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THE RESEARCH OF NANOSTRUCTURAL MATERIALS' PROPERTIES OBTAINED THROUGH PARTIAL CRYSTALLIZATION OF AMORPHOUS ALLOYS

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The research of heat treatment influence and thermomechanical processing concerning amorphous alloys stability has been conducted. It has been shown that these effects significantly enhance the thermal stability of amorphous alloys based on iron. The increase of thermal stability and diminishing of microhardness of amorphous alloys is explained by the fact that the conducted treatment results in substantial displacement of phase equilibrium in the heterogeneous system, amorphous matrix–frozen crystallization centers which is accompanied by diminishing of frozen crystallization centers sizes and amorphous-nanocrystalline state forming.

Keywords: amorphous alloys, crystallization, thermal stability.
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INTRODUCTION

The topical matter of metallic glasses research is the development of nanostructure receipt methods through partial crystallization of amorphous alloys due to external influences. These influences are as following – heat treatment (isothermal and unisothermal annealing at temperatures below than temperature of crystallization, thermocycling, cryotreatment); intensive plastic deformation; irradiation of different nature particles. The great attention to heat treatment of alloys with the amorphous structure can be explained by acquisition of the special properties option in the nanorystalline state. In this regard, the study of the amorphous alloys properties under external influences is of keen interest. Moreover the issues of the external factors influence mechanisms on the materials properties are still underestimated [1-2].

For a number of amorphous alloys the certain experiments have been carried out on heat treatment and thermomechanical processing for the purpose of enhancing the alloys thermal stability and the developing of the ways to obtain the nanostructured alloys. The mechanical properties of the nanostructured materials obtained have been also researched.

1. METHOD OF EXPERIMENT

The parameter that determines thermal stability of amorphous alloys is the temperature of intensive crystallization beginning T_k which has been determined by means of highly sensitive dilatometer method. The method of the conducted dilatometric researches is as follows [3]. While amorphous alloy heating its volume grows droningly (density goes down correspondingly), at certain temperature (the temperatures of

beginning of intensive crystallization) the volume sharp diminishing and alloy density increasing can be observed that proves the beginning of crystallization. Consequently, it is possible to probe the process of crystallization of amorphous alloy, fixing the change of length of standard and transferring it in volume changes or changes of density. The temperatures of beginning of intensive crystallization for the initial amorphous alloys and after the executed thermal or termomechanical treatment have been determined by dilatometer.

For a number of amorphous alloys in the initial amorphous state and after the processing conducted microhardness by Vikkers on the device PMT-3 has been measured. The method of microhardness measuring is based on of the measuring of imprint diagonal linear size that appears while pressing of a diamond pyramid in the probed material under the certain loading. The device allows to measure microhardness at pressing of the diamond pyramid with the square basis and the top corner of 136^0 between the opposite verges with the appendix of loadings (2-200) gramme. As a result of measurings the length of diagonal of imprint obtained by an eyepiece-micrometer has been determined. While measuring microhardness volume deformed by pressure must be less than the amount of a grain being measured. The sample has being pressed 10 seconds.

The number of hardness (for Vikkers) is accounted by the formula:

$$H = \frac{1854P}{d^2}\left(\frac{\kappa Gf}{mm^2}\right),$$

where P is the pressure $\left(\frac{\kappa Gf}{mm^2}\right)$, d is the length of diagonal of imprint in microns.

At the microhardness measuring it has been taken into account the possibility to spread the values of microhardness due to the influence of neighboring structural components with different microhardness. The measurings have been carried out 10 times in the same conditions, the load equals 200 g, and the repeated measuring has been carried out in a new place of structural constituent.

2. THE EXPERIMENT'S RESULTS AND THEIR DISCUSSION

By means of high-sensitivity dilatometry there have been obtained the dependences on the relative change of density for initial alloys and alloys underwent thermal or termomechanical processing. From the dependencies received there have been identified certain temperatures of intensive crystallization beginning for initial samples and those which have been earlier treated. Three types of thermal treatment have been conducted, namely: thermocycling (3 cycle of heating to $T = T_k - 50^0 C$); isothermal annealing during 1 hour at $T = T_k - 50^0 C$; heating to $T = T_k - 50^0 C$ (time under this temperature is 1 minute) and sharp cooling to the temperature of liquid nitrogen 77 K with the purpose of stabilizing of the nanostructural state obtained.

