Mechanical behavior of Fe\textsubscript{65.5}Cr\textsubscript{4}Mo\textsubscript{4}Ga\textsubscript{4}P\textsubscript{12}C\textsubscript{5}B\textsubscript{5.5} bulk metallic glass

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Abstract

Fe\textsubscript{65.5}Cr\textsubscript{4}Mo\textsubscript{4}Ga\textsubscript{4}P\textsubscript{12}C\textsubscript{5}B\textsubscript{5.5} bulk amorphous rectangular bars with a cross-section of 2×2 mm\textsuperscript{2} and a length of 30 mm were produced by copper mold casting. The as-cast bars as well as annealed samples were investigated by compression and Vickers hardness tests. The fracture strength for the as-cast samples is 2.8 GPa and the fracture strain is 1.9%. Upon annealing at 715 K for 10 min, i.e. at a temperature below the calorimetric glass transition, the fracture strain drops to 1.6% and no plastic deformation is observed. The Vickers hardness HV for the as-cast samples is about 885, and increases to 902 upon annealing. The fracture behavior of this Fe-based bulk glassy alloy is significantly different in comparison with the well-studied Zr-, Cu- or Ti-based good glass-formers. The fracture is not propagating along a well-defined direction and the fractured surface looks irregular. Instead of veins, the glassy alloy develops a high number of microcracks.

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1. Introduction

Multicomponent alloys with high glass-forming ability and a wide supercooled liquid region between the glass transition temperature \(T_g\) and the crystallization temperature \(T_x\), give promise to expand the application field of iron-base amorphous alloys as soft magnetic materials [1]. Because of the absence of crystalline anisotropy, the Fe\textsubscript{65.5}Cr\textsubscript{4}Mo\textsubscript{4}Ga\textsubscript{4}P\textsubscript{12}C\textsubscript{5}B\textsubscript{5.5} amorphous alloy exhibits good soft magnetic properties, characterized by a low coercive force and a high permeability [2]. The presence of Cr and Mo in the composition not only improves the glass-forming ability, but also increases the corrosion resistance of the material in comparison with conventional steels used for magnetic applications [3,4]. Besides the good soft magnetic properties, such alloys also require good mechanical strength for possible use in magnetic devices as magnetic sensors, magnetic valves or magnetic clutches.

However, despite an increasing number of published papers about the mechanical properties of bulk metallic glasses (BMG), most of these reports deal only with non-ferrous Zr-, Ti- or Cu-based [5–7]. The mechanical properties of bulk Fe-based glasses started to be investigated only in the past few years [8–12]. One reason is the difficulty to cast such ferrous glasses in bulk form, because of their relatively low glass-forming ability. The maximum achievable diameter for soft magnetic Fe-based BMGs is limited to about 3–4 mm. This is in contrast to Zr- or Cu-based glassy alloys, which can easily reach even 10 mm diameter [7]. This is because the critical cooling rate necessary for amorphization in the case of soft magnetic Fe-based alloys is \(10^2–10^3\) K/s, whereas for Zr- or Cu-based metallic glasses, the required critical cooling rate is only \(10^0–10^2\) K/s [7], i.e. at least one order of magnitude lower than that for the Fe-based BMGs. Only very recently, Ponnambalam et al. [11] and, independently, Lu et al. [12] succeeded to cast Fe-based BMGs with a thickness larger than one centimeter (using some small addition of Y,
Bulk amorphous FeCrMoGaPCB: Preparation and magnetic properties

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Abstract

The Fe\textsubscript{65.5}Cr\textsubscript{4}Mo\textsubscript{4}Ga\textsubscript{4}P\textsubscript{12}C\textsubscript{5}B\textsubscript{5.5} bulk amorphous alloy exhibits good soft magnetic properties. Amorphous rods with diameters of 1.5–3 mm and discs with 10 mm diameter and 1 mm thickness were prepared by copper mold casting. The coercivity of as-cast rods and discs is around 5 A/m, decreasing up to less than 1 A/m upon annealing. Bulk amorphous samples with larger sizes or various shapes can be prepared by ball milling combined with subsequent consolidation of the resulting powders. Using this route, we prepared amorphous discs with 10 mm diameter and 3 mm thickness. The coercivity of as-milled powder decreases after hot compaction and subsequent annealing, reaching 25 A/m.

