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Low-temperature elastic properties of $Zr_{55}Al_{10}Ni_5Cu_{30}$ bulk metallic glass doped with yttrium

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The temperature dependence of elastic constants $c_{ij}(T)$ of zirconium $Zr_{55}Al_{10}Ni_5Cu_{30}$-based, 1 % yttrium-doped bulk metallic glass (BMG) within the temperature range of 78 to 300 K was examined using the method of resonance spectroscopy. The measurements helped determine low-temperature behavior of elastic Young's modulus (E), shear modulus (G) and bulk modulus. BMG doping with yttrium allowed to obtain high value of the Poisson's ratio (σ) and the B/G ratio and note weak dependence of $B(T)$ stemming from the appearance of an efficient dense pack of atomic clusters with icosahedral ordering symmetry within their internal structure. It was discovered that under 300 K, 1 % of yttrium reduces E by 5.4 % in comparison with the size of original BMG matrix. Analysis of the Debye temperature (θ_D) pattern points out the predominant contribution of phonon anharmonicity to BMG's elastic properties. It was assumed that high value of the Gruneisen parameter (γ) is due to manifestation of particularities of oscillatory properties.

Keywords: zirconium-based bulk metallic glass, elastic constants, elastic modules, Gruneisen parameter, Debay temperature, acoustic studies.

Методом резонансной спектроскопии изучена температурная зависимость упругих постоянных c_{ij} (T) объемного металлического стекла (ОМС) на основе циркония $Zr_{55}Al_{10}Ni_5Cu_{30}$ легированного 1 % иттрия в температурном интервале 78–300 К. Измерения позволили определить низкотемпературное поведение упругих модулей Юнга (E), сдвига (G) и объемного модуля. Легирование ОМС иттрием позволило получить высокое значение коэффициента Пуассона (σ), отношения B/G и отметить слабую зависимость $B(T)$, что связано с проявлением эффективной плотной упаковки атомных кластеров с икосаэдрической симметрией упорядочения в их внутренней структуре. Обнаружено, 1 % иттрия снижает E при 300 К на 5,4 % в сравнении с величиной исходной матрицы ОМС. Анализ характера температуры Дебая (θ_D) указывает на преобладающий вклад фононного ангармонизма на упругие свойства ОМС. Предполагается, что высокое значение параметра Грюнайзена (γ) вызвано проявлением особенности колебательных свойств.

Низькотемпературні пружні властивості $Zr_{55}Al_{10}Ni_5Cu_{30}$ об'ємного металевого скла, легованого ітрієм. *С.О.Бакай, О.С.Булатов, В.Ф.Долженко, В.С.Клочко, А.В.Корнієць, В.І.Спіцина.*

Методом резонансної спектроскопії вивчено температурну залежність пружних постійних c_{ij} (T) об'ємного металевого скла (ОМС) на основі цирконію $Zr_{55}Al_{10}Ni_5Cu_{30}$, легованого 1 % ітрію у температурному інтервалі 78–300 К. Вимірювання дозволили визначити низькотемпературну поведінку пружних модулів Юнга (E), зсуву (G) і

об'ємного модуля. Легування ОМС ітрієм дозволило отримати високе значення коефіцієнта Пуассона (σ), відносини B/G і відзначити слабку залежність $B(T)$, що пов'язано з проявом ефективної щільної упаковки атомних кластерів з ікосаедричною симетрією упорядкування в їх внутрішній структурі. Виявлено, 1 % ітрію знижує E при 300 К на 5,4 % у порівнянні з величиною вихідної матриці ОМС. Аналіз характеру температури Дебая (θ_D) вказує на переважаючий вклад фононного ангармонізму на пружні властивості ОМС. Передбачається, що високе значення параметра Грюнайзена (γ) викликано проявом особливості коливальних властивостей.

