Materials and Design 106 (2016) 69–73

Contents lists available at ScienceDirect

Materials and Design

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

Formation and structure-property correlation of new bulk Fe–B–Si–Hf metallic glasses

Yaoxiang Geng [a], Yingmin Wang [a,b,*], Zengrui Wang [b], Jianbing Qiang [a,b,*], Haibin Wang [a], Chuang Dong [a,b], Ojied Tegus [c]

[a] School of Materials Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China
[b] Key Laboratory of Materials Modification (Ministry of Education), Dalian University of Technology, Dalian 116024, China
[c] Inner Mongolia Key Laboratory for Physics and Chemistry of Functional Materials, Inner Mongolia Normal University, Hohhot 010022, China

ARTICLE INFO

Article history:
Received 17 March 2016
Received in revised form 11 May 2016
Accepted 26 May 2016
Available online 27 May 2016

Keywords:
Cluster-plus-glue-atom model
Fe–B–Si–Hf bulk glassy alloys
Soft magnetic properties
Mechanical properties
Structure-property correlation

ABSTRACT

The present work is devoted to designing new Fe–B–Si–Hf multi-component bulk glassy alloys with good soft magnetic and mechanical properties, and also explored the structure-property correlation in the microalloyed Fe–B–Si amorphous alloy with Hf. Based on the cluster-plus-glue-atom model, a series of Fe–B–Si–Hf alloys with cluster formulas $[Si–B_2Fe_{8-x}Hf_x]Fe$ (x = 0–0.6) are produced. Our experiments show that a large glass-forming ability along with a critical glass formation size of 2.5 mm is reached at $[Si–B_2Fe_{7.7}Hf_{0.3}]Fe$ (in at.%: $Fe_{72.5}B_{16.7}Si_{8.3}Hf_{2.5}$). This glassy alloy shows a high fracture strength ~4000 MPa with a plastic strain of 0.5%, a high saturation magnetization ~1.45 T and a low coercive force ~1.5 A/m. The monotonic variations of the thermal glass stability, microhardness and the magnetic ordering parameters with the concentration of micro-alloying element Hf, the accessibility of calorimetric glass transition and the glass-forming ability of the Fe–B–Si–Hf glassy alloys are explained in terms of the intra- and inter-atomic cluster correlations in the amorphous structures.

1. Introduction

Fe-based amorphous alloys are well known for their excellent soft magnetic properties including high saturation magnetization (B_s), very low coercive force (H_c), high magnetic permeability (μ) and low core loss [1–3]. The materials have found industrial applications in transformers cores and magnetic sensors [4]. Fe-based amorphous alloys in ribbon or wire form were made in early times due to their poor glass forming abilities (GFAs), which require cooling rates as high as 10^6 K/s to avoid crystallization. The maximum dimension sizes of these Fe-based amorphous alloys are limited to several tens of micrometers. During the past decade, much research efforts have been made on Fe-based amorphous alloys with high GFA to explore further industrial applications [5]. Driven by the technical demands on GFA, a variety of Fe-based bulk glassy alloys have been synthesized recently [6]. The known ferromagnetic Fe-based bulk glassy alloys can generally be classified into three categories [7,8]: LTM-SM-Metalloid (LTM: late transition metal, e.g., Fe, Co, Ni; SM: simple metal, e.g., Al, Ga), LTM-ETM-Metalloid (ETM: early transition metal, e.g., Zr, Nb, Mo, Hf, Ta, W) and LTM-RE-Metalloid (RE: rare earths). Among them, Fe–TM–B–Si glassy alloys exhibit good soft magnetic properties including high B_s (>1.5 T) and low H_c (<3.0 A/m), and high fracture strength (>4000 MPa) [9–11]. In quaternary Fe–TM–B–Si systems, bulk glassy alloys with critical size greater than 1.0 mm was previously reached only in the Fe–B–Si–Nb system. Magnetic powder cores named 'SENNTIX-I' are made from Fe–B–Si–Nb glassy alloys, which have been used in choke coils of AC-DC and DC-DC converters, noise suppression sheets, etc. [6]. New Fe–TM–B–Si bulk glassy alloys with high GFA are desirable for these applications.

