Journal of Non-Crystalline Solids 358 (2012) 470–473

Contents lists available at SciVerse ScienceDirect

Journal of Non-Crystalline Solids

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

Low expansion in $[(Fe_{0.9}Co_{0.1})_{0.72}B_{0.24}Nb_{0.04}]_{95.5}Y_{4.5}$ bulk metallic glass

M.B. Tang [a,*], J. Yi [b], J.Q. Wang [b], W.H. Wang [b], J.T. Zhao [a]

[a] *Key Laboratory of Transparent and Opto-functional Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China*
[b] *Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*

ARTICLE INFO

Article history:
Received 11 July 2011
Received in revised form 8 October 2011
Available online 22 November 2011

Keywords:
Bulk metallic glass;
Thermal expansion;
Magnetic material

ABSTRACT

The thermal expansion behavior of an iron-based bulk metallic glass (BMG) $[(Fe_{0.9}Co_{0.1})_{0.72}B_{0.24}Nb_{0.04}]_{95.5}Y_{4.5}$ is studied. The expansion coefficient in the wide temperature range of 100–300 K keeps in a constant, which is close to that of the Kovar alloy. Furthermore, the expansion coefficient of the BMG can be tuned by annealing below glass transition temperature. The results have implication for understanding the origin of low expansion, and the BMG may have a potential for commercial low expansion material.

1. Introduction

The thermal expansion behavior of Fe-rich alloys has been studied for many years owing to its significance relating to the application, for example, the Invar alloy. Invar is the original low expansion iron alloy, and was discovered in 1897 by Guillaume [1]. He received the Nobel Prize in Physics due to this work in 1920. With the development in industrial technology, there is an ever increasing demand for a more advanced degree of process accuracy. The prevention of heat deformation to ensure accuracy in processing machines, measuring machines, optical instruments, and various precision parts is critical for the promotion of higher performance. In other words, the best solution is to maintain the accuracy of various equipments, parts and components by using alloy materials that have low thermal expansion coefficient. Consequently, there is a growing interest in low-expansion alloys especially in recent years [2–6].

Low-expansion alloys such as Invar and Super Invar develop volume changes caused by spontaneous volume magnetostriction in temperatures lower than the Curie point. Since this negates the content change caused by lattice vibration, low thermal expansion property is obtained. It has long been realized that the effect is related to magnetism; but a full understanding is still lacking. A number of theoretical models have been suggested for Invar explanation [7]. The most known model for the Invar phenomenon in Fe–Ni is the phenomenological 2γ-state model, which was proposed by Weiss [8]. According to this model there are two possible states for face-centred cubic γ-Fe: the high-spin/high-volume state and the low-spin/low-volume state. In some theoretical models, the disorder effect has been taken into account [7,9], which is only a weak chemical disorder in crystalline alloys. The structure disorder effect on thermal expansion has not been studied by both experiments and theories, which is an important question.

In low expansion crystalline alloys, Fe–Ni alloys are the best studied Invar materials [8,10,11]. In recent years, Fe-rich bulk metallic glasses (BMGs) were discovered as a new class of multicomponent alloys with high glass forming ability and excellent engineering properties [12–19], which are helpful to study the structure disorder effect on thermal expansion. While little work has been done on the thermal expansion of Fe-based amorphous alloys [20–22]. In this paper, the temperature-dependent thermal expansion, magnetization, and specific heat C_p of the as-cast and annealed $[(Fe_{0.9}Co_{0.1})_{0.72}B_{0.24}Nb_{0.04}]_{95.5}Y_{4.5}$ BMG is studied. The results indicate that the Fe-based BMG exhibits low thermal expansion, which is close to that of the known Kovar alloy (Fe-29Ni-17Co) in wide temperature range from 100 K to 300 K, and the thermal expansion coefficient can be tuned by annealing. The low expansion in the Fe-based BMG is related to the structural disorder, which is important to understand the origin of low expansion.

