous alloy before treatment was equal to 400°C and after treatment with pressure – 480°C , i.e. it increased by 80°C .

In Fig. 2 we show the temperature dependence of the relative volume change $\Delta V/V$ with constant heating and cooling of $\text{Fe}_{78}\text{Mo}_2\text{Si}_6\text{B}_{14}$ amorphous alloy in the initial state and after treatment with pressure of $P = 5$ GPa; the temperature of the beginning of intensive crystallization before treatment was 500°C , after pressure treatment it reached 525°C , i.e. it increased by 25°C .

In Table 1 we give the temperatures of the beginning of intensive crystallization for the initial samples and after 5 GPa quasi-hydrostatic pressure treatment.

The analysis of the results given in Table 1 showed that external pressure treatment leads to an expansion of the temperature-time stability interval of amorphous alloys by (20-80) $^\circ\text{C}$, as evidenced by an increase in the temperature of the beginning of intensive crystallization.

A more significant increase in the temperature of the beginning of intensive crystallization after pressure treatment for binary alloys can be explained by the fact that

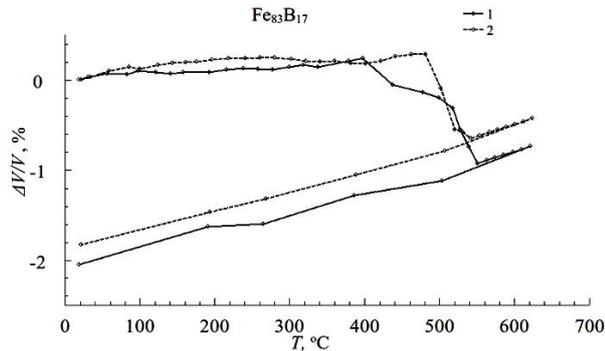


Fig. 1 – Temperature dependences of the relative volume change $\Delta V/V$ at constant heating and cooling of $\text{Fe}_{83}\text{B}_{17}$ amorphous alloy in the initial state (1) and after 5 GPa pressure treatment (2)

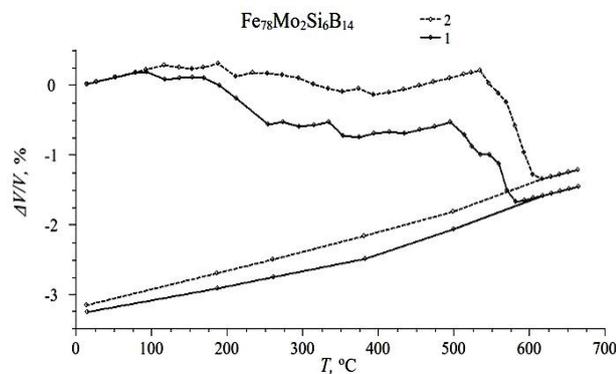


Fig. 2 – Temperature dependences of the relative volume change $\Delta V/V$ at constant heating and cooling of $\text{Fe}_{78}\text{Mo}_2\text{Si}_6\text{B}_{14}$ amorphous alloy in the initial state (1), after 5 GPa pressure treatment (2)

Table 1 – Temperatures of the beginning of intensive crystallization T_k for the initial samples and after treatment with quasi-hydrostatic pressure of $P = 5$ GPa

Composition of the amorphous alloy	$T_k, ^\circ\text{C}$ for the initial amorphous alloy	$T_k^o, ^\circ\text{C}$ after treatment with pressure of $P = 5$ GPa	$T_k - T_k^o, ^\circ\text{C}$
$\text{Fe}_{80}\text{B}_{20}$	380	440	60
$\text{Fe}_{83}\text{B}_{17}$	400	480	80
$\text{Fe}_{76}\text{Ni}_4\text{Si}_6\text{B}_{14}$	475	500	25
$\text{Fe}_{78}\text{Mo}_2\text{Si}_6\text{B}_{14}$	500	525	25
$\text{Ni}_{78}\text{Si}_4\text{B}_{18}$	460	480	20

multicomponent amorphous alloys are more stable compared with binary ones, since the addition of silicon and high-temperature doping impurities to the base binary Fe-B alloys inhibits the diffusion of boron in alloys and, thus, the crystallization process.

Let us analyze the obtained experimental results. The numerical electron microscopic studies show that even in the case of ultrafast quenching from the liquid phase, with quenching rates of the order of $(10^4\text{--}10^6)$ K/s, the crystallization centers frozen into an amorphous matrix exist in amorphous alloys; at that, the volume fraction of the crystalline phase in the sample cannot exceed 10^{-6} that is the condition for amorphous material. Frozen crystallization centers have different sizes; as a rule, their radius does not exceed (20-100) nm. After prolonged isothermal exposure, heat treatment or plastic treatment, their size varies. The frozen crystallization centers can increase with time (at $\Delta\mu_i > 0$) to sizes of (200-500) nm; at that, the temperature-time stability of an amorphous alloy will decrease. Such a process is typical for most binary alloys; the multicomponent alloys are much more stable. Under the action of external influences, the size of frozen crystallization centers can decrease (at $\Delta\mu_i < 0$), as well as their destruction and dissolution in an amorphous matrix; at that, the thermal stability interval of an alloy will increase.