On Fig. 1 the temperature dependence of relative change of density $\frac{\Delta\rho}{\rho}(T)$ is resulted for amorphous alloy $Fe_{80}B_{14}Si_6$ in initial state (Curve 1) and after thermal treatment: thermocycling (3 cycle of heating to $T = T_k - 50^0 C$) (Curve 2); isothermal annealing during 1 hour at $T = T_k - 50^0 C$ (Curve 3) and heating to $T = T_k - 50^0 C$ (time under this temperature is 1 minute) with following cryotreatment (Curve 4).

The tempererure of intensive crystallization beginning for $Fe_{80}B_{14}Si_6$ makes 500^0C, consequently the previous thermal treatment has been conducted under T=450^0C. From Fig.1 it is evidently that the temperature of intensive crystallization beginning after thermocycling has been increased to 15^0C, after the isothermal annealing – to 30^0C, and after cryotreatment – up to 40^0C.

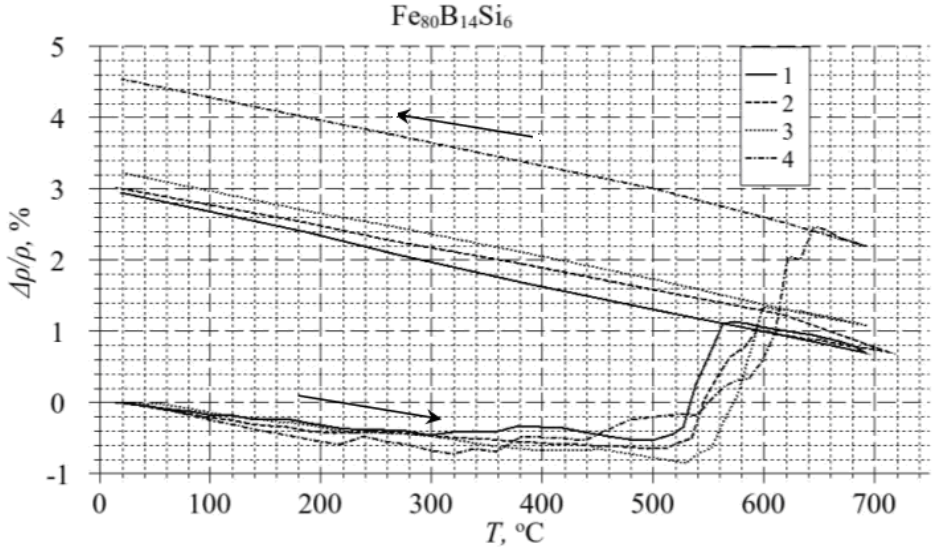

Fig. 1. Relations between relative changes in density and temperature for amorphous alloys $Fe_{80}B_{14}Si_6$ obtained with continuous heating and cooling: (1) initial sample; (2) after thermocycling; (3) after isotermal annearling; (4) after cryotreatment.

On Fig. 2 temperature dependence of relative change of density $\frac{\Delta\rho}{\rho}(T)$ is resulted for amorphous alloy $Fe_{70}Cr_{15}B_{15}$ in initial state (Curve 1) and after thermal treatment: thermocycling (3 cycle of heating to $T = T_k - 50^0 C$) (Curve 2); isothermal annealing during 1 hour at $T = T_k - 50^0 C$ (Curve 3) and heating to $T = T_k - 50^0 C$ (time under this temperature is 1 minute) with following cryotreatment (Curve 4). The temperature of intensive crystallization beginning for $Fe_{70}Cr_{15}B_{15}$ makes 480^0C. Consequently, the

previous thermal treatment has been conducted at T=430^{0}C. From Fig.2 it is evident that the temperature of intensive crystallization beginning after thermocycling has not changed, after the isothermal annealing it has increased to 60^{0}C, and after cryotreatment – to 20^{0}C.