2. Experimental details

The alloy ingot of $[(Fe_{0.9}Co_{0.1})_{0.72}B_{0.24}Nb_{0.04}]_{95.5}Y_{4.5}$ was prepared by arc melting the mixture of pure (better than 99.9% at%) Fe, Co, Nb and Y metals, and B metalloid, in a Ti-gettered high-purity argon atmosphere. The master alloy was remelted several times for homogenization, and the melt was suction-cast into a Cu mould under argon atmosphere to get cylindrical rods of 3 mm diameter. The glassy structure of the as-cast BMG (BMG1) is ascertained by X-ray diffraction (XRD) using a Rigaku D\max-2550 with Cu K_α radiation, and Differential scanning calorimeter (DSC). DSC measurement was carried out in a NETZSCH STA 409 PC. The isothermal annealing (for relaxation) was performed under a high vacuum at 800 K (BMG2) and

---

* Corresponding author. Tel.: +86 21 52412517; fax: +86 21 52413122.
E-mail address: mbtang@mail.sic.ac.cn (M.B. Tang).

0022-3093/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2011.10.030

825 K (BMG3) for 1 h (below the glass transition temperature T_g). The linear thermal expansion $\Delta L/L(300\ \mathrm{K})$ was measured using a foil strain gage (KYOWA; model KFL-02-120-C1). The gauge was bonded with PC-6, and measured using Physical Property Measurement System (PPMS, Quantum Design Inc.). This method is simple but requires a material of known expansion. We used aluminum (purity: 99.99%) and the corresponding thermal expansion data of pure aluminum to calibrate the gauge [23]. Thus, although the precision of the gauges is better than 10^{-7} strain, the accuracy is only about 20%. The C_p measurements (error<2%) were carried out with PPMS. The magnetization was measured using PPMS.

3. Experimental results

Fig. 1(a) shows the XRD pattern of the as-cast $[(\mathrm{Fe_{0.9}Co_{0.1}})_{0.72}\mathrm{B_{0.24}Nb_{0.04}}]_{95.5}\mathrm{Y_{4.5}}$ BMG (BMG1). The BMG1 exhibits a broad diffraction maxima characteristic of metallic glass characterizing of amorphous structure of alloys with the limitation of the XRD. The DSC trace of the alloy in Fig. 1 (b) shows an obvious endothermic characteristic before crystallization demonstrating a distinct glass transition with the onset at $T_g = 890$ K. Following the glass transition, the alloy exhibits obvious two exothermic heat release events associated with the transformations from undercooled liquid state to the equilibrium crystalline intermetallic phases. The crystalline temperature is 933 K. The distinct glass transition and sharp crystallization event further confirm the glassy structure of the BMG.

Fig. 2(a) displays the thermal expansion $\Delta L/L(300\ \mathrm{K})$ as a temperature function from 5 to 300 K for the as-cast Fe-based BMG (BMG1), the BMG annealed at 800 K (BMG2) and the BMG annealed at 825 K (BMG3). The $\Delta L/L(300\ \mathrm{K})$ of both BMG1 and BMG2 exhibits a positive T-coefficient from 5 to 300 K. The $\Delta L/L(300\ \mathrm{K})$ of the BMG2 is smaller than that of the BMG1. The $\Delta L/L(300\ \mathrm{K})$ of the BMG3 is obviously different from that of the BMG1 and BMG2, and shows a negative T-coefficient below about 115 K. So the BMG3 shows a negative thermal expansion behavior below 115 K.