The thermodynamic conditions of existence of frozen crystallization centers in an amorphous matrix taking into account the additional pressure arising from the elastic stresses at the crystalline nucleus/amorphous matrix interface are obtained in [1].

For function $\Delta\mu_i$, which determines the difference in chemical potentials in the amorphous (α) and crystalline (β) phases, for the deviation of the system from the thermodynamic equilibrium state, the formula

$$\Delta\mu = -(P_\beta V_\beta - P_\alpha V_\alpha) + \Delta\mu_0$$

is true, where $\Delta\mu_0 = \mu_0^\alpha - \mu_0^\beta$, $\mu_0^\alpha, \mu_0^\beta$ are the chemical potentials of undeformed α - and β -phases, respectively, P_α is the pressure in the α -phase at the boundary of the α/β - interphase, P_β is the pressure in the β -phase, V_α, V_β are the molar volumes of α - and β -phases, respectively.

If $\Delta\mu_i < 0$, then there is a transition from the β - to the α -phase, i.e. stable nuclei dissolve in the metastable α -phase. And if $\Delta\mu_i > 0$, then the normal crystallization – a transition from the α - to the β -phase – occurs.

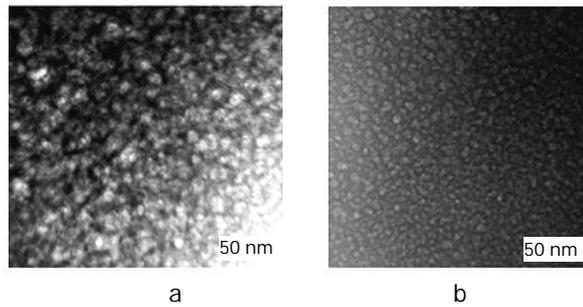


Fig. 3 – Electron microscopic dark field images for $\text{Fe}_{80}\text{B}_{20}$ alloy in the initial state (a) and after pressure treatment (b)

In Fig. 3 we illustrate the results of electron microscopic studies for $\text{Fe}_{80}\text{B}_{20}$ alloy in the initial state and after quasi-hydrostatic pressure treatment. The electron microscopic results showed that the initial amorphous state is characterized by the presence of frozen crystallization centers with an average size of the order of (20-30) nm (Fig. 3a). The size of crystalline nuclei decreases to (2-5) nm after pressure treatment (Fig. 3b).

Thus, by the action of external influences, such as, for example, creation of additional pressure, it is possible to effect the magnitude of function $\Delta\mu_i$ and for $\Delta\mu_i < 0$ to create conditions, under which the frozen crystallization centers dissolve, and, as a result, the thermal stability of amorphous alloys increases. Moreover, in the treatment of amorphous alloys by an external pressure, mechanical destruction and fragmentation of frozen crystallization centers, which are present in the initial samples, may also occur.

The occurrence of processes of partial destruction and dissolution of frozen crystallization centers takes place due to the formation of significant mechanical stresses in

the shear bands of an amorphous matrix as a result of plastic deformation and an increase in the local temperature in these bands.

Significant stresses in the shear bands lead to the mechanical destruction of frozen crystallization centers, and a local temperature increase in the shear bands transfers them into that temperature range, where the dissolution of frozen crystallization centers occurs according to the thermodynamic theory of high-temperature stability of amorphous alloys in a heterogeneous system amorphous matrix – frozen crystallization centers.

4. CONCLUSIONS

1. It is shown that treatment of amorphous alloys by quasi-hydrostatic pressure of $P = 5$ GPa leads to an increase in the temperature of the beginning of intensive crystallization of binary alloys by (60-80) °C, and of the multicomponent ones – by (20-25) °C.

2. An increase in the thermal stability interval of amorphous alloys can be explained by the fact that the mechanical treatment leads to a significant shift of the phase equilibrium in a heterogeneous system amorphous matrix – frozen crystallization centers; at that, there is dissolution of frozen crystallization centers, which are present in the initial samples, that is confirmed by the results of electron microscopic studies.

3. A more significant increase in the temperature of the beginning of intensive crystallization after pressure treatment for binary alloys can be explained by the fact that multicomponent amorphous alloys are more stable compared with binary ones, since the addition of silicon and high-temperature doping impurities to the base binary Fe-B alloys inhibits the diffusion of boron in alloys and, thus, the crystallization process.

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