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Effect of Ultrasonic Treatment on Phase Formation Processes in Amorphous Alloy $Fe_{76}Ni_4Si_{14}B_6$

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One of the most important trends in modern physics of condensed state is the study of amorphous metallic alloys in metastable state, because their properties essentially depend on the influence of external conditions, especially in the region of phase transitions. External actions, such as low temperature annealing and mechanical treatment, lead to a change in the structure and physical properties of amorphous alloys. Effect of ultrasonic mechanical activation on the structure and properties of amorphous metal alloys is studied not enough, so such research is a relevant task. The aim of the work is an experimental study of the effect of ultrasonic treatment on thermal stability of the amorphous alloy $Fe_{76}Ni_4Si_{14}B_6$. The results of dilatometric studies show the increase in crystallization temperature of the samples of amorphous alloy $Fe_{76}Ni_4Si_{14}B_6$, that is, the expansion of thermal stability interval of the alloy, after ultrasound treatment. When intensity of ultrasonic treatment is 1 W/cm^2, the temperature of intensive crystallization beginning increases by 30 K regardless of processing time (1-100 min), and with intensity of ultrasonic treatment of 2 W/cm^2, the temperature of intensive crystallization beginning increases by 50 K regardless of processing time (1-80 min). As a parameter for comparing the mechanical properties of the amorphous alloy before and after ultrasonic treatment, microhardness was used. Microhardness of the amorphous alloy after ultrasonic treatment is reduced by 15 %, which indirectly confirms the fact that percentage of crystalline phase in the alloy is reduced by reducing size of frozen-in crystallization centers. Increasing of the thermal stability interval of $Fe_{76}Ni_4Si_{14}B_6$ amorphous alloy and reducing of the microhardness can be explained by the fact that ultrasonic treatment leads to decrease in the size or dissolution of frozen-in crystallization centers, resulting in homogenization of the amorphous alloy structure.

Keywords: Amorphous alloy, Frozen crystallization centers, Ultrasonic treatment, Thermal stability.

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1. INTRODUCTION

Amorphous metallic alloys obtained by the method of ultrafast quenching of the melt have unique physical properties, which made these materials very promising in many applications [1-4]. In recent years, much attention has been paid to the investigation of structural-phase state changes of amorphous alloys (which don't have such structural defects as dislocations and intergranular boundaries as is known) under conditions of intense plastic deformation [5-7]. The question of deformation mechanism and formation of deformed structure in amorphous metallic alloys is one of the most important and interesting in the search for new ways to modify structure and properties of such materials. Intensive plastic deformation of alloys in amorphous state can be one of controlled methods for obtaining nanocrystalline materials with new physical properties [8, 9]. A method based on ultrasonic vibration energy use is one of the effective methods of intensive plastic deformation. For the first time, the effect of ultrasonic oscillations on structure change of solids was found during crystallization of metals and alloys from liquid state. Ultrasonic treatment is extensively used in the refining and degassing of melt alloys by using the nonlinear effects such as cavitation and acoustic streaming caused by ultrasound [10-13]. Effect of ultrasonic oscillations on the melt can reduce the size of formed crystalline grains, prevent dendrite structure formation and significantly reduce the grain size distribution. In addition, ultrasonic action affects the formation of secondary phases and their distribution by volume of the alloy, that is, it allows to obtain a more uniform structure of the material, what significantly improves both physical and mechanical properties of alloys [14]. A large number of different substances as objects for ultrasonic mechanoactivation were tested: from metals (to obtain alloys of various composition – the effect of mechano-alloying) to minerals (to increase removal degree of a valuable component) [15]. However, ultrasonic treatment of the melt has some deficiencies such as contact with the melt and limitation of processing time [16]. The contact of ultrasonic probe with the melt requires special materials for the probe to endure high temperature and corrosion [16]. Therefore, it is interesting to study the effect of ultrasonic treatment after hardening of an amorphous alloy.

In general, effect of ultrasonic treatment, especially after hardening, on structure and properties of amorphous metallic alloys is not well enough explored. Thus, investigation of the effect of ultrasonic treatment on thermal stability and properties of amorphous alloys is a relevant task.

2. STATEMENT OF THE PROBLEM AND EXPERIMENTAL TECHNIQUE

Amorphous metallic alloys are heterogeneous systems: amorphous matrix – frozen-in crystallization centers that are in a metastable state, and therefore their properties are substantially dependent on the influence of external conditions, especially in phase transitions region. In the newly prepared amorphous samples, frozen-in crystallization centers are always present, while volume of crystalline phase fraction in the sample cannot exceed 10^{-6} (the condition of amorphous material). Frozen-in crystallization centers have different sizes; their average radius is usually about 20 nm. The processes of nucleation and growth of crystallization centers in amorphous metallic alloys are affected by the difference in chemical potentials $\Delta\mu_i$ of amorphous and crystalline phases of the components. Thermodynamic equilibrium condition for heterogeneous system amorphous matrix-frozen-in crystallization centers for the *i*-th component is described by equality $\Delta\mu_i = 0$. Reducing difference in chemical potentials between amorphous and crystalline phases contributes to an increase in thermal stability of alloys [6]. In a heterogeneous system amorphous matrix-frozen-in crystallization centers there are elastic stresses, which result in additional pressure on the interface between crystalline nucleus and amorphous phase. Taking into account this additional pressure caused by elastic stresses results in a significant decrease in chemical potentials between amorphous and crystalline phases. When the system deviates from the state of thermodynamic equilibrium, function $\Delta\mu_i$ is described by the formula [17]:

