Journal of Alloys and Compounds 504S (2010) S95–S97

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Annealing effect on mechanical constants for $Ca_{48}Mg_{27}Cu_{25}$ bulk metallic glass

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ARTICLE INFO

Article history:
Received 3 July 2009
Received in revised form 23 February 2010
Accepted 9 March 2010
Available online 17 March 2010

Keywords:
$Ca_{48}Mg_{27}Cu_{25}$
Metallic glass
Crystallization
Elastic stiffness constant
Ultrasonic velocity

ABSTRACT

An annealing effect on elastic moduli of a $Ca_{48}Mg_{27}Cu_{25}$ bulk metallic glass has been investigated. The elastic moduli of $Ca_{48}Mg_{27}Cu_{25}$ bulk metallic glass were estimated using a technique of ultrasonic velocity measurements. The Young's modulus (E), Poisson's ratio (ν), shear modulus (G) and bulk modulus (B) for the as-cast $Ca_{48}Mg_{27}Cu_{25}$ alloy at room temperature were found out to be sensitive to the change of amorphous structure for the alloy. The crystallization of $Ca_{48}Mg_{27}Cu_{25}$ bulk metallic glass led to the increases of E, G and B, and the decrease of ν for the alloy.

1. Introduction

Metallic glasses have superior mechanical properties as comparison with crystalline metallic alloys. For example, a $Zr_{55}Cu_{20}Al_{15}Ni_{10}$ bulk metallic glass exhibits high charpy impact fracture energy of 160 kJ/m^2, tensile fracture strength of 1850 MPa, bending flexural strength of 3894 MPa and low Young' modulus of 90 GPa [1]. The mechanical properties of metallic glass are attributable to the amorphous structure of the alloy. The relationships between the glassy structure and mechanical properties for metallic glasses have been investigated. It has been reported that the charpy impact value, tensile fracture strain and Young' modulus of metallic glasses are affected by free volume contains in the glass structure for a $Zr_{50}Cu_{30}Ni_{10}Al_{10}$ bulk metallic glass [2]. A $Zr_{55}Cu_{29}Al_{10}Ni_5Nb_1$ bulk glassy alloy with nanocrystalline particle of 2–6 nm size in the amorphous matrix exhibits high bending flexural strength of 4300 MPa, which is much higher than 2000 MPa of a $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk metallic glass consists of only amorphous structure [3]. These results point out that the mechanical properties of metallic glasses remarkably depend on the glassy structure of the alloy.

Recently, Ca–Mg–Cu bulk metallic glasses with significantly low density, low Young's modulus and low glass transition temperature have been developed [4,5]. The mechanical constants of Ca–Mg–Cu bulk metallic glass have been reported [6,7]. The Ca–Mg–Cu metallic glasses with the essential characteristics have a potential for practical applications. In this study, the annealing effect on mechanical constants of metallic glass was investigated for a $Ca_{48}Mg_{27}Cu_{25}$ bulk metallic glass. The amorphous solid state of metallic glass, which is a metastable state, finally changes to crystalline state by heat treatments. The relationships between the glassy structure and the elastic moduli for the $Ca_{48}Mg_{27}Cu_{25}$ bulk metallic glass have been reported. The elastic moduli of the $Ca_{48}Mg_{27}Cu_{25}$ bulk metallic glass were examined using a technique of ultrasonic measurements.

2. Experimental procedures

An alloy ingot of $Ca_{48}Mg_{27}Cu_{25}$ was prepared from pure Ca, Mg and Cu metals using an induction melting technique in an argon atmosphere. The $Ca_{48}Mg_{27}Cu_{25}$ bulk metallic glass was fabricated using a copper-mold casting technique in an argon gas atmosphere. The plate-shaped bulk metallic glass with a width of 10 mm and thickness of 4 mm was fabricated. The amorphous structure of the sample was examined by X-ray diffraction with Cu Kα radiation. The thermal stability of the sample was measured using a differential scanning calorimetry (DSC) under a flowing argon gas atmosphere with a heating rate of 20 K/min. The ultrasonic velocities for specimen were measured using mechanical resonance of continuous ultrasonic waves [8,9]. The longitudinal and transverse ultrasonic waves propagating through the sample were generated by $LiNbO_3$ transducers with 36° Y cut and 41° X cut, respectively. The transducers with a diameter of 5 mm and fundamental frequency of 10 MHz were used for the ultrasonic velocity measurements.