1. Introduction

The new class of multicomponent bulk amorphous metallic alloys called bulk metallic glass (BMG) has a unique set of mechanical, physical and chemical properties: high strength, hardness and elasticity, higher wear and corrosion resistance, and super magnetic characteristics [1, 2]. Thanks to these properties, they are successfully used as functional and structural materials. However, in a number of structural applications BMG faces technical difficulties manifesting through low plasticity in the case of tensile deformation (compression), which limits BMG's potential engineering application. A technological method of enhancing BMG's mechanical and physical properties has been found recently; this method involves additional microdoping of amorphous matrix with a rare-earth element, such as yttrium, within a concentration range of 0.05 to 2.0 at. % [2–6]. The positive effect is achieved in increasing the glass-forming ability of a supercooled melt by removing oxygen impurities to form harmless Y_2O_3 oxides and by inhibiting nucleation of crystalline phases. Yttrium is used with especial effectiveness in commercially-promising zirconium-based BMGs where the presence of oxygen leads to increased brittleness of the alloy. In addition, zirconium oxide helps produce intermetallic crystalline phases. That is the main reason for high sensitivity of the zirconium-based BMG to the content of oxygen impurities. The goal of this work is to offer a detailed study of the temperature dependence (78–300 K) of elastic constants $c_{ij}(T)$ of zirconium-based, 1 % yttrium-doped BMG's elastic modulus tensor for BMG with narrow-component composition $(Zr_{55}Al_{10}Ni_5Cu_{30})Y_1$. Amorphous matrix has high glass-forming ability and allows to achieve the critical ingot diameter of 30 mm [7]. Research was performed using resonant ultrasound technology. The temperature behavior of the following mechanical parameters was determined on the basis of experimental data: Young's (E), transverse (G) and bulk (B) elastic modules, Poisson's ratio (σ) and the phonon spectrum characteristics: Gruneisen parameter (γ) and Debye temperature (θ_D). The research has revealed the effect of yttrium on the temperature behavior of elastic properties of zirconium-based BMG's amorphous matrix. The analysis of $c_{ij}(T)$ provides additional information about bulk configurations of short-range order and BMG's dynamic properties.

2. Experimental

An $(Zr_{55}Al_{10}Ni_5Cu_{30})Y_1$ alloy ingot was prepared by arc melting of its components with over 99.95 % purity in the ultrapure argon atmosphere. To achieve chemical homogeneity the alloy was remelted three times, and a sample 2 mm in diameter and 5 mm long was cut out of it for acoustic research. The alloy's amorphous state was monitored by X-ray in $Cu\ K_\alpha$ radiation. The alloy had the density of $\rho = 7.38$ g/cm^3 (under 300 K) measured using the Archimedes method. Low-temperature acoustic studies (78–300 K) were carried out in the pulsed mode using a phase-sensitive method for the pass scheme. Excitation and detection of 50 MHz ultrasonic waves was achieved by lithium niobate piezoelectric transducers. The propagation velocities V_L and V_S (where L and S mean longitudinal and transverse polarization, respectively) within the investigated temperature range were measured by heating at the rate of 50 K/h in 1 K temperature increments with the precision of ±0.3. The heating rate and temperature stabilization were achieved using high-precision RIF 101 heating controller.

3. Results and discussion

Since the amorphous alloy is an isotropic material, it is characterized by only two independent elastic constants, $c_{11} = \rho V_L^2$ and $c_{44} = \rho V_S^2$ which help determine the elastic constant $c_{12} = c_{11} - 2c_{44}$. Values of the elastic modules E, B, G and the Poisson's ratio (σ) are determined from the known concepts:

$$E = (c_{11} - c_{12})(c_{11} + 2c_{12})/(c_{11} + c_{12});$$
$$G = c_{44} = (c_{11} - c_{12})/2;$$
$$B = (c_{11} + 2c_{12})/3$$

and

$$\sigma = c_{12}/(c_{11} + c_{12}).$$

The Gruneisen parameter γ is calculated from the equation:

$$\gamma = \frac{9(V_L^2 - 4V_S^2/3)}{2(V_L^2 + 2V_S^2)},$$

while the characteristic Debye temperature (θ_D) can be found from the equation:

$$\theta_D = \frac{h}{k_B}\left(\frac{3N}{4\pi}\right)^{1/3}\left(\frac{\rho}{\mu}\right)^{1/3} V_m,$$
$$\frac{3}{V_m^3} = \frac{2}{V_S^3} + \frac{1}{V_L^3},$$

where k_B, N and h are the Boltzmann, Avogadro and Plank constants, respectively, μ is the average atomic mass in the system and V_m is the average sound speed.