$$\Delta\mu_i = -\left(P_\beta V_\beta - P_\alpha^0 V_\alpha\right) + \Delta\mu_{i0},$$

where $\Delta\mu_{i0} = \mu_{i0}^{\alpha} - \mu_{i0}^{\beta}$; μ_{i0}^{α}, μ_{i0}^{β} are the chemical potentials of undeformed α- and β-phases, respectively, P_α is the pressure in α- phase at interface between α- and β-phases; P_β is the pressure in β-phase, V_α, V_β are the molar volumes of α- and β-phase, respectively.

Thus, displacement of phase equilibrium in a heterogeneous system amorphous matrix–frozen-in crystallization centers can occur not only due to thermal effects, but also mechanical, one of which is ultrasonic treatment.

The treatment of the amorphous alloy samples was carried out in ultrasonic bath Ya Xun YX-3560 (made in China), which generates ultrasonic pressure and cavitation effects and has two modes of operation at a power of 30 W and 50 W. The bath was filled with distilled water; samples of the amorphous alloy were immersed in it and were held under ultrasonic load for a certain time. Ultrasonic mechanoactivation of the amorphous alloy samples was carried out at room temperature of 18 °C, which is below than structural relaxation temperature of the material. The specimens were exposed to ultrasound of 1 W/cm^2 at a frequency of 20 kHz (30 W mode) and 2 W/cm^2 at 40 kHz (50 W mode). Duration of ultrasonic treatment ranged from 1 to 100 min.

The temperature of intensive crystallization beginning of the amorphous alloy by the method of high sensitive dilatometry was determined after ultrasonic treatment and compared with this parameter for the initial alloy.

Four-component amorphous $Fe_{76}Ni_4Si_6B_{14}$ alloy obtained by the melt spinning method in G.V. Kurdyumov Institute for Metal Physics of the National Academy of Sciences of Ukraine was selected as a research object at this stage of the work.

The main characteristic of the thermal stability of amorphous alloys is the temperature of the intensive crystallization beginning, which is determined using a highly sensitive dilatometric technique [8], the essence of which is as follows. 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 %.

For the amorphous alloys in the initial amorphous state and after ultrasonic treatment, measurements of microhardness by Vickers on the PMT-3 device were performed. The method of measuring microhardness is based on measuring linear value of diagonal of the imprint, which is formed when diamond pyramid is squeezed out into the examined material under a certain loading. As a result of measurements, the length of the imprint diagonal is determined using an eyepiece-micrometer. When microhardness is measured, the possibility of scattering of microhardness values due to the influence of neighboring structural components with other microhardness was taken into account, measurements were carried out 10 times under the same conditions, repeated measurements were carried out in a new place of the structural component.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The main characteristic of thermostability of amorphous alloys is temperature of intensive crystallization beginning, which determination is carried out by using dilatometric method. Fig. 1 shows the temperature dependences of relative change in volume $\Delta V/V$ of amorphous $Fe_{76}Ni_4Si_{14}B_6$ alloy under continuous heating and cooling: for the initial alloy (1) and for samples after ultrasonic treatment at various modes (2, 3).

It can be seen from Fig. 1 that ultrasonic treatment affects temperature of intensive crystallization beginning, that is, thermal stability of the amorphous alloy. After ultrasonic treatment, thermal stability interval of the alloy increases. Table 1 shows the results of experimental studies of ultrasonic treatment effect carried out at different modes on thermal stability of amorphous alloy $Fe_{76}Ni_4Si_{14}B_6$.

The results presented in Table 1 indicate that crystallization temperature of the amorphous alloy $Fe_{76}Ni_4Si_{14}B_6$ increases after ultrasonic treatment, that is, thermostability interval of the amorphous alloy is expanded.

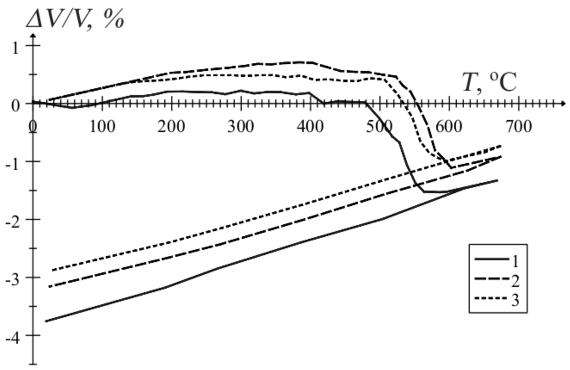

Fig. 1 – Temperature dependence of relative change in volume Δ*V*/*V* of amorphous $Fe_{76}Ni_4Si_{14}B_6$ alloy with continuous heating and cooling: 1 – initial alloy, 2 – after 4 min of ultrasonic treatment (2 W/cm^2, 40 kHz), 3 – after 2 min of ultrasonic treatment (1 W/cm^2, 20 kHz).