A wave length (λ_r) of ultrasonic wave with a mechanical resonance frequency (f_r), which propagates into sample have a relationship to thickness of sample (L) as $\lambda_r = 2L/n$ where n is a constant associated with the resonance order. Velocity of ultrasonic wave (V_s) is given as $V_s = \lambda_r \times f_r$. Therefore, the V_s is rewritten as $V_s = 2L \times f_r/n$. The ultrasonic velocity is obtained by the measurements of a series of resonance frequencies. The elastic stiffness constants of c_{11} and c_{44} are related to the velocities of longitudinal and transverse waves (V_l and V_t) as $c_{11} = \rho(V_l)^2$ and $c_{44} = \rho(V_t)^2$ where ρ is a mass density of sample. For isotropic materials such as amorphous

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doi:10.1016/j.jallcom.2010.03.103

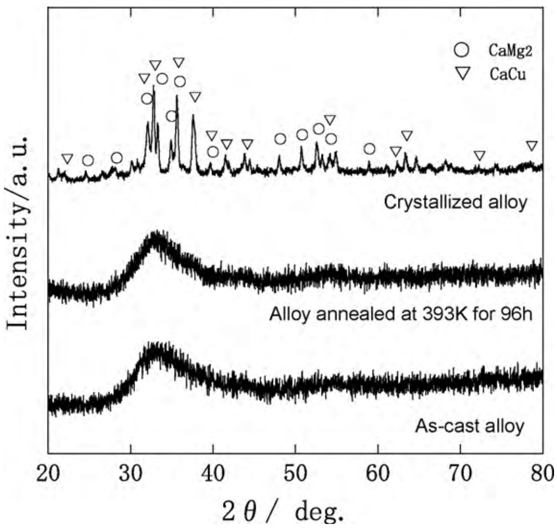

Fig. 1. X-ray diffraction patterns of $Ca_{48}Mg_{27}Cu_{25}$ alloys.

materials, Young's modulus (E), Poisson's ratio (ν), shear modulus (G), bulk modulus (B) depend on elastic stiffness constants of c_{11}, c_{44} and c_{12} ($c_{12} = c_{11} - 2c_{44}$). The E, ν, G and B are presented as $E = (c_{11} - c_{12})(c_{11} + 2c_{12})/(c_{11} + c_{12})$, $\nu = c_{12}/(c_{11} + c_{12})$, $G = c_{44} = (c_{11} - c_{12})/2$ and $B = (c_{11} + 2c_{12})/3$, respectively.

The density of sample was measured by an Archimedes method at room temperature. The n-tridecane ($CH_3(CH_2)_{11}CH_3$) as working fluid for the density measurements was used to prevent sample from the surface oxidization. The density and thermal expansion of the n-tridecane were taken into account for accurate density-measurement of sample. The air buoyancy was also calibrated to estimate the density with high accuracy. The rate of structure relaxation and crystallization for the metallic glass was estimated from the density of alloy. The annealing treatments of $Ca_{48}Mg_{27}Cu_{25}$ alloy were performed at $T_g - 10$ K in a vacuum atmosphere. The sufficiently crystallized sample was obtained by the heat treatment at 573 K for 15 min.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the $Ca_{48}Mg_{27}Cu_{25}$ alloys. The broadened diffused-diffraction peak for the as-cast alloy is the typical characterization of amorphous structure. The X-ray diffraction pattern for the alloy annealed at 393 K for 96 h also consists only of a broad peak. The crystallized alloy consists of $CaMg_2$, CaCu and unknown phases. Fig. 2 shows the DSC curve for the as-cast $Ca_{48}Mg_{27}Cu_{25}$ alloy. The glass transition temperature (T_g) and onset temperature of crystallization (T_x) of the $Ca_{48}Mg_{27}Cu_{25}$ alloy are 403 K and 435 K, respectively. The thermodynamic parameters of the $Ca_{48}Mg_{27}Cu_{25}$ alloy are close to those reported for $Ca_{50}Mg_{25}Cu_{25}$ alloy [5].

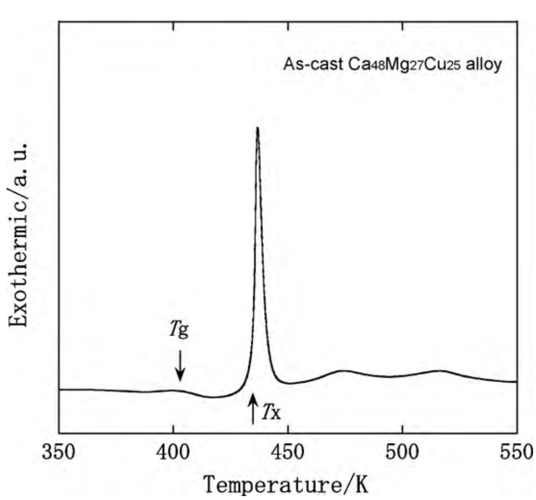

Fig. 2. DSC curve for the as-cast $Ca_{48}Mg_{27}Cu_{25}$ alloy.