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Because of the absence of crystalline anisotropy, Fe-based amorphous alloys can achieve good soft magnetic properties\cite{[1]}. Nevertheless, residual anisotropies may be present, such as shape anisotropy or stress-induced anisotropies, caused by internal mechanical stress induced during the preparation procedure, which can be successfully reduced by annealing the samples at elevated temperatures\cite{[2]}. The present study is focused only on the composition Fe\textsubscript{65.5}Cr\textsubscript{4}Mo\textsubscript{4}Ga\textsubscript{4}P\textsubscript{12}C\textsubscript{5}B\textsubscript{5.5}, which has a high glass-forming ability and exhibits good soft magnetic properties\cite{[3,4]}. This alloy can be directly prepared in the amorphous state by copper mold casting in shapes suitable for use as magnetic parts in various devices. However, the critical cooling rate of about 100 K/s required for glass formation is higher than the value of about 1–10 K/s characteristic for non-magnetic alloys with very good glass-forming ability. Thus, the maximum achievable diameter of this Fe-based alloy is limited to only a few millimeters\cite{[5]}. On the other hand, bulk amorphous samples with larger sizes or various shapes can be prepared by powder metallurgical methods, i.e. ball milling of amorphous ribbons combined with subsequent consolidation of the resulting powders in the viscous state at temperatures in the supercooled liquid region\cite{[6]}. Using the copper mold casting method, we produced amorphous cylindrical rods with diameters up to 3 and 70 mm length, and discs with 10 mm in diameter and 1 mm in thickness. By the
New ternary Fe-based bulk metallic glass with high boron content

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To satisfy thermodynamic and kinetic requirements, Fe-based alloys capable of forming bulk metallic glasses often contain five or more elements. Usually, such compositions are of the type transition-metals/metalloids, with metalloid content around 20 atomic%. Starting from known Fe-based compositions used to make melt-spun glassy ribbons, purifying the master alloy by fluxing with B₂O₃ and using copper mould casting, a ternary Fe₆₆Nb₄B₃₀ bulk metallic glass was obtained. To our knowledge this is the first Fe-based fully amorphous bulk metallic glass with just three atomic constituents. The alloy is ferromagnetic with Curie temperature \( T_c = 646 \text{ K} \), glass transition temperature \( T_g = 845 \text{ K} \), crystallization temperature \( T_x = 876 \text{ K} \), liquidus temperature \( T_{\text{liq}} = 1451 \text{ K} \) and having a mechanical strength of 4 GPa.

1. Introduction

Since the first synthesis of a metallic glass in the Au–Si system by rapid solidification in 1960 [1], a large number of alloys have been prepared in the vitreous state over the last four decades. The Fe-, Co- and Ni-based metallic glasses found before 1990 required high cooling rates, above \( 10^5 \text{ K/s} \), for glass formation and the resulting sample thickness was limited to less than about 50 \( \mu \text{m} \). More recently, Inoue and co-workers [2, 3] succeeded in finding new multicomponent alloy systems that required much lower critical cooling rates for vitrification in the Mg-, Ln- (Ln = lanthanide metals), Zr-, Fe-, Pd-Cu-, Pd-Fe-, Ti- and Ni-based alloy systems. Typical alloy systems reported to date, which may form bulk metallic glasses (BMGs), are summarized in various papers [3]. It is apparent that initial bulk glassy alloys were non-ferrous, followed by the Fe- and Co-based alloy systems. Furthermore, Cu-based bulk glassy alloys defined by Cu contents above 50 at.% have been developed most recently [4, 5], though other bulk glassy alloys also contain Cu as the main additive [6, 7].