The cluster-plus-glue-atom model has proven effective in understanding and designing alloy compositions with large GFA in many systems [12–15]. In this model, the average composition and local structure of an ideal amorphous alloy is described by a specific cluster formula, namely, $[cluster](glue\ atom)_{1\ or\ 3}$, where the cluster is the characteristic first-neighbor coordination polyhedron and the glue atom is located in between the clusters, 1 or 3 being designated as the number of glue atoms per cluster [16]. The cluster in the composition formula is usually termed as the principal cluster, which is derived from the devitrification phases of metallic glasses [17–19]. Considering the electronic structure stability, the total number of valence electrons

* Corresponding authors at: Key Laboratory of Materials Modification (Ministry of Education), Dalian University of Technology, Dalian 116024, China
E-mail addresses: apwangym@dlut.edu.cn (Y. Wang), qiang@dlut.edu.cn (J. Qiang).

http://dx.doi.org/10.1016/j.matdes.2016.05.102
0264-1275/

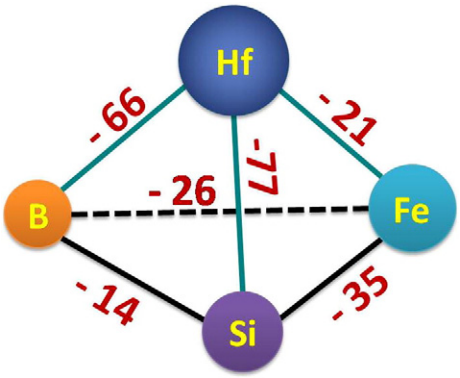

Fig. 1. The equal-atomic ratio enthalpy of mixing (kJ/mol) data of B, Si, and Fe with Hf.

per unit formula (e/u) is assumed to be close to 24 [20]. Using this model, new Fe–B–Si–Zr and Fe–B–Si–Ta bulk metallic glasses with good soft magnetic and mechanic properties were successfully designed in our previous studies [21,22]. In the present work, the model is used to design Fe–B–Si–Hf bulk glassy alloys, and the mechanism of micro-alloying effects of Hf on the structure-property correlation of Fe–B–Si amorphous alloy is explained in terms of the local structure model.

2. Composition design of Fe–B–Si–Hf metallic glasses

In binary Fe–B system, melt-spun amorphous alloys are readily obtained in the vicinity of the Fe-rich eutectic composition of $Fe_{83}B_{17}$ (in atom percent, at.%). Fe_2B phase is the eutectic-related intermetallic phase. There exist two non-equivalent atomic sites in the Fe_2B structure, which are occupied by Fe and B atoms, respectively. Based on the highest atomic density principle [23], the local structure of Fe_2B phase is characterized by a Fe-centered [Fe–B_4Fe_{11}] and a B-centered Archimedean octahedral antiprism [B–B_2Fe_8] atomic cluster, respectively. The [B–B_2Fe_8] cluster, which has a relatively large degree of isolation in the crystal structure, is determined to be the principal cluster [19]. Therewith, the cluster formula of ideal metallic glass in the Fe–B system becomes, [B–B_2Fe_8](glue atom)$_{1\ or\ 3}$, where the number and nature of glue atoms can be one Fe, three Fe, one B, three B, one B and two Feor one Fe and two B.

To reach the optimal composition for glass formation, the electron concentration factor should be taken into account. Our calculation result show that the cluster formula of [B–B_2Fe_8]Fe has an e/u value close to the ideal one of 24 [21]. So the composition with large GFA should appear in the vicinity of [B–B_2Fe_8]Fe = $Fe_{75}B_{25}$. Notice that the enthalpy of mixing between Si and Fe ($\Delta H_{Si-Fe} = -35$ kJ/mol) is more negative than that of Fe–B pair ($\Delta H_{B-Fe} = -26$ kJ/mol) [24] (Fig. 1), and since the immediate neighbors of the B center atom in the model structure [B–B_2Fe_8] are eight Fe atoms, replacement of the B center by Si is expected to result in enhanced local structure stability. The early transition metal Hf exhibits strongly negative enthalpies of mixing with Si and B, $\Delta H_{Si-Hf} = -77$ kJ/mol and $\Delta H_{B-Hf} = -66$ kJ/mol [24]. Enhanced local structural stability may be reached by partial substituting Hf for the shell Fe atoms in the [Si–B_2Fe_8] cluster. A series of quaternary compositions, [Si–$B_2Fe_{8-x}Hf_x$]Fe (x = 0.0–0.6), are finally generated for bulk glassy alloy formation in the Fe–B–Si–Hf system.