The thermal expansion of both BMG1 and BMG2 is close to linear behavior below 50 K and above 100 K, respectively. Fig. 2(b) shows the linear fitting results for BMG1 and BMG2. The thermal expansion coefficient $\alpha = d[\Delta L/L(300\ \mathrm{K})]/dT$ of both BMG1 and BMG2 in different temperature range can be gotten by the fitting. The thermal expansion coefficient α of the BMG1 is a constant $6.05 \times 10^{-6}\ \mathrm{K}^{-1}$ in the temperature range from 100 K to 300 K, and is close to that of the Kovar alloy Fe-29Ni-17Co $5.5 \times 10^{-6}\ \mathrm{K}^{-1}$ (300 K–473 K), which is known for a long time as the alloy used for hard glass sealing. The α of the BMG1 increases rapidly with decreasing temperature, and is up to $27.7 \times 10^{-6}\ \mathrm{K}^{-1}$ in the temperature range from 50 K to 5 K. The α of the BMG2 is like that of the BMG1, and is $3.32 \times 10^{-6}\ \mathrm{K}^{-1}$ in the temperature range from 100 K to 300 K, which is smaller than that of the BMG1 and is between that of the Kovar alloy and that of the Invar alloy Fe-36Ni. The α of the BMG2 in the temperature range from 50 K to 20 K is $22.9 \times 10^{-6}\ \mathrm{K}^{-1}$. The α in both BMG1 and BMG2 above 100 K is very low in the wide temperature range, and is close to hard glass and ceramics, which has potential applications.

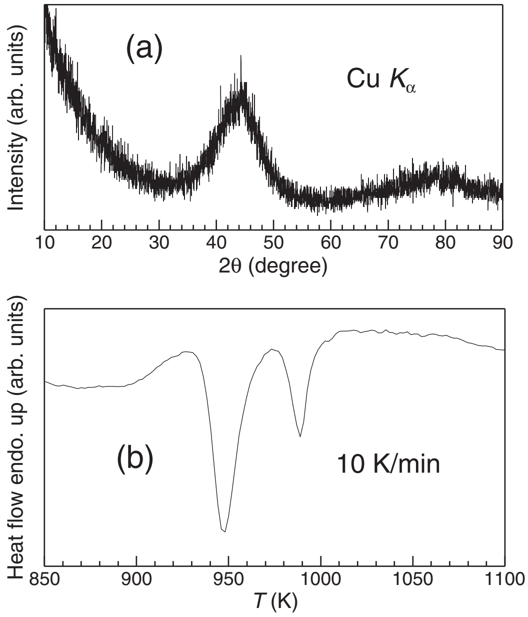

Fig. 1. (a): XRD pattern for the as-cast $[(\mathrm{Fe_{0.9}Co_{0.1}})_{0.72}\mathrm{B_{0.24}Nb_{0.04}}]_{95.5}\mathrm{Y_{4.5}}$ BMG; (b): DSC trace of the alloy showing the glass transition, crystallization and the melting process at the scanning rate 10 K/min.

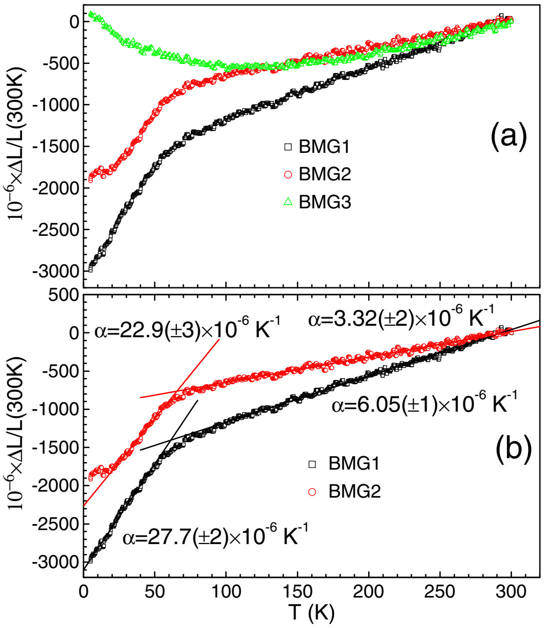

Fig. 2. (Color online) (a): Thermal expansion of the BMG1, BMG2 and BMG3. (b): the linear fitting results of the thermal expansion for BMG1 and BMG2.