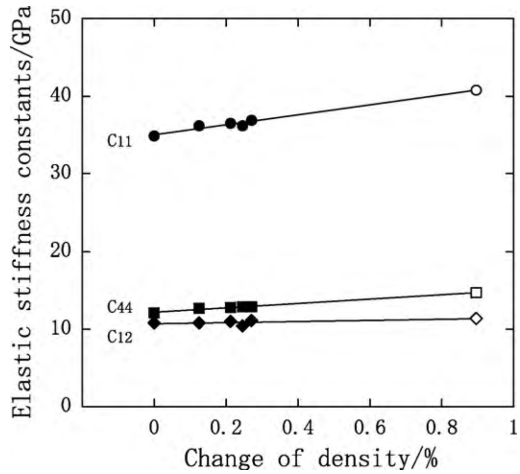

Fig. 3. The relationships between the elastic stiffness constants and the density of the $Ca_{48}Mg_{27}Cu_{25}$ alloy. The symbols of closed circle, diamond and square denote the elastic stiffness constants for the as-cast amorphous and glassy alloys. The symbols of open circle, diamond and square denote the elastic stiffness constants for the fully crystallized alloy.

Fig. 3 shows the relationships between the elastic stiffness constants and the density of the $Ca_{48}Mg_{27}Cu_{25}$ alloy. The elastic stiffness constants of c_{11}, c_{44} and c_{12} increased with increasing the density of alloy. The increase of density for the alloy is attributed to the structural relaxation and crystallization of alloy. Fig. 4 shows the elastic moduli versus the density for the $Ca_{48}Mg_{27}Cu_{25}$ bulk metallic glass. The E, G and B for $Ca_{48}Mg_{27}Cu_{25}$ alloy increased with increasing the density of the alloy. On the other hand, the ν value for $Ca_{48}Mg_{27}Cu_{25}$ alloy decreased with increasing the density of the alloy. These results indicate that the elastic moduli for the $Ca_{48}Mg_{27}Cu_{25}$ alloy are influenced by the structural relaxation and crystallization of the alloy. The structural relaxation for the glass alloy led to a loss of flexibility of metallic bonds for atoms. The elastic properties for the $Ca_{48}Mg_{27}Cu_{25}$ alloy shifted monotonously for the transition from amorphous phase to crystalline phase of the alloy.

Table 1 shows the elastic moduli of the as-cast and annealed $Ca_{48}Mg_{27}Cu_{25}$ alloys. The elastic properties of a $Ca_{50}Mg_{20}Cu_{30}$ bulk

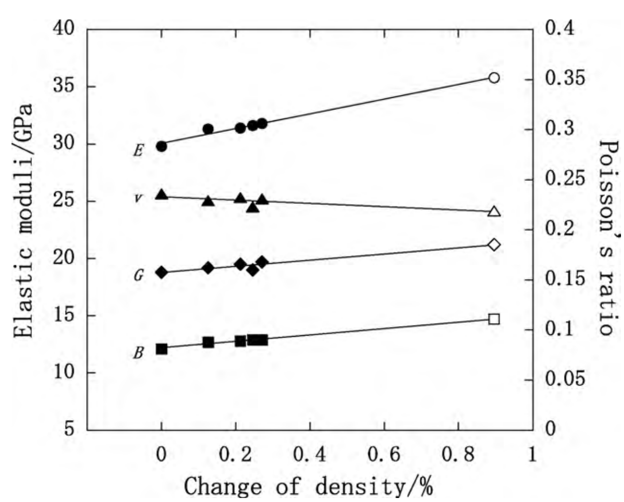

Fig. 4. The elastic moduli versus the density for the $Ca_{48}Mg_{27}Cu_{25}$ alloy. The symbols of closed circle, diamond, square and triangle denote the elastic moduli for the as-cast amorphous and glassy alloys. The symbols of open circle, diamond, square and triangle denote the elastic moduli for the fully crystallized alloy.

Table 1
The mass density, ultrasonic velocities and elastic moduli for the as-cast and annealed $Ca_{48}Mg_{27}Cu_{25}$ alloys.