3. Experimental

The purities of raw elements are 99.999 wt.% for Fe and Si, 99.9 wt.% for Hf, and 99.5 wt.% for B, respectively. Alloy ingots with compositions of [Si–$B_2Fe_{8-x}Hf_x$]Fe (x = 0, 0.2, 0.3, 0.4, 0.5 and 0.6) were prepared by arc melting mixtures of the raw materials under a Ti-gettered argon

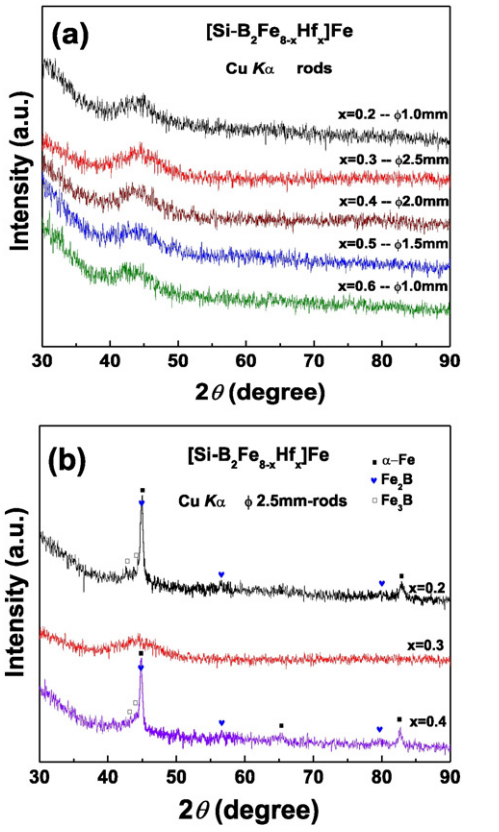

Fig. 2. XRD patterns of [Si–$B_2Fe_{8-x}Hf_x$]Fe (x = 0.2, 0.3, 0.4, 0.5 and 0.6) as-cast rods (a) with critical diameter sizes and (b) of 2.5 mm diameter.

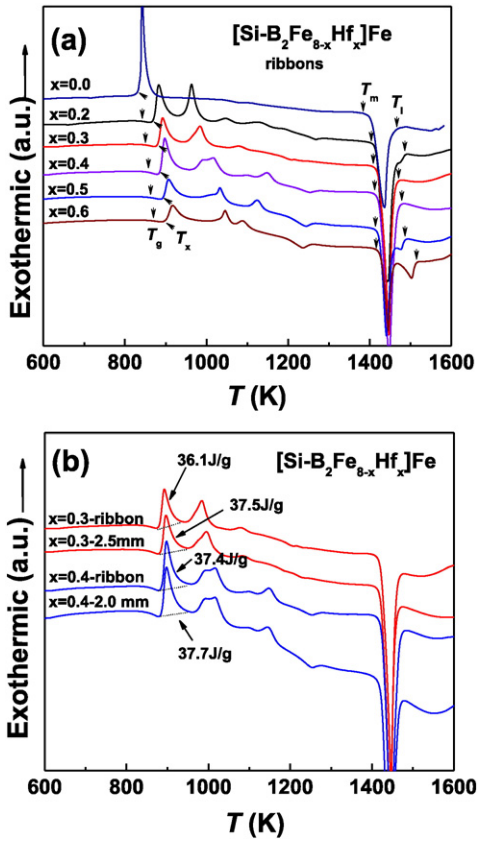

Fig. 3. DTA curves of (a) [Si–$B_2Fe_{8-x}Hf_x$]Fe (x = 0.0, 0.2, 0.3, 0.4, 0.5 and 0.6) ribbon samples and (b) [Si–$B_2Fe_{7.7}Hf_{0.3}$]Fe and [Si–$B_2Fe_{7.6}Hf_{0.4}$]Fe rods with critical glass formation diameters.