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Influence of Constant Magnetic Field on Mechanical Properties and Thermal Stability of the Amorphous Alloys Based on Co, Fe and Ni

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To develop new amorphous, amorphous-nanocrystalline and nanocrystalline materials, optimize their unique properties and successfully operate their products, knowledge of changes in their structure under the influence of external factors is required. For the practical use of amorphous metal alloys, it is important to have data on the stability or changes in their properties under the action of magnetic fields, since products based on them are often operated under conditions of prolonged exposure to this factor. An experimental study of the influence of a constant weak ($B = 0.64$ T) magnetic field on the micromechanical properties and thermal stability of amorphous $Co_{67}Fe_3Cr_3Si_{15}B_{12}$ and $Fe_{40}Ni_{40}B_{20}$ alloys was conducted. It is established that the long-term action of a weak constant magnetic field leads to a magnetoplastic effect: the microhardness of amorphous alloys decreases up to 18-21 % per 100 days. Results of dilatometric experiments indicate that after treatment of amorphous $Co_{67}Fe_3Cr_3Si_{15}B_{12}$ and $Fe_{40}Ni_{40}B_{20}$ alloys by a weak magnetic field, the temperature of the intense crystallization onset increases by 40-80 K, that is, the interval of thermal stability of the alloy expands. The established effects can be explained by the fact that the magnetic field creates magnetoelastic dynamic stresses that destroy borides and silicides in the amorphous alloy, which promotes the homogenization of its structure. This causes the destruction of frozen-in crystallization centers and the formation of a new, more stable structural state with other short-range parameters and the level of internal stresses caused by the processes of structural relaxation.

Keywords: Amorphous alloy, Microhardness, Magnetoplastic effect, Thermal stability.

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1. INTRODUCTION

The level of requirements for the properties and reliability of products made of modern functional materials is increasing. To develop new amorphous, amorphous crystalline and nanocrystalline materials, optimize their properties and successfully operate the end-products, knowledge of changes in their structure under the influence of external factors is required. A magnetic field, similar to other destabilizing effects (temperature, pressure, ultrasound, irradiation), can affect the processes of phase formation, cause changes in the topological and compositional short order and influence the physical properties of amorphous alloys [1]. For practical use of amorphous metal alloys, it is important to have data on the stability of their properties under the action of magnetic fields, since products based on them are often operated under conditions of prolonged exposure to this factor.

Strong magnetic fields (greater than 1 T) are means of controlling the structure and properties of materials, as they are an additional thermodynamic factor that, along with temperature and pressure, affects the kinetics and mechanism of structural-phase transformations [2]. Under the influence of weak magnetic fields (for which condition $\mu_B B < kT$ is satisfied, where μ_B is the Bohr magneton, B is the induction of a magnetic field), magnetic energy does not contribute to the thermodynamic state of the material, as is the case with strong magnetic fields. When exposed to a weak magnetic field, there is a magnetoplastic effect, which is to increase the plasticity in the tensile test of magnetic metals. Not only the magnitude of the magnetoplastic effect but also its sign can change over a wide temperature range in the presence of or after its magnetic field [3]. The combination of changes in mechanical properties as a result of exposure to a weak magnetic field is called the magnetomechanical effect.

The influence of weak magnetic fields on the mechanical properties of materials is complex, both in the process of direct impact of the field and after its shutdown. The analysis of the literature shows that the influence of weak magnetic fields on the processes of phase formation depends on the composition of the alloy, and the manifestations of the effect may vary. For example, annealing of an amorphous $Ni_{80}P_{20}$ alloy in the presence of a weak constant magnetic field slowed down the rate of crystalline phase formation, and $Fe_{83}B_{12}Si_5$ alloy was found to accelerate the crystallization process in a magnetic field [4]. In [5], it is established the existence of a non-monotonic dependence of microhardness on the residence time of amorphous metal alloys in a magnetic field.

Therefore, there are many unresolved questions regarding the physical nature of the magnetic field effect of the structure and properties of amorphous metal alloys, which substantiates the relevance of the conducted research.

