ARTICLE IN PRESS

Intermetallics xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Intermetallics

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

Invar effect of Fe-based bulk metallic glasses

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A R T I C L E I N F O

Keywords:
A. Metallic glasses
B. Magnetic properties
Mechanical properties
Thermal properties

A B S T R A C T

Invar alloys have a wide application owing to its low expansion characteristics. Recently, it is revealed that some Fe-based bulk metallic glasses (BMGs), which have much higher strength than that of traditional Fe-Ni Invar alloys, also have the Invar effect. Combining the low expansion of the Invar effect and the good mechanical properties of Fe-based BMGs has an attractive potential for applications, for which firstly systematic study on the Invar effect of Fe-based BMGs is needed. In this work, the thermal expansion of 14 FeSiPCBM, (Fe,Co)BSiNb, FeNiPC and FeMoPCB BMGs are investigated. The results show all the alloys have the Invar effect, but can be categorized in two types, depending on whether the low expansion occurs in a wide temperature range below the Curie temperature T_c, or in a narrow temperature range near T_c. It is found the former type of alloys have lower T_c and saturation magnetic induction density, i.e., weaker magnetic properties. The substitution of Fe by Co and Ni weakens the Invar effect. These findings are explained based on the characteristics of the amorphous structure and the Bethe-Slater curve. The findings in this paper help to further develop low expansion Fe-based BMGs.

1. Introduction

In 1896, Guillaume found that the $Fe_{65}Ni_{35}$ alloy has a very low and constant thermal expansion coefficient α of 1.5×10^{-6}/°C [1], which was used to fabricate the International Prototype Metre. The discovery of this low expansion Fe-Ni alloy, named as the Invar alloy, made great contribution to the precision measurement at that time and won the Nobel Prize in Physics in 1920 [2]. Until now, it is still the sole Nobel Prize in the filed of metals. A unified explanation on the Invar effect, i.e., the effect that some ferromagnetic alloys have low thermal expansion near or below the Curie temperature T_c, is however still a difficulty in the field of magnetism [3–8]. Now the Invar alloys are widely used in many fields, such as aerospace, microwave communication, hair spring in watches, display devices, LNG carriers, core wires of long-distance power cables, in which a high dimensional precision mechanical system under different temperatures are need. However, the traditional Fe-Ni Invar alloys have a low strength of about 550 MPa and are thus incompetent in some applications [9].

Apart from in the face centered cubic (FCC) Fe-Ni alloys, the Invar effect is also found in many Fe-based amorphous alloys [10–15]. These amorphous alloys are all ribbons with a thickness of dozens of micrometers, due to the very limited glass-forming ability (GFA), and thus can hardly be used as low expansion structural materials. Bulk metallic glasses (BMGs) are amorphous alloys larger than 1 mm in all three dimensions, and have better thermal stability than that of ribbon alloys [16]. In previous works [17,18], we found that the $(Fe_{71.2}B_{24}Y_{4.8})_{96}Nb_4$ BMG has a clear Invar effect, with a low average α of 5.5×10^{-6}/°C below 200 °C [19,20]. Fe-based BMGs usually have a strength above 3000 MPa, which is much larger than that of traditional Fe-Ni Invar alloys. Replacing the Fe-Ni alloys by Fe-based BMGs would make the low expansion parts lighter, thinner, smaller, and more compact, which is important in some applications, such as the weight-bearing part of optical systems, the arm of precise balances, the length measurement devices, the passive layer of thermostatic bimetal plates. Especially, for the long distance overhead power transmission, aluminum cladded Fe-Ni alloy cables are usually used to avoid the elongation of the cable under the Joule heating. The Invar alloy core bears most of the tension applied between pylons, and the outer aluminum conducts most of the current. The use of low expansion, high strength Fe-based BMGs would make the core much thinner, and thus increase the cross-section of aluminum wire and reduce the transmission losses effectively. It must also point out that a good bending ductility [21,22] of the core wire is also needed when stranding the cable. However, only a small part of Fe-based BMGs [23–27], not including $(Fe_{71.2}B_{24}Y_{4.8})_{96}Nb_4$, have some ductility.