Fig. 1 shows the temperature dependence of $(Zr_{55}Al_{10}Ni_5Cu_{30})Y_1$ elastic modulus tensor's elastic constants c_{11} and c_{44}. The monotonous nature of the curves $c_{11}(T)$ and $c_{44}(T)$ suggests that its atomic structures do not undergo critical changes within the investigated temperature range. It is worth noting that there is still no uniform perception of the amorphous alloy's structure. Only various constructions of structural models are based on the observance of three empirical rules:

1) achieving high degree of packing of atomic configurations;

2) new local atomic configuration must be completely different from the structure of crystalline phases of the constituent elements;

3) long-range uniformity of interacting attraction forces is maintained.

Recently, structural models created by computer simulation have been widely used for the multicomponent (Zr–Al–Ni–Cu)Y BMG [7]. The topological model of a single cluster is based on the coordination polyhedron, for example, icosahedron featuring average ordering order, i.e., a structure with icosahedral ordering featuring the five-fold symmetry is created. The ratio of atomic radii of BMG's constituent elements represents a structural parameter. Elementary clusters are packed in three spatial directions according to the hcp or fcc scheme. For the time being, these structural models have explained the BMG's global property: high density. The topological model [7] involves understanding of BMG's formation by destabilizing basic element's crystal lattice (in this case, zirconium), which involves substitution or introduction of constituent elements. Destabilization of the crystal lattice leads to amorphization, when the alloy's constituent components create internal critical stresses to change local coordinate numbers. When an atom Y with large atomic radius (1.74 Å) replaces a relatively small atom Zr (1.58 Å), the effective packaging remains unbroken, but internal stresses which affect the elastic properties of amorphous alloy are induced in the cluster configuration space. Fig. 2 shows the temperature dependence of the Young's (E) and bulk (B) elastic modules. The set of dependencies $E(T)$, $G(T)$ and $B(T)$ shows the general trend in the temperature behavior of the alloy's elastic modules: their values increase monotonically as the temperature decreases. Weak dependence $B(T)$ is also worth mentioning. At the same time, under 300 K the E value of doped alloy is 5.3 % lower than the known value of 90 GPa for the original $Zr_{55}Al_{10}Ni_5Cu_{30}$ amorphous matrix [8]. It is quite possible that the softening of elastic properties by adding yttrium has effect on the values of G and B.

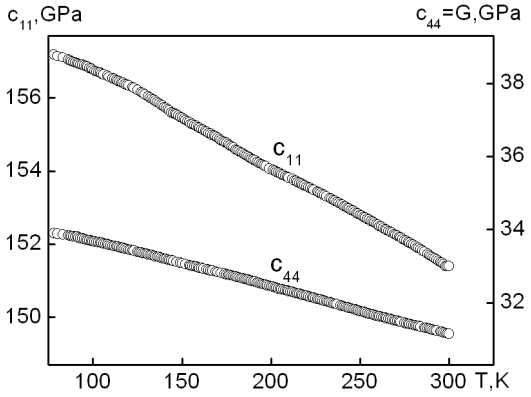

Fig. 1. Dependences on the temperature of the elastic constants of elasticity tensor modulus in $(Zr_{55}Al_{10}Ni_5Cu_{30})Y_1$ bulk metallic

Fig. 3 shows the temperature dependence of the Poisson's ratio (σ) and the B/G module ratio. In contrast to the temperature behavior of the elastic modules, both characteristics show continuous decrease of their values as the temperature decreases. If we take into account the well-known cor-

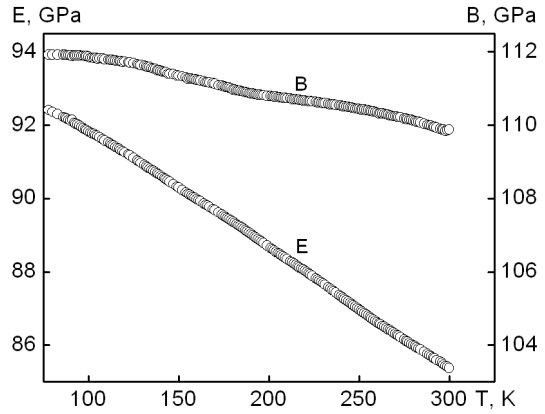

Fig. 2. Temperature dependences of Young's modulus (E) and bulk modulus (B) in $(Zr_{55}Al_{10}Ni_5Cu_{30})Y_1$ bulk metallic glass.