2. STATEMENT OF THE PROBLEM AND EXPERIMENTAL TECHNIQUE

Amorphous $Co_{67}Fe_3Cr_3Si_{15}B_{12}$ and $Fe_{40}Ni_{40}B_{20}$ alloys in the form of a foil with a thickness of 25-30 microns were investigated. The alloys were obtained by spinning with a cooling rate of 10^6 K/s at G.V. Kurdyumov Institute for Metal Physics of the National Academy of Sciences of Ukraine.

The small ribbon thickness of amorphous metal alloys obtained by the melt spinning method makes it difficult to study the mechanical properties by traditional methods. Therefore, the main method for studying the mechanical properties of amorphous alloys is the method of microhardness measuring.

For treatment in the magnetic field, the sample was placed between two plates of permanent magnets, providing a uniform field strength ($B = 0.64$ T). After exposure in a magnetic field, Vickers microhardness was measured (in air at room temperature) for a given time [6]. For the amorphous alloys in the initial amorphous state and after treatment, measurements of Vickers microhardness on the PMT-3 device were performed.

The value of hardness (by Vickers) accounts by the formula

$$H_V = \frac{1854P}{d^2}\left(\frac{\kappa Gf}{mm^2}\right), \qquad (1)$$

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

During the measurement, the possibility of microhardness value variation as a result of the influence of nearby structural constituents with other microhardness was taken into account: measurements were conducted 10 times under identical conditions, loading was made by 30 g, the repeated measurements were executed in a new place of structural constituent. The measurement error was 5 %. Indentations were performed on the shiny side of the amorphous ribbon, which did not come into contact with the rotating drum during its manufacturing.

The main characteristic of the thermal stability of amorphous alloys is the temperature of the intensive crystallization onset, which is determined using a highly sensitive dilatometric technique [7], 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. During heating of an amorphous alloy with a constant rate, its volume increases monotonically, when the temperature reaches a certain value (the temperature of the intensive crystallization onset), the transition of an amorphous alloy into the crystalline state occurs. This process is accompanied by a sharp decrease in volume. The temperature of the intensive crystallization onset is determined from the temperature dependence of the relative volume change $\Delta V/V$ when an amorphous alloy is heated.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Two types of studies of the influence of a weak constant magnetic field on the properties of an amorphous alloy were conducted: a study of microhardness and thermal stability. Before exposure to the magnetic field, the alloys were in the air for two years, which provided a significant relaxation of the basic thermal stresses existing in freshly quenched amorphous alloys. The results of the microhardness measurements, as well as the relative changes in the microhardness between the initial alloys and alloys that have undergone the corresponding treatment in the magnetic field are shown in Table 1.

Table 1 – The values of the microhardness of the initial samples and after the magnetic field treatment

Mode and time processing	H_v, GPa	$\frac{(H_v - H_0)}{H_0}$, %
Initial alloys $Co_{67}Fe_3Cr_3Si_{15}B_{12}$	9.38	–
Treatment with constant magnetic field of 0.64 T		
10 days	8.91	– 5
20 days	7.88	– 16
50 days	8.08	– 14
100 days	7.70	– 18
Initial alloys $Fe_{40}Ni_{40}B_{20}$	9.63	–
Treatment with constant magnetic field of 0.64 T		
20 days	8.14	– 15
80 days	7.42	– 23
100 days	7.58	– 21

Studies have shown that holding an amorphous $Co_{67}Fe_3Cr_3Si_{15}B_{12}$ alloy in a magnetic field for 10 days does not lead to a change in microhardness (a change within the error of the experiment). As the exposure time in the magnetic field increases, the changes increase and after 100 days of exposure, the microhardness decreases by 18 %. Similar results were obtained for the alloy $Fe_{40}Ni_{40}B_{20}$: exposure in a magnetic field for 80-100 days leads to a noticeable magnetoplastic effect – the microhardness decreases (by 21-23 %).

Therefore, the analysis of the data in Table 1 shows that under the influence of the magnetic field $B = 0.64$ T the microhardness of the samples decreases, i.e. there is a magnetoplastic effect.