	As-cast alloy	Alloy annealed at 393 K for 12 h	Fully crystallized alloy
ρ (g/cm^3)	2.400	2.403	2.421
V_l (km/s)	3.81	3.88	4.10
V_t (km/s)	2.24	2.30	2.46
c_{11} (GPa)	34.9	36.2	40.8
c_{44} (GPa)	12.1	12.7	14.7
c_{12} (GPa)	10.8	10.8	11.4
E (GPa)	29.8	31.3	35.8
ν	0.236	0.229	0.219
G (GPa)	12.1	12.7	14.7
B (GPa)	18.8	19.2	21.2
B/G	1.56	1.51	1.44
G/B	0.641	0.661	0.692

metallic glass measured by a resonant ultrasound spectroscopy have been reported to be 33.16 GPa for E, 12.56 GPa for G, 29 GPa for B and 0.311 for ν [7]. The E and G measured for the $Ca_{48}Mg_{27}Cu_{25}$ alloy were close to those reported for the $Ca_{50}Mg_{20}Cu_{30}$ alloy. On the other hand, the B and ν for the $Ca_{48}Mg_{27}Cu_{25}$ alloy were smaller than those for the $Ca_{50}Mg_{20}Cu_{30}$ alloy.

The elastic moduli for the glass solid state for metallic glass have been pointed to be related to a property of the supercooled liquid [10]. The fragility (m) of supercooled liquid for the $Ca_{48}Mg_{27}Cu_{25}$ alloy was estimated from the experimental data of shear and bulk moduli for the glass solid state. The m is given by $m = 29(B/G - 0.41)$ [10]. The m value calculated for the as-cast alloy was approximately 33.2. This implies that the supercooled liquid of the $Ca_{48}Mg_{27}Cu_{25}$ alloy is a strong liquid.

The heat treatment at 393 K for 12 h of $Ca_{48}Mg_{27}Cu_{25}$ alloy led to the structural relaxation of approximately 0.1% for the alloy. Here, the volume of structural relaxation for bulk metallic glass has been reported to be approximately 0.1% for a $Pd_{40}Ni_{40}P_{20}$ alloy [11]. Compared to the as-cast $Ca_{48}Mg_{27}Cu_{25}$ alloy, the $Ca_{48}Mg_{27}Cu_{25}$ alloy with a structural relaxation of approximately 0.1% exhibited the increases of about 5% for E, 6% for G and 2% for B, and the decrease of about 3% for ν.

The elastic moduli for the crystallized $Ca_{48}Mg_{27}Cu_{25}$ alloy were changed about 20% for E, 22% for G, 13% for B and 7% for ν compared to the as-cast alloy. The measurement results indicate that the elastic moduli of $Ca_{48}Mg_{27}Cu_{25}$ metallic glass are sensitive to the change of glass structure for the alloy. The G of the alloy was influenced most remarkably among the elastic moduli of the alloy by the change of the glass structure. The $Ca_{48}Mg_{27}Cu_{25}$ bulk metallic glass lost the intrinsic elasticity of the alloy by the crystallization of alloy.

4. Conclusions

The annealing effect on the mechanical constants of metallic glass was investigated for a $Ca_{48}Mg_{27}Cu_{25}$ alloy. The elastic moduli of the $Ca_{48}Mg_{27}Cu_{25}$ alloy were measured by a continuous ultrasonic method. The acoustic mechanical properties of the $Ca_{48}Mg_{27}Cu_{25}$ bulk metallic glass were sensitive to the change of glass structure for the alloy. The crystallization of the $Ca_{48}Mg_{27}Cu_{25}$ bulk metallic glass led to the increases of Young's modulus (E), shear modulus (G) and bulk modulus (B), and the decrease of Poisson's ratio (ν) for the alloy. The G for the $Ca_{48}Mg_{27}Cu_{25}$ alloy was affected most significantly among the elastic moduli for the alloy by the crystallization of alloy.

References

[1] T. Zhang, A. Inoue, Mater. Trans. JIM 39 (1998) 1230–1237.
[2] Y. Yokoyama, T. Yamasaki, A. Inoue, Rev. Adv. Mater. Sci. 18 (2008) 131–136.
[3] Y. Yokoyama, K. Yamano, K. Fukaura, H. Sunada, A. Inoue, Mater. Trans. JIM 40 (1999) 1015–1018.
[4] K. Amiya, A. Inoue, Mater. Trans. JIM 43 (2002) 81–84.
[5] O.N. Senkov, J.M. Scott, D.B. Miracle, J. Alloys Comp. 424 (2006) 394–399.
[6] V Keppens, Z. Zhang, O.N. Senkov, D.B. Miracle, Philos. Mag. 87 (2007) 503–508.
[7] Z. Zhang, V. Keppens, O.N. Senkov, D.B. Miracle, Mater. Sci. Eng. A 471 (2007) 151–154.
[8] D.I. Bolef, J.G. Miller, in: W.P. Mason, R.N. Thurston (Eds.), Physical Acoustics, vol. VIII, Academic Press, New York, 1971, p. 95.
[9] T. Fukami, Jpn. J. Appl. Phys. 29 (1990) 206–207.
[10] V.N. Novikov, A.P. Sokolov, Nature 431 (2004) 961–963.
[11] O. Haruyama, Appl. Phys. Lett. 88 (2006) 131906.