Fe-, Co- or Ni-based metallic glasses are good candidates for application as soft magnetic materials due to the lack of crystal anisotropy. Although conventional

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Strain distribution in Zr$_{64.13}$Cu$_{15.75}$Ni$_{10.12}$Al$_{10}$ bulk metallic glass investigated by in situ tensile tests under synchrotron radiation

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We report on the evolution of the atomic-scale strain tensor of ductile Zr$_{64.13}$Cu$_{15.75}$Ni$_{10.12}$Al$_{10}$ bulk metallic glass under tensile loading by using x-ray synchrotron radiation. The same kind of samples was previously investigated under compressive loading and revealed yielding at 1690 MPa together with large deformability of up to 160% strain. In tension the samples fracture at a lower stress, 1500 MPa, with no sign of yielding or plastic deformation. With no macroplasticity observed under tension, large differences in the elastic constants obtained from the strain tensor and from ultrasonic sound velocity measurements are revealed. This paper presents in detail the measuring procedure as well as the calculation of the tensile tensor and pair distribution functions of Zr$_{64.13}$Cu$_{15.75}$Ni$_{10.12}$Al$_{10}$ at different stages of deformation. The results are discussed in comparison with other reported data obtained from x-ray diffraction measurements using synchrotron radiation. © 2008 American Institute of Physics. [DOI: 10.1063/1.2952034]

I. INTRODUCTION

Bulk metallic glasses (BMGs) have many potential applications due to their unique properties as, for example, superior strength and high hardness, excellent corrosion resistance, and high wear resistance.\textsuperscript{1,2} The high strength of BMGs is often accompanied by more or less pronounced plastic deformation and their deformation and fracture mechanisms are quite different from crystalline materials.\textsuperscript{3–12} At temperatures below or around the glass transition and rather high strain rates metallic glasses deform by the formation of localized shear bands,\textsuperscript{3–5,8} whereas homogeneous flow of the supercooled liquid is observed at elevated temperatures and/or low strain rates.\textsuperscript{13,14} For the former case, it was previously considered that the compressive fracture usually proceeds along a shear plane inclined by 45° to the loading axis,\textsuperscript{15} i.e., the maximum shear stress plane. However, several recent systematic investigations on glasses in different alloy systems indicate that the shear fracture always deviates from the maximum shear stress plane either under compression or under tension.\textsuperscript{16–19}

High strength has been a long-standing objective pursued in metals and alloys. BMGs have strengths approaching the theoretical limit,\textsuperscript{20} but their plasticity at room temperature is typically very low. In uniaxial tension, the plastic strain is almost zero.\textsuperscript{21} For the majority of the known BMGs, the plastic strain at room temperature is very limited (<2%) even under compression, resulting from pronounced shear localization and work softening. The lack of plasticity makes BMGs prone to catastrophic failure in load-bearing conditions and restricts their application. This also hinders the precise study of some fundamental issues in glasses, such as the deformation mechanism and the dynamics of plastic deformation, in which large plasticity is needed for detailed analysis.\textsuperscript{21} Plastic deformation of metallic glasses at room temperature occurs through the formation and evolution of shear bands and is localized in thin shear bands.\textsuperscript{22} Therefore, brittleness is regarded as an intrinsic defect of metallic glasses. Efforts have been made to enhance the plasticity of BMGs, mostly focusing on the fabrication of BMG composites.\textsuperscript{23–27} Very recently, Liu et al.\textsuperscript{28} succeeded to prepare several Zr-based BMGs which show an exceptional deformability and a high strain as revealed by compression tests. The samples which were able to endure maximum deformation (yielding at 1690 MPa, maximum true strain of 160%) had a composition of Zr$_{64.13}$Cu$_{15.75}$Ni$_{10.12}$Al$_{10}$. In order to correlate the extraordinary plasticity of the glasses with their structure, transmission electron microscopy (TEM) investigations were performed to reveal their microstructural features. It was found that the BMGs are composed of isolated dark zones, ranging from 2 to 5 μm in size, surrounded by continuous bright zones of about 0.5–1 μm in width.\textsuperscript{28} The volume fraction of the bright zones was estimated to be ~10%. The selected-area electron diffraction patterns of both bright and dark zones showed only broad rings, confirming the glassy nature of both zones. The detailed structure of the bright and dark zones was also examined by means of high resolution TEM and a mazelike pattern without any crystalline fringes was observed. The structural studies confirmed the chemical and compositional homogeneities and the single glassy nature of the BMGs (i.e., no indications for phase separation were found). It was supposed\textsuperscript{28} that the very high deformability of these BMGs stems from this particular kind of structure, in which hard regions (the black zones) are surrounded by soft regions (the bright zones).