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http://dx.doi.org/10.1016/j.intermet.2017.10.012
Received 1 August 2017; Received in revised form 25 September 2017; Accepted 17 October 2017
0966-9795/

Please cite this article as: Hu, Q., Intermetallics (2017), http://dx.doi.org/10.1016/j.intermet.2017.10.012

To date, more than 10 Fe-based BMG alloy systems and more than 400 alloy compositions have been reported [16]. Except $(Fe_{71.2}B_{24}Y_{4.8})_{96}Nb_4$, which BMG systems have the Invar effect and how the detailed composition affects the Invar effect are still unknown. Especially, whether those Fe-based BMGs with a certain amount of plasticity can have the low expansion is an attractive issue. In this work, the thermal expansion behavior of 4 ferromagnetic BMG systems with 14 alloy compositions, including some BMGs with obvious plasticity, are investigated. The results and analyses can help to further develop Fe-based BMGs with better comprehensive performance.

2. Experimental procedures

The purity of raw materials are 99.99% for metals (Fe, Co, Ni, Nb, Mo), 99.999% for metalloids (C, B, Si), and 99.9% for commercial Fe-P alloys. The lightest B powder was firstly put into the bottom of a clear fused quartz tube and then covered by the C powder and subsequently the Fe-P powder, finally Si and metal pieces were added. The inner diameter of the tube was 18 mm, and the mass of the raw materials were 12 g. The raw materials in the tube were melted to form a flat cylinder by induction heating under a high-purity argon atmosphere. The flat cylinder alloys were then re-melted for 4 times by arc melting under a Ti-gettered high-purity argon atmosphere. The master alloy was smashed into small pieces, and 1.2 g alloys were loaded into a fused quartz tube with an inner diameter of 8 mm. A hole with a diameter of 1 mm was located in the end of the tube. The tube was assembled onto the injection machine (Rapid Quench Machine System VF-RQT50, Makabe Co. Ltd. Japan), then the chamber of machine was evacuated to 4×10^{-3} Pa and back-filled by a high-purity argon atmosphere with pressure of 0.05 MPa. The pieces of alloys were melted by induction heating and then injected through the tube hole into a copper mold under a high-purity argon gas flow with a pressure of 0.25 MPa. The copper mold was carefully polished by the alumina polisher (PIKAL Metal Polish, Japan) before use. The diameter and length of the injecting formed BMG rods are 1 and 50 mm, respectively.

The amorphous state of the rods was confirmed by x-ray diffraction (Bruker D8 Advance) tests. The thermal expansion behavior was measured in a thermal dilatometer (NETZSCH DIL 402C) using samples with the length of 20 mm cut from the middle part of as-cast samples. The equipment was calibrated with the standard alumina sample and the applied push load was 30 cN, corresponding to a stress of 0.38 MPa. The samples were flushed by a high-purity argon flow during the tests, and the heating rates of the tests were 5 K/min. The results are presented by the change of relative length change ($\Delta L/L_0$) and the linear thermal expansion coefficient α with varying temperatures, respectively.

3. Results

$Fe_{76-x}Si_{3.3}P_{8.7}C_{7.0}B_{5.0}M_x$ BMGs system have good magnetic properties, especially for the alloys with minor addition of Cu [28]. As shown in Fig. 1(a1) and (a2), all the investigated alloys have the Invar effect, manifesting as a turn in the thermal expansion trace, and this turn can be seen more clearly in the α trace. The temperature at the turning point is T_c [15,17]. The minor addition of Cu does not change T_c much and these alloys have similar α traces, i.e., a negative peak near T_c and a similar α value before and after this peak. The addition of Mo decreases T_c significantly and gradually changes the shape of the α trace. $Fe_{75}Si_{3.3}P_{8.7}C_{7.0}B_{5.0}Mo_1$ (Mo1) has a typical peak-type α trace. The shape of the α trace of Mo3 can still be categorized as the peak-type, although the α value before the peak is slightly smaller than that after the peak. When the content of Mo increases to 5%, a step-type turn instead of a peak occurs in the α trace. The main characteristic of the step-type turn is that α below T_c is obviously smaller than that above T_c. The difference between the step-type and peak-type turns is also reflected in the thermal expansion traces. As shown in Fig. 1(a1), all alloys have two stages of thermal expansion, but only for Mo5 the extension line of the low temperature stage is under the high temperature stage; for other alloys, the extension line is above the high temperature stage.