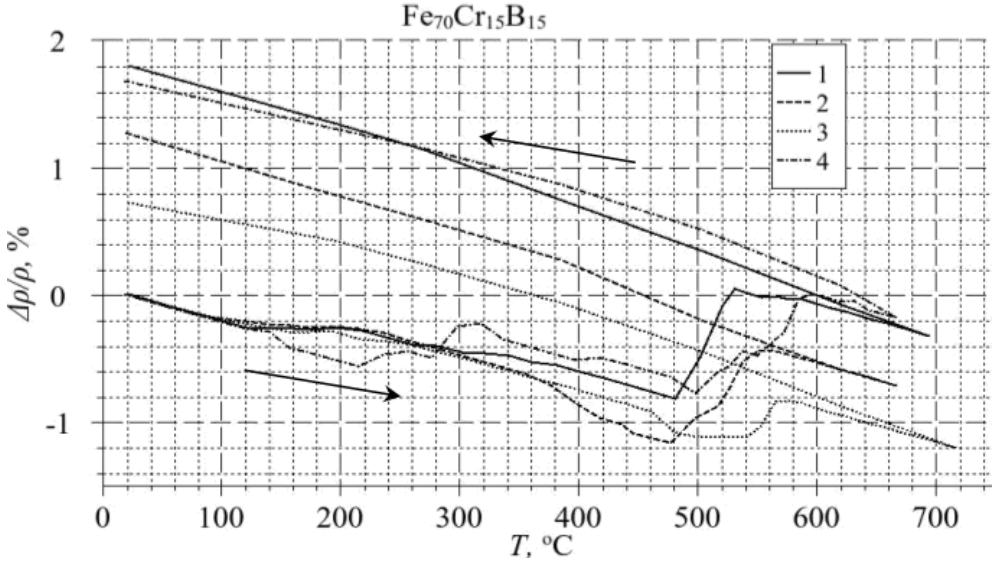

Fig. 2. Relations between relative changes in density and temperature for amorphous alloys $Fe_{70}Cr_{15}B_{15}$ obtained with continuous heating and cooling: (1) initial sample; (2) after thermocycling; (3) after isotermal annearling; (4) after cryotreatment.

For amorphous alloys $Fe_{80}B_{14}Si_6$ and $Fe_{76}Ni_4Si_6B_{14}$ the influence of the combined thermomechanical treatment on thermal stability has been researched.

The thermomechanical processing of amorphous alloy samples has been performed in two steps. Thermal treatment has meant isothermal annealing at temperature $T = T_k - 50^0 C$ for 10 min, while mechanical treatment has been performed on a hydraulic press with a quintuple cyclic loading of 225 MPa.

Fig. 3 and Fig. 4 show the temperature dependence of density relative change $\frac{\Delta\rho}{\rho}(T)$ for amorphous alloys $Fe_{80}B_{14}Si_6$ and $Fe_{76}Ni_4Si_6B_{14}$ in initial state (Curve 1) and after thermomechanical treatment (Curve 2). The temperature of intensive crystallization beginning for amorphous alloy $Fe_{80}B_{14}Si_6$ makes 500^{0}C, so the previous thermal treatment has been conducted under T=450^{0}C. The temperature of intensive crystallization beginning for amorphous alloy $Fe_{76}Ni_4Si_6B_{14}$ makes 450^{0}C, thus the previous thermal treatment has been conducted under T=400^{0}C. It becomes clear from Fig.3 and Fig.4 that the temperature of intensive crystallization beginning for amorphous alloy $Fe_{80}B_{14}Si_6$ after combined thermomechanical treatment has increased to 40^{0}C and for amorphous alloy $Fe_{76}Ni_4Si_6B_{14}$ – to 50^{0}C.

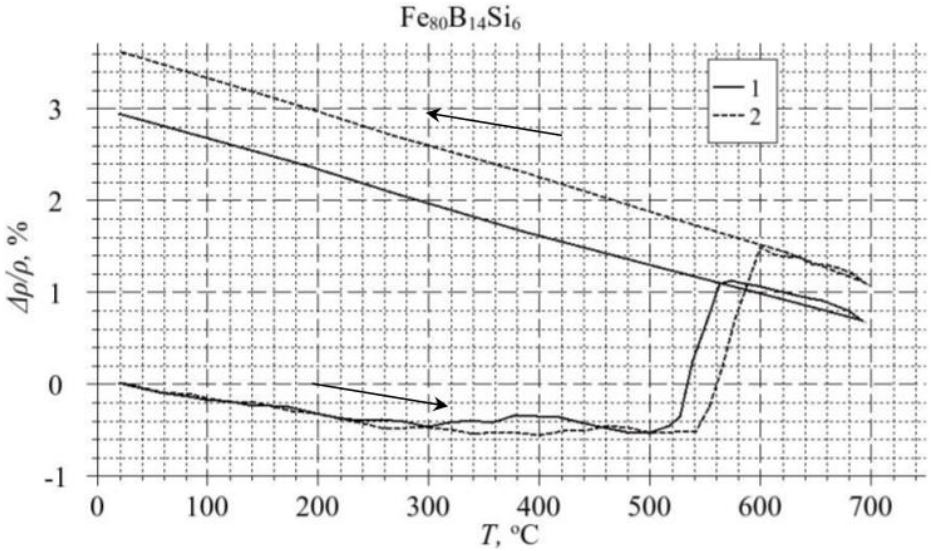

Fig. 3. Relations between relative changes in density and temperature for amorphous alloys $Fe_{80}B_{14}Si_6$ obtained with continuous heating and cooling: (*1*) initial sample; (*2*) thermomechanically processed sample.