Several properties of amorphous materials including fa-
Mechanical Response of Metallic Glasses: Insights from In-situ High Energy X-ray Diffraction

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The term “metallic glass” usually refers to a metallic alloy rapidly quenched in order to “freeze” its structure from the liquid state. A metallic glass is a metastable alloy, which lacks the symmetry typical for crystalline materials and at room temperature shows an amorphous liquid-like structure. Bulk metallic glasses (BMGs) represent a class of amorphous alloys. The most notable property of BMGs is their ultra-high (near theoretical) strength and hardness. Because the known BMGs usually miss tensile plasticity and thus exhibit catastrophic failure upon tension it is important to understand deformation mechanisms involved and thus improve their performance. This article analyzes the use of synchrotron radiation for evaluating the elastic-plastic response of such materials.

INTRODUCTION

Due to the lack of crystalline structure, bulk metallic glasses (BMGs) may achieve interesting properties, including high strength and high hardness, excellent corrosion resistance, high wear resistance, very good soft magnetic properties, and, depending on composition, biocompatibility.1,2 The high strength of BMGs is sometimes accompanied by plastic deformation and their deformation and fracture mechanisms are quite different from crystalline materials.3–7 Bulk metallic glasses have strengths approaching the theoretical limit,8 but their plasticity at room temperature is typically very low. In uniaxial tension, the plastic strain is almost zero.9 For most of the known BMGs, plastic strain at room temperature is limited, less than 2%, even under compression, resulting from pronounced shear localization and work softening. The lack of plasticity makes BMGs prone to catastrophic failure in load-bearing conditions and restricts their application. This also hinders the precise study of some fundamental issues in glasses, such as the deformation mechanism and the dynamics of plastic deformation, in which large plasticity is needed for detailed analysis.9 Plastic deformation of metallic glasses at room temperature occurs through the formation and evolution of shear bands and is localized in thin shear bands.10 Therefore, brittleness is regarded as an intrinsic defect of metallic glasses.

Many methods have been developed and employed to rule out the deformation mechanisms characteristic to BMGs.11 Recently, characterization of amorphous materials by diffraction methods for the purpose of strain scanning was established.12 Several glasses were investigated since then, using different synchrotron sources: HASYLAB at Deutsches Elektronen-Synchrotron (DESY) Hamburg, Germany; European Synchrotron Radiation Facilities (ESRF) Grenoble, France; or Advanced Photon Source (APS) at Argonne National Laboratory, USA. Monochromatic hard x-rays with energies at 80–100 keV were used for these experiments.

Ex-situ compression tests are usually performed to study the mechanical behavior of BMGs. This method is relatively simple and suitable for small samples. Tensile tests have technical limitations. First, for such tests a dog-bone shaped plate or rod sample is necessary, with a length of a few centimeters. This requires a BMG sample with quite large geometrical dimensions, which cannot be achieved by a poor glass former. The sample should be homogeneous, but in practice some small voids (as pores or oxides inclusions) may be present upon casting. Another limitation comes from the device used for tests—it is quite difficult to create a proper clamping system. Due to the difference in hardness between BMGs and the hardened steel used for tools, the BMG sample tends to slide from the grips.