(Fe,Co)BSiNb BMGs have very high strength but zero plasticity [22]. As shown in Fig. 1(b2), in spite of a small negative peak around T_c, the Co-free alloy has a clear step-type α trace, because α below T_c is obviously lower than that above T_c. The addition of Co increases T_c significantly and results in the peak-type α trace, in which the α value before the peak is obviously larger than that after the peak. The location of the extension line also indicates the obvious difference between the Invar effect of these two types of alloys.

$Fe_{80-x}Ni_xP_{13}C_7$ alloys without boron addition have a relative low strength, but a very good plasticity which improves with more addition of Ni [25,26]. The plastic strain of $Fe_{50}Ni_{30}P_{13}C_7$ is as high as 22% and the thin and long rod can even be bent. However, the magnetic properties, including T_c and the saturation magnetic induction, B_s, decrease with the increase of Ni addition, as listed in Table 1. This phenomenon is mostly attributed to the decrease of exchange interaction by 3d electrons, since the number of 3d electron numbers of Ni and Fe are 8 and 6, respectively [26,29,30]. Seen from Fig. 1 (c1) and (c2), all these alloys have the peak-type Invar effect and the negative peak becomes smaller with the increase of Ni. The low α value only occurs in a very narrow range near T_c, while in a wide temperature range below T_c the α value is still in the order of magnitude of 10^{-5}/ C, which means these alloys have a limited application potential as low expansion alloys.

FeMoPCB BMGs containing a small amount of boron have a plasticity of about 3%–5% [23,27]. As shown in Fig. 1(d1) and (d2), these BMGs have typical step-type Invar effect and the alloy with more Fe content has obviously lower α below T_c. The addition of Ni can improve the plasticity [23,31,32], but it also increases the average α below T_c.

4. Discussion

4.1. Universal invar effect of ferromagnetic Fe-based BMGs

The alloy systems investigated in this work are quite different but are all soft magnetic alloys. The thermal expansion tests show all alloys have the Invar effect. The previously reported amorphous ribbon alloys that have the Invar effect are also soft magnetic alloys [11–15]. However, the non-ferromagnetic (Fe,Co)CrMoCBRe BMGs [34,35], named as "amorphous steels" due to their large GFA and very high strength [36], do not have the Invar effect. Therefore, the Invar effect is a universal characteristics of ferromagnetic Fe-based amorphous alloys. On the other hand, most crystalline steels, except the FCC Fe-Ni alloy, do not have obvious Invar effect even if they are ferromagnetic.

The detailed mechanism of the Invar effect, is a longstanding question in the field of magnetism. In most models, from the early Weiss' 2γ-state model to the modern electronic-structure model, the Invar effect is explained as the anomalous large spontaneous volume magnetostriction produced by the competition and transition between two magnetic states [3–8]. The two magnetic states are the ferromagnetic high-volume state and the antiferromagnetic low-volume state, or the low-spin low-volume state and the high-spin high-volume state. In all models, the competition and transition between two magnetic states is closely related to the exchange coupling in the TM-TM nearest neighbor atomic pair. Here TM is the transition metal element. The degree of exchange coupling is expressed by the exchange integral A. The Bethe-Slater curve shown in Fig. 2 describes the schematic correlation between A and r_a/r_{3d}, where r_a and r_{3d} are the TM-TM nearest neighbors' distance and the radius of the 3d electron shell, respectively [37,38]. Several transition metals and the $Fe_{65}Ni_{35}$ Invar alloys are presented in the curve as scattered data points because these crystalline metals and alloys have a fixed r_a which can be simplified as their lattice constant a. The Bethe-Slater curve have two parts, as divided by the dotted line in Fig. 2. In the left part, A has a positive correlation with a.