Usually, the anomalous thermal expansion coefficient in magnetic alloys, for example, the Invar alloy, is due to the ferromagnetic property [8,10]. Fig. 3(a) displays the hysteresis M–H loops of the BMG1, BMG2 and BMG3 with low coercive field at $T = 300$ K. And the BMGs show soft magnetic property at room temperature. The saturation magnetization of the as-cast BMG1 is a little lower than that of the annealed BMG2 and BMG3. Fig. 3(b) exhibits *dc* magnetic susceptibility M *vs.* T for the as-cast and annealed BMGs at $H = 200$ Oe from 2 K to 300 K. The magnetic susceptibility M in low magnetic field of the BMGs is almost a constant from 2 K to 300 K, is about 910 emu/mol, 760 emu/mol and 610 emu/mol for the BMG1, BMG2 and BMG3, respectively. There is no obvious difference in the magnetization of the bulk specimens. And the M in low magnetic field decreases by annealing, which maybe is due to a structural relaxation.

The metastable state of metallic glasses can relax structurally by annealing below glass transition temperature T_g [24–28]. The measured specific heat C_p of the BMG1, BMG2 and BMG3 from 2 K to 300 K is shown in Fig. 4 (a). There is no phase transition, and the C_p of the BMG decreases slightly by annealing, which is in accord with that in Zr-based BMG [29]. In order to study the annealing effect, the excess specific heat ΔC_p in the annealed BMGs is obtained by subtracting the C_p of the as-cast BMG1. Fig. 4(b) shows $-\Delta C_p/T$ *vs.* T for both BMG2 and BMG3, which exhibits a peak near 40 K in both annealed BMGs. The annealing temperature is higher, the excess

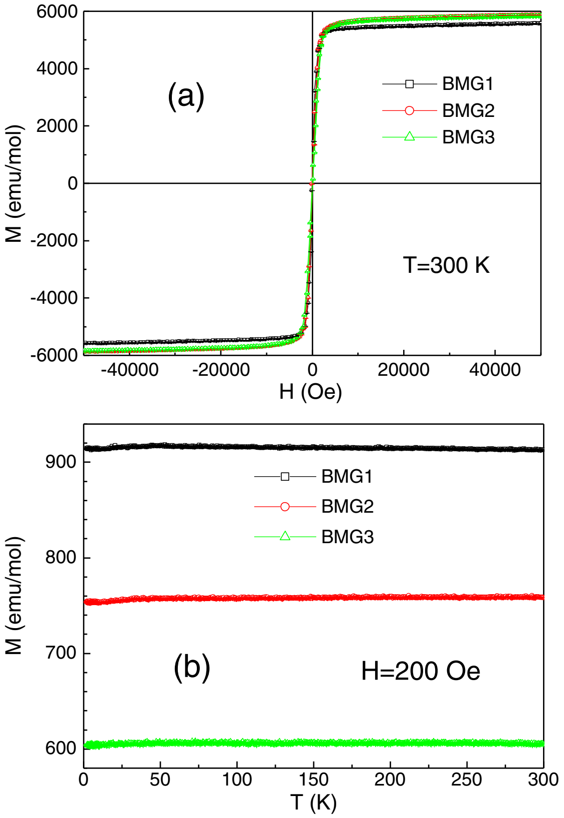

Fig. 3. (Color online) (a): Hysteresis *M–H* loops of the as-cast and annealed [(Fe$_{0.9}$Co$_{0.1}$)$_{0.72}$B$_{0.24}$Nb$_{0.04}$]$_{95.5}$Y$_{4.5}$ BMGs at $T=300$ K (b) *dc* magnetic susceptibility *M vs. T* for the BMGs at $H=200$ Oe.

specific heat ΔC_p is stronger, which shows that the structural relaxation is obvious. The α can be tuned by annealing below glass transition temperature [30,31]. The structural relaxation may play an important role in the thermal expansion of the Fe-based BMG.