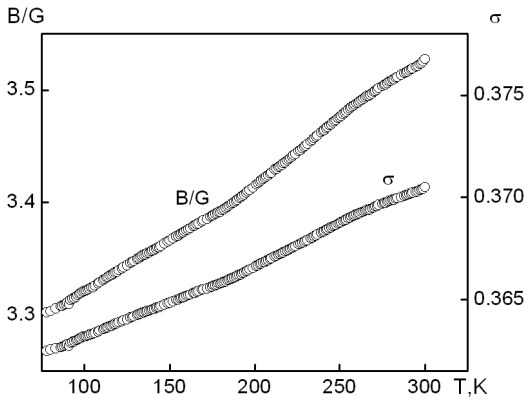

Fig. 3. Temperature dependences of Poisson's ratio (σ) and B/G ratio in $(Zr_{55}Al_{10}Ni_5Cu_{30})Y_1$ bulk metallic glass. G — shear modulus, B — bulk modulus.

relation that high values of σ (or B/G) correspond to the increased ductility of zirconium alloys [9, 10], our data points out the loss of ductility under cryogenic temperatures. But this statement requires a direct experiment. It is worth noting that according to [11], the 0.6 % yttrium doping of BMG with a composition closely resembling our alloy allowed to achieve high strength (2700 MPa) and ductility under 300 K.

Fig. 4 illustrates the temperature dependences of the Gruneisen parameter ($\gamma(T)$) and Debye temperature ($\theta_D(T)$) for $(Zr_{55}Al_{10}Ni_5Cu_{30})Y_1$ BMG. As the temperature decreases, γ continuously falls down and reflects the declining anharmonicity level of interatomic interaction (or oscillation of atoms) in an amorphous alloy. In this case, γ retains slightly higher value in comparison with the metallic components. The results in their entirety — decrease of the Young's modulus, weak dependence $B(T)$ and high degree of anharmonicity — indicate manifestation of the prominent role of phonon spectrum's soft modes in the elastic properties of amorphous alloy. The growing pattern of $\theta_D(T)$ as the temperature decreases proves the strengthening of interatomic bond that occurs, in particular, as a result of hybridization of Zr d-orbitals and s-, p-, d-orbitals of neighboring atoms in the cluster [12]. In addition, $\theta_D(T)$ indicates that phonon anharmonicity needs to be taken into account when studying the temperature dependence of BMG's elastic properties, which manifests itself through the link of θ_D with the bulk modulus and Poisson's ratio. Our study of $B(T)$ and $\theta_D(T)$ has revealed a general trend: the increase of B and θ_D.

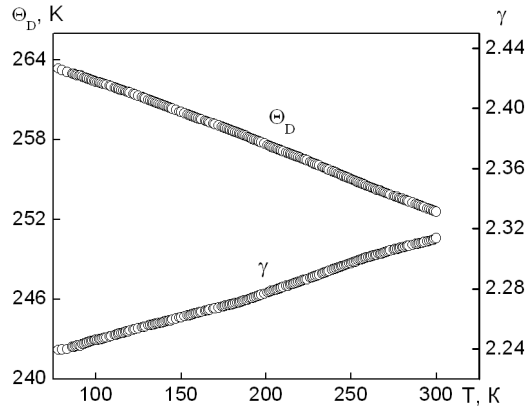

Fig. 4. Debye temperature (θ_D) and Gruneisen parameter (γ) as a temperature function for $(Zr_{55}Al_{10}Ni_5Cu_{30})Y_1$ bulk metallic glass.

4. Conclusions

The temperature dependence of zirconium $Zr_{55}Al_{10}Ni_5Cu_{30}$-based, 1 % yttrium-doped BMG's elastic constants ($c_{ij}(T)$), oscillatory properties ($\theta_D(T)$) and degree of anharmonicity ($\gamma(T)$) within the temperature range of 78 to 300 K was examined using the method of resonance spectroscopy. A study of the temperature dependence of the elastic modules $E(T)$, $G(T)$ and $B(T)$ has revealed normal behavior: as the temperature decreases, their values begin to grow. Doped alloy shows high value of σ and B/G and weak dependence of $B(T)$ within the entire investigated temperature range due to the packing efficiency of atomic clusters. The presence of 1 % yttrium in the amorphous alloy led to a 5.4 % decrease of E under 300 K comparing to the original matrix.

The increase of $\theta_D(T)$ as the temperature drops reflects the substantial contribution of phonon anharmonicity to BMG's elastic properties. The results indicate high degree of anharmonicity of interatomic interaction.

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