Let us analyze the reasons for the change of microhardness under the influence of a magnetic field. The micromechanical properties of amorphous alloys, including microhardness, depend on the amount of free volume, the chemical composition of both the amorphous matrix, and the frozen crystallization centers and internal mechanical stresses.

The influence of the magnetic field can be explained by the set of actions of such mechanisms: accumulation and annihilation of the free volume, redistribution and relaxation of internal stresses, redistribution of chemical elements. It is established that, in the presence of internal mechanical stresses in the amorphous alloys [8, 9], there is an intense migration of elements, manifesting itself in the redistribution of the components of the sample both in the surface region and in the volume of the amorphous sample. This migration is due to the field of internal stresses whose relaxation is facilitated by the diffusion of elements along the thickness of the amorphous band. The hardness of amorphous alloys significantly increases when crystalline phases appear. In particular, this effect is manifested by the presence of borides in the structure. The stiffness of the nanostructured state with rare exceptions is higher than that of the corresponding amorphous one. Crystallization of amorphous metal-metalloid alloys results in borides, silicides and other high-strength phases associated with the presence of metal atoms in the amorphous matrix.

The magnetic field creates magnetoelastic and dynamic stresses that destroy borides and silicides [10]. That is, when exposed to a magnetic field, the decay of borides, silicides results in a decrease in hardness.

The peculiarity of the structure of amorphous metal alloys after rapid quenching of the melt is the presence of frozen crystallization centers, which may respond differently to external influences. The decrease in the microhardness value indirectly indicates the possible dissolution of the frozen-in crystallization centers.

Consider the effect of long-acting constant weak magnetic fields on the thermal stability of an amorphous alloy. Fig. 1 shows the temperature dependences of the relative change in volume of the amorphous $Co_{67}Fe_3Cr_3Si_{15}B_{12}$ alloy in the initial state (curve 1) and after treatment in the magnetic field of 0.64 T for 20 days (curve 2) and 90 days (curve 3).

When heated to 400 ^{0}C, the dependences (1) and (2), (3) are identical. For the original alloy, the onset temperature of intense crystallization is 500 °C, the crystallization interval is 100 °C. For an amorphous alloy that has been treated in a magnetic field of 0.64 T for 20 days, the onset temperature of intensive crystallization is 540 °C, and after treatment for 90 days, the onset temperature of intensive crystallization is 580 °C.

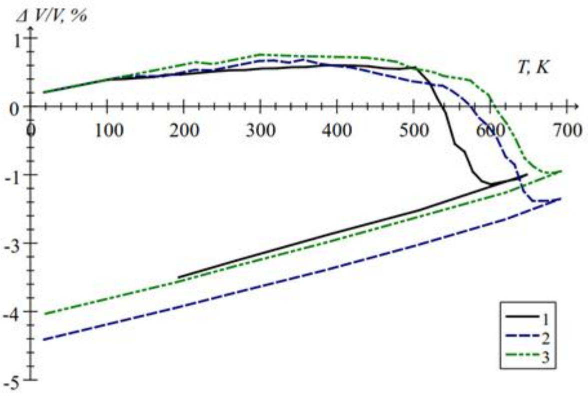

Fig. 1 – Temperature dependence of the relative change in the volume of the amorphous $Co_{67}Fe_3Cr_3Si_{15}B_{12}$ alloy in the initial state (curve 1) and after treatment in the magnetic field of 0.64 T for 20 days (curve 2) and 100 days (curve 3)

At these intervals, there is a slight decrease in the relative volume change, similar to the changes characteristic for the structural relaxation process.

For amorphous alloys that have undergone treatment in a magnetic field, the temperature dependence in the range of 440 °C prior to the onset of intense crystallization has differences compared to the original alloy.

The analogy between the processes of magnetic and low-temperature structural relaxation of the amorphous state can be explained by the fact that the influence of the magnetic field leads to the transition of the initial metastable amorphous state to a new, more stable level.

Table 2 shows the values of the thermal stability parameters of the initial samples and after the magnetic field treatment obtained by the dilatometric method.