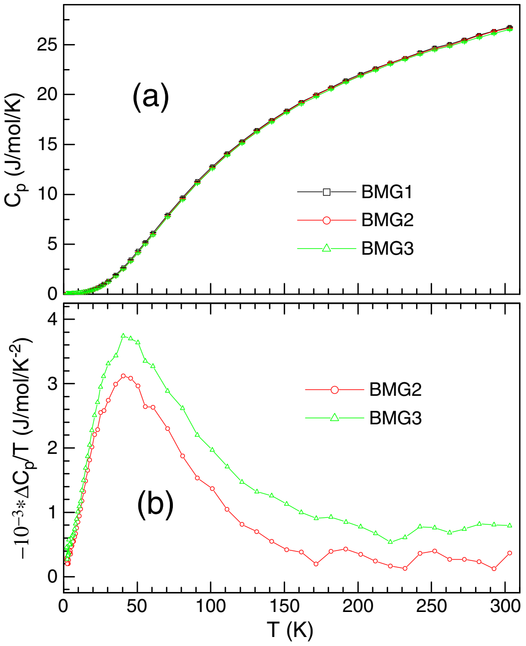

Fig. 4. (Color online) (a): Specific heat C_p of the as-cast and annealed Fe-based BMGs in the temperature range from 2 K to 300 K. (b): excess specific heat -$\Delta C_p/T$ *vs. T* of the annealed BMG2 and BMG3.

4. Discussion

The Fe-based BMG is a new class of low expansion materials with α value (6.059×10^{-6} K^{-1} for BMG1) close to that of the Kovar alloy and is only about 1/2 to 1/4 of iron or ordinary alloys. The experiments verify that the negative or low thermal expansion in Invar alloys is directly associated with vibrational anharmonicity due to the magnetoelastic interaction [32]. The structure of metallic glasses is strongly disordered, and the vibrational properties are complicated comparable to that of crystals. The low thermal expansion in Fe-based BMG maybe is related to the complicated vibrational properties. On the other hand, because metallic glasses are metastable, there is a distribution of the energy minima in the landscape [33,34]. Annealing can shift the state point of a glass to a deeper and lower-energy minimum, and change the interatomic interactions. Both energy minimum and the anharmonic force determine the vibrational properties in glasses. So the thermal expansion in metallic glasses is easily tuned by annealing, which is an important method to tune and control the thermal expansion in amorphous materials.

5. Conclusions

The Fe-based BMG exhibits low thermal expansion behavior at low temperature. Their thermal expansion coefficient α in the wide temperature range from 100 K to 300 K keeps in a constant, and is close to that of the Kovar alloy. The α in the Fe-based BMG is related to the structural disorder, and can be tuned by annealing below glass transition temperature, which is an important method to tune and control the thermal expansion in amorphous materials. So the Fe-based BMG may have a potential for both structural and functional applications.

Acknowledgments

The financial support of the National Science Foundation of China (Grant Nrs: 51001113, 50731008 and 50921091), the National Basic Research Program of China (MOST, Nr. 2007CB613904 and 2009CB939904), and the MPG-CAS Partner Group Program is appreciated.