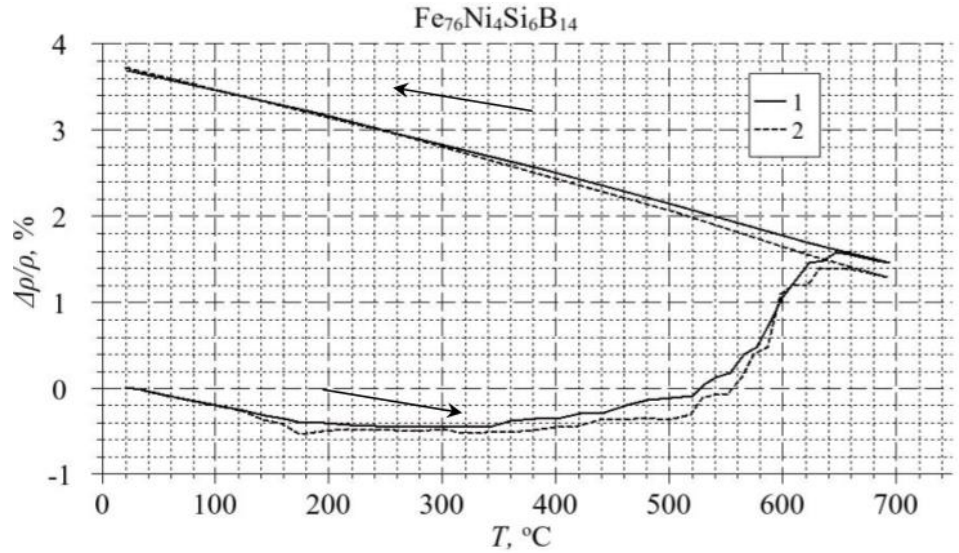

Fig. 4. Relations between relative changes in density and temperature for amorphous alloys $Fe_{76}Ni_4Si_6B_{14}$ obtained with continuous heating and cooling: (*1*) initial sample; (*2*) thermomechanically processed sample.

Table 1 shows the beginning of intensive crystallization temperature for a number of initial amorphous alloys and after the thermal or thermomechanical processing.

Table 1

The onset intense crystallization temperatures for initial amorphous alloys and the alloys after heat treatment or thermomechanical processing

Composition of amorphous alloy	The beginning of intensive crystallization temperature T_k , ^0C				
	initial alloys	*after thermo-cycling*	*after isotermal annearling*	*after cryotreat-ment*	*thermomecha-nically proces-sed alloys*
$Fe_{80}B_{20}$	380	440	420	440	460
$Fe_{83}B_{17}$	400	460	440	480	480
$Fe_{70}Cr_{15}B_{15}$	480	480	540	500	500
$Fe_{80}B_{14}Si_6$	500	515	530	540	540
$Fe_{76}Ni_4Si_6B_{14}$	500	520	520	540	550
$Fe_{77,5}B_{16}Si_2Ni_{3,5}Mo_1$	480	500	520	500	520

As a comparison parameter elastic properties of metallic glasses in the initial state and after a processing used the microhardness *H*. Table 2 shows the results of microhardness measurements.

Table 2

Microhardness for initial amorphous alloys and after a processing

Composition of amorphous alloy	H , $\left(\frac{\kappa Gf}{mm^2}\right)$	
	initial alloys	*alloys after isotermal annearling*
$Fe_{83}B_{17}$	758±38	658±330
$Fe_{70}Cr_{15}B_{15}$	526±21	416±26
	initial alloys	*thermomechanically processed alloys*
$Fe_{80}B_{14}Si_6$	747±37	648±32
$Fe_{76}Ni_4Si_6B_{14}$	605±30	512±25