See the sidebar for experimental details.

DATA TREATMENT AND THEORETICAL BACKGROUND

The elastic scattering intensity \( I(Q) \) is measured as a function of the scattering vector (or wave vector) \( Q \), which is defined as \( 4\pi \sin \theta / \lambda \), where \( \theta \) is half of
Crystallization kinetics and magnetic properties of Fe\(_{66}\)Nb\(_4\)B\(_{30}\) bulk metallic glass

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Abstract

Fe-based bulk metallic glasses (BMGs) have a high application potential because of their unique soft magnetic properties, mechanical behaviour and high corrosion resistance. Also, they can be obtained directly in the final shape suitable for use as magnetic sensors, magnetic valves, magnetic clutches etc. in different devices. Fe-based alloys able to form magnetic BMGs are of the type transition metal–metalloid and often contain 5 or more elements. Usually, the metalloid content is around 20 at.%. Recently, a new Fe-based BMG containing only 3 elements and a very high boron content was synthesized. The preparation of this BMG was done by employing the copper mold casting method and using the fluxing technique. This new BMG is ferromagnetic, with a Curie temperature around 550 K and a saturation magnetization of 105 Am\(^2\)/kg. Differential scanning calorimetry (DSC) investigations revealed a reduced glass transition temperature of 0.55 and an extension of the supercooled liquid region of about 31 K, values which indicate a relatively good thermal stability. Despite of numerous studies about Fe-based BMGs, there is still a lack of data about the crystallization kinetics. Also, the intermediate metastable phases, which form upon crystallization from the amorphous state, as well as the mechanism of their formation, are not fully understood. The present work discusses the kinetics of the phase formation using the Kissinger analysis and Johnson–Mehl–Avrami plots, correlated with the results obtained upon X-ray diffraction (XRD) of samples with different metastable structures. Additionally, the magnetic behaviour of different phase(s) is presented.

1. Introduction

Generally, Fe-based glassy alloys are well known for their good soft magnetic properties depending on compositions, constituents and subsequent heat treatment of alloy. The soft magnetic properties arise because of absence of any crystalline anisotropy. Since the preparation of amorphous alloys in Fe-metalloid systems which exhibit good soft-magnetic properties in 1974 [1,2], a large number of studies on the development of soft-magnetic amorphous alloys have been carried out for the subsequent decades. However, the shape and dimension of Fe-based amorphous magnetic alloys had been limited to thin ribbon form with thicknesses below 30 \(\mu\)m because of the necessity of a high cooling rate of almost 10\(^8\) K/s for the formation of an amorphous phase [3].

In 1995, a distinct glass transition before crystallization was found in the Fe\(_{72}\)Al\(_5\)Ga\(_2\)P\(_{11}\)C\(_6\)B\(_4\) rapidly solidified alloy [4], and an Fe\(_{72}\)Al\(_5\)Ga\(_2\)P\(_{11}\)C\(_6\)B\(_4\) ferromagnetic BMG was synthesized through the stabilization of supercooled liquid [5]. Subsequently, a variety of Fe-based ferromagnetic BMGs have been developed because of their potential magnetic applications [6,7]. Now, the development of Fe-based BMGs with high glass forming ability (GFA) has become a very hot research topic not only because of the soft-magnetic properties [8,9] but also of the high fracture strength [10,11] and corrosion resistance [12,13]. Fe-based alloys able to form magnetic BMGs are of the type transition metal–metalloid and often contain 5 or more elements. Usually, the metalloid content is around 20 at.%. In some cases, the magnetic properties of such BMGs can be enhanced by partial devitrification upon heating at a constant rate or by isothermal annealing. The change in magnetic properties is due to structural changes induced upon heating/annealing. Usually, Fe-based BMGs form intermetallic metastable phases at elevated temperatures, which finally transform into crystalline stable phases if the heating goes further. Very recently [14], we reported that the
Thermal stability and magnetic properties of FeCoBSiNb bulk metallic glasses