References

[1] C.E. Guillaume, C. R. Acad. Sci. 125 (1897) 235.
[2] A.W. Sleight, Inorg. Chem. 37 (1998) 2854.
[3] G. Ernst, C. Broholm, G.R. Kowach, A.P. Ramirez, Nature 396 (1998) 147.
[4] J.S.O. Evans, J. Chem. Soc. Dalton Trans. (1999) 3317.
[5] G.D. Barrera, J.A.O. Bruno, T.H.K. Barron, N.L. Allan, J. Phys. Condens. Matter 17 (2005) R217.
[6] A.L. Goodwin, C.J. Kepert, Phys. Rev. B 71 (2005) (R).
[7] A.V. Ruban, S. Khmelevskyi, P. Mohn, B. Johansson, Phys. Rev. B 76 (2007) 014420.
[8] R.J. Weiss, Proc. R. Soc. London, Ser. A 82 (1963) 281.
[9] S. Khmelevskyi, I. Turek, P. Mohn, Phys. Rev. Lett. 91 (2003) 037201.
[10] M.V. Schilfgaarde, I.A. Abrikosov, B. Johansson, Nature 400 (1999) 46.
[11] S. Chikazumi, J. Magn. Magn. Mater. 10 (1979) 113.
[12] Z. Han, J. Zhang, Y. Li, Intermetallics 15 (2007) 1447.
[13] B.L. Shen, C.T. Chang, A. Inoue, Intermetallics 15 (2007) 9.
[14] Z.P. Lu, C.T. Liu, J.R. Thompson, W.D. Porter, Phys. Rev. Lett. 92 (2004) 245503.
[15] V. Ponnambalam, S.J. Poon, G.J. Shiflet, V.M. Keppens, R. Taylor, G. Petculescu, Appl. Phys. Lett. 83 (2003) 1131.
[16] M.D. Demetriou, G. Kaltenboeck, J.Y. Suh, G. Garrett, M. Floyd, C. Crewdson, D.C. Hofmann, H. Kozachkov, A. Wiest, J.P. Schramm, W.L. Johnson, Appl. Phys. Lett. 95 (2009) 041907.
[17] J. Zhang, H. Tan, Y.P. Feng, Y. Li, Scr. Mater. 53 (2005) 183.
[18] D.H. Kim, J.M. Park, D.H. Kim, W.T. Kim, J. Mater. Res. 22 (2007) 471.
[19] M. Stoica, V. Kolesar, J. Bednarcic, S. Roth, H. Franz, J. Eckert, J. Appl. Phys. 109 (2011) 054901.
[20] K. Fukamichi, M. Kikuchi, S. Arakawa, T. Masumoto, Solid State Commun. 23 (1977) 955.
[21] K. Fukamichi, H. Hiroyoshi, M. Kikuchi, T. Masumoto, J. Magn. Magn. Mater. 10 (1979) 294.
[22] M. Hatate, J.S. Garitaonandia, K. Suzuki, J. Appl. Phys. 103 (2008) 07B909.
[23] F.R. Kroeger, C.A. Swenson, J. Appl. Phys. 48 (1977) 853.
[24] K. Ratzke, P.W. Huppe, F. Faupel, Phys. Rev. Lett. 68 (1992) 2347.
[25] B.C. Wei, W. Löser, L. Xia, S. Roth, M.X. Pan, W.H. Wang, J. Eckert, Acta Mater. 50 (2002) 4357.
[26] H.S. Chen, S.Y. Chuang, Appl. Phys. Lett. 31 (1977) 255.

[27] M.B. Tang, H.Y. Bai, W.H. Wang, D. Bogdanov, K. Winzer, K. Samwer, T. Egami, Phys. Rev. B 75 (2007) 172201.
[28] D. Srolovitz, T. Egami, V. Vitek, Phys. Rev. B 24 (1981) 6936.
[29] P. Wen, G.P. Johari, R.J. Wang, W.H. Wang, Phys. Rev. B 73 (2006) 224203.
[30] S. Tyagi, J. Steinberg, A.E. Lord Jr., Appl. Phys. Lett. 37 (1980) 618.
[31] A. Fujita, T. Suzuki, N. Kataoka, K. Fukamichi, Phys. Rev. B 50 (1994) 6199.
[32] L. Maosa, G.A. Saunders, H. Rahdi, U. Kawald, J. Pelzl, H. Bach, Phys. Rev. B 45 (1992) 2224.
[33] M. Goldstein, J. Chem. Phys. 51 (1969) 3728.
[34] F.H. Stillinger, Science 267 (1995) 1935.