It has been experienced thermal stability increasing, as it is evidenced by increasing of temperature of intensive crystallization beginning and microhardness diminishing, for all investigational amorphous alloys after thermal conducted or termomechanical

treatment. This fact can be explained by dissolution of existing in the amorphous phase some frozen crystallization centers and the amorphous-nanocrystalline state forming [4-5]. The amorphous alloys are the heterogeneous systems: amorphous matrix is frozen crystallization centers existed in the metastable state, therefore their properties depend on external terms influence substantially (temperature, pressure, time, etc), especially in the area of phase transitions. There are always some frozen crystallization centers in the amorphous samples newly obtained, while the volume fraction of crystalline phase in the sample don't not exceed $X = 10^{-6}$ (condition amorphous material). Over time and under the influence of external influences the size of frozen crystallization centers can vary. They can grow, and then temperature and time stability of amorphous alloys become decreasing. It is observed while aging of amorphous binary alloys. The size of frozen crystallization centers can also decrease and dissolve which result in increased thermal stability of amorphous alloys. The condition of the thermodynamic equilibrium of a system with an amorphous matrix and frozen crystallization centers for component *i* is described by the equality $\Delta\mu_i = 0$ [1]. Nucleation is therefore influenced considerably by the difference $\Delta\mu_i$ between the chemical potentials of the amorphous and crystal phases, with a drop in $\Delta\mu_i$ raising the alloy's thermal stability.

The conducted treatment of amorphous alloys has resulted in substantial displacement of phase equilibrium in the heterogeneous system: amorphous matrix as frozen centers of crystallization which leads to an increase in thermal stability interval. More considerable increase of temperature of intensive crystallization beginning for binary alloys can be explain by the fact that multicomponent amorphous alloys are more stable in comparing to binary ones, since the addition of silicon and high temperature alloying admixtures such as molybdenum and niobium, the basic binary alloys of the system F_E-B, inhibit the diffusion of boron in alloys, thus the crystallization process.

Thus, the results of the experimental studies confirm the conclusions of the theory of amorphous alloys thermodynamic stability [1], which shows the possibility to shift the phase equilibrium in the system amorphous matrix-freezes centres of crystallization by directional external influences (temperature, pressure) and can be defined by modes of the temperature interval extension of amorphous state existence.

CONCLUSIONS

1. It is shown that for binary and multicomponent amorphous alloys based on iron the increase in thermal stability after thermal or termomechanical treatment conducted on $(20\text{-}80)^0$C has been observed.

2. It is established that microhardness of materials received has been reduced compared to the initial amorphous state, which can be explained by the dissolution of freezes centers crystallization in the initial samples and the formation of nanostructural state.

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Лисов В. І. Дослідження властивостей наноструктурних матеріалів, отриманих частковою кристалізацією аморфних сплавів / В. І. Лисов, Т. Л. Цареградська, О. В. Турков, Г. В. Саєнко, П. О. Теселько // Вчені записки Таврійського національного університету імені В. І. Вернадського. Серія : Фізико-математичні науки. – 2013. – Т. 26 (65), № 2. – С. 143-150.

Проведено дослідження впливу термічної і термомеханічної обробки на стабільність аморфних сплавів та показано, що ці впливи значно підвищують температуру початку інтенсивної кристалізації. Збільшення термічної стабільності та зменшення мікротвердості аморфних сплавів пояснюється тим, що проведена обробка призводить до істотного зміщення фазової рівноваги в гетерогенній системі: аморфна матриця–вмережені центри кристалізації, що супроводжується зменшенням розмірів вмережених центрів кристалізації та формуванням аморфно-нанокристалічного стану.

Ключеві слова: аморфні сплави, кристалізація, термічна стабільність.

Лысов В. И. Исследование свойств наноструктурных материалов, полученных частичной кристаллизацией аморфных сплавов / В. И. Лысов, Т. Л. Цареградская, О. В. Турков, Г. В. Саенко, П. О. Теселько // Ученые записки Таврического национального университета имени В. И. Вернадского. Серия : Физико-математические науки. – 2013. – Т. 26 (65), № 2. – С. 143-150.

Проведено исследование влияния термической и термомеханической обработки на стабильность аморфных сплавов и показано, что эти влияния значительно повышают температуру начала интенсивной кристаллизации. Увеличение термической стабильности и уменьшение микротвердости аморфных сплавов объясняется тем, что проведенная обработка приводит к существенному смещению фазового равновесия в гетерогенной системе: аморфная матриця–вмороженные центры кристаллизации, что сопровождается уменьшением размеров вморожених центров кристаллизации и формированием аморфно-нанокристаличного состояния.

Ключевые слова: аморфные сплавы, кристаллизация, термическая стабильность.

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