Table 1 – Results of experimental studies of ultrasonic treatment effect carried out at different modes on thermal stability of amorphous alloy $Fe_{76}Ni_4Si_{14}B_6$

Mode and time of ultrasonic treatment	Temperature of intensive crystallization beginning, *K*
Initial sample	750
Intensity of ultrasonic treatment: 1 W/cm^2 (20 kHz)	
1 min, 4 min, 40 min, 60 min, 100 min	780
Intensity of ultrasonic treatment: 2 W/cm^2 (40 kHz)	
1 min, 4 min, 40 min, 60 min, 80 min	800

When intensity of ultrasonic treatment is 1 W/cm^2, temperature of intensive crystallization beginning increases by 30 K regardless of processing time (1-100 min), and with intensity of ultrasonic treatment of 2 W/cm^2, temperature of intensive crystallization beginning increases by 50 K regardless of processing time (1-80) min.

As a parameter for comparing the mechanical properties of the amorphous alloy before and after ultrasonic treatment, microhardness was used. Table 2 shows the results of microhardness measurements of initial amorphous alloy and after ultrasonic treatment performed under different modes.

Microhardness decreases by (9-17) % after performed ultrasonic treatment, which indirectly confirms the fact that proportion of crystalline phase in the alloy is reduced by reducing size of frozen-in crystallization centers.

Consequently, under the action of ultrasonic treatment, the size of frozen-in crystallization centers can decrease, as well as their destruction, dissolution in amorphous matrix. This leads to an increase in thermal stability interval and a decrease in microhardness of the alloy.

Table 2 – Results of microhardness measurements of initial amorphous alloy $Fe_{76}Ni_4Si_{14}B_6$ and after ultrasonic treatment carried out at different modes

Mode and time of ultrasonic treatment	*H*, kgf/mm^2
Initial sample	788
Intensity of UT: 1 W/cm^2 (20 kHz)	
1 min	718
40 min	686
Intensity of UT: 2 W/cm^2 (40 kHz)	
1 min	693
40 min	657

4. CONCLUSIONS

It is shown that ultrasonic treatment of the amorphous alloy $Fe_{76}Ni_4Si_{14}B_6$ contributes to extending the thermal stability interval by 30-50 K.

Microhardness of the amorphous alloy after ultrasonic treatment decreases by (9-17) %.

An increase in temperature of intensive crystallization beginning and a reduction of microhardness after ultrasonic treatment of the amorphous $Fe_{76}Ni_4Si_{14}B_6$ alloy can be explained by a decrease in the sizes of frozen-in crystallization centers resulting in homogenization of the amorphous alloy structure.

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Вплив ультразвукової обробки на процеси фазоутворення в аморфному сплаві $Fe_{76}Ni_4Si_{14}B_6$

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Одним з актуальних напрямів сучасної фізики конденсованого стану є дослідження аморфних металевих сплавів, які знаходяться в метастабільному стані, тому їх властивості істотно залежать від впливу зовнішніх умов, особливо в області фазових переходів. Зовнішні дії, такі як низькотемпературний відпал та механічна обробка приводять до зміни структури та фізичних властивостей аморфних сплавів. Вплив ультразвукової механоактивації на структуру та властивості аморфних металевих сплавів виявляється недостатньо вивченим, отже такі дослідження впливу є досить актуальною задачею. Метою роботи було експериментальне дослідження впливу ультразвукової обробки на термічну стабільність аморфного сплаву $Fe_{76}Ni_4Si_{14}B_6$. Результати дилатометричних досліджень вказують на те, що після обробки ультразвуком зразків аморфного сплаву $Fe_{76}Ni_4Si_{14}B_6$ температура кристалізації зростає, тобто розширюється інтервал термостабільності сплаву. При інтенсивності ультразвукової обробки 1 Вт/см^2, незалежно від часу обробки (1-100 хвилин), температура початку інтенсивної кристалізації збільшується на 30 К, а при інтенсивності ультразвукової обробки 2 Вт/см^2, незалежно від часу обробки (1-80 хвилин), температура початку інтенсивної кристалізації збільшується на 50 К. В якості параметра порівняння механічних властивостей аморфного сплаву до та після дії ультразвукової обробки було використано мікротвердість. Мікротвердість аморфного сплаву після проведеної ультразвукової обробки зменшується на 15%, що непрямим чином підтверджує факт зменшення частки кристалічної фази в сплаві за рахунок зменшення розмірів вморожених центрів кристалізації. Збільшення інтервалу термічної стабільності аморфного сплаву $Fe_{76}Ni_4Si_{14}B_6$ та зменшення мікротвердості можна пояснити тим, що проведена ультразвукова обробка призводить до зменшення розмірів або розчинення вморожених центрів кристалізації, внаслідок чого відбувається гомогенізація структури аморфного сплаву.

Ключові слова: Аморфний сплав, Вморожені центри кристалізації, Ультразвукова обробка, Термічна стабільність.