Table 2 – The values of the thermal stability parameters of the original samples and after the magnetic field treatment

Mode and time of magnetic field action	Temperature of onset intensive crystallization, °C	Crystallization interval, °C
Initial state $Co_{67}Fe_3Cr_3Si_{15}B_{12}$	500	100
Treatment with a constant magnetic field of 0.64 T		
10 days	500	105
20 days	510	110
50 days	540	120
100 days	580	140
Initial state $Fe_{40}Ni_{40}B_{20}$	440	100
Treatment with a constant magnetic field of 0.64 T		
10 days	445	100
20 days	455	100
50 days	465	110
100 days	480	120

Treatment with a magnetic field for 10 days does not change the thermal stability parameters of the amorphous alloys. By increasing the processing time in the magnetic field up to 100 days, a noticeable effect of increasing thermal stability is observed. The thermal stability interval of the amorphous $Co_{67}Fe_3Cr_3Si_{15}B_{12}$ alloy increases by 80 °C and for amorphous $Fe_{40}Ni_{40}B_{20}$ alloy – by 40 °C.

The explanation of the revealed effect of increasing thermal stability of amorphous metal alloys may be the dissolution of frozen crystallization centers, the formation of a new structural state with other short-range parameters and the level of internal stresses.

4. CONCLUSIONS

It has been established that the continuous action of a weak constant magnetic field ($B = 0.64$ T) leads to a magnetoplastic effect in amorphous $Co_{67}Fe_3Cr_3Si_{15}B_{12}$ and $Fe_{40}Ni_{40}B_{20}$ alloys: the microhardness value decreases by 18-21 % in 100 days.

At long exposure (100 days) in the magnetic field, the thermal stability interval of the amorphous alloy increases by 40-80 °C.

The established effects of increasing plasticity and increasing thermal stability can be explained by the fact that the magnetic field creates magnetic elastic dynamic stresses that destroy borides and silicides in the amorphous alloy, which promotes the homogenization of its structure.

This causes the destruction of frozen-in crystallization centers and the formation of a new, more stable structural state with other short-range parameters and the level of internal stresses caused by the processes of structural relaxation.

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Вплив постійного магнітного поля на механічні властивості та термостабільність аморфних сплавів на основі Co, Fe та Ni

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Для розробки нових аморфних, аморфно-кристалічних та нанокристалічних матеріалів, оптимізації їх унікальних властивостей та успішної експлуатації виробів з них необхідні знання про зміни їх структури під дією зовнішніх чинників. Для практичного використання аморфних металевих сплавів важливо мати дані про стабільність або зміни їх властивостей під дією магнітних полів, оскільки вироби на їх основі часто експлуатуються в умовах тривалого впливу даного чинника. Було проведено експериментальне дослідження впливу постійного слабкого (B = 0,64 Т) магнітного поля на мікромеханічні властивості та термічну стабільність аморфних сплавів $Co_{67}Fe_3Cr_3Si_{15}B_{12}$ та $Fe_{40}Ni_{40}B_{20}$. Встановлено, що тривала дія слабкого постійного магнітного поля призводить до магнітопластичного ефекту: мікротвердість аморфних сплавів зменшується на 18-21 % за 100 діб. Результати дилатометричних досліджень вказують на те, що після обробки слабким магнітним полем аморфних сплавів $Co_{67}Fe_3Cr_3Si_{15}B_{12}$ та $Fe_{40}Ni_{40}B_{20}$ температура початку інтенсивної кристалізації зростає, тобто розширюється інтервал термостабільності сплаву. Встановлені ефекти можна пояснити тим, що магнітне поле створює магнітопружні динамічні напруги, які руйнують бориди та силіциди в аморфному сплаві, що сприяє гомогенізації його структури. При цьому відбувається формування нового, більш стабільного структурного стану з іншими параметрами ближнього порядку та рівнем внутрішніх напружень, викликаного процесами структурної релаксації.

Ключові слова: Аморфний сплав, Мікротвердість, Магнітопластичний ефект, Термічна стабільність.