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\textbf{Abstract}

For the present study, \([\text{Fe}_{0.5}\text{Co}_{0.5}\text{Si}_{0.05}\text{B}_{0.25}\text{Nb}_{0.05}]\) bulk metallic glasses (BMGs) were cast as cylinders with 2 mm diameter and 50 mm length. The first crystallized product, the metastable \(\text{Fe}_{23}\text{B}_{6}\)-type like phase, forms as a result of primary crystallization. The thermal stability and the crystallization kinetics were studied using the isochronal and isothermal DSC curves, measured at different heating rate and temperatures. Despite their good glass-forming ability (GFA) and high stability against crystallizations, their incubation time prior crystallization is almost zero. In order to rule-out the complete crystallization mechanism, in situ time resolved studies using the synchrotron radiation were done. The magnetic properties of the BMGs are strongly related to their structure and will be presented as well.

\section{1. Introduction}

Since Fe–C–P amorphous alloys were produced in 1965 \cite{1}, ferromagnetic metallic glasses and the corresponding nano-crystalline alloys such as FINEMET and NANOPEARL \cite{2–4}, produced through crystallization from the corresponding amorphous precursors, were intensively investigated because of their excellent soft magnetic properties including relatively high saturation magnetization (\(M_s\)) and permeability (\(\mu\)) as well as low coercive force (\(H_c\)) and core loss (\(W\)) \cite{5}. Up to now, ferromagnetic amorphous alloys have shown great industrial value for commercial application. Many products consisting of these kinds of metallic glasses have been widely used, for example anti-theft labels and high efficient magnetic transformers in electronic industry. Multi-component ferromagnetic alloys, such as Fe–\((\text{AlGa})–(\text{P,C,B,Si})\), Fe–\((\text{Zr,Hf,Nb,Ta})–\)B and Fe–\((\text{Cr,Mo})–(\text{C,B,P})\) systems \cite{6–13}, allow to decrease the critical cooling rate of glass formation, and enable the formation of bulk metallic glasses (BMGs), which not only ensure the fabrication stability during glass formation, subsequent heat treatment processes and shaping operations, but also give ferromagnetic metallic glasses potential applications as advanced structural materials because of their high fracture strength (\(\sigma_f\)) and high corrosion resistance \cite{14}.

Recently, (Fe–Co)–B–Si–Nb BMGs were produced which exhibit high glass-forming ability (GFA) as well as good mechanical and magnetic properties (\(\sigma_f\): \(\sim\)4000 MPa; \(M_s\): \(\sim\)1 T; \(\mu\): \(\sim\)12,000; \(H_c\): \(\sim\)2 A/m) \cite{15,16}. These alloys are regarded as one of the most attractive candidates for application combining the advantages of functional and structural materials. Thus, enormous efforts have been undertaken for this alloy system, especially for the \([\text{Fe}_{0.5}\text{Co}_{0.5}\text{Si}_{0.05}\text{B}_{0.25}\text{Nb}_{0.05}]\) glassy alloy, in order to elucidate GFA, thermal stability, mechanical and soft magnetic properties, as well as the effect of minor Cu addition on the physical properties \cite{17–21}. Studies of crystallization and its effect on the magnetic properties in this system are essential for possible commercial application, similar like in case of FINEMET. However, few works have been devoted to this topic so far \cite{20–22}. It is believed that some small additions of Cu may promote the nanocrystallization \cite{23} due to its positive heat of mixing with Fe, Co and Nb \cite{24}. Subsequently, the magnetic properties, as well as the mechanical properties, may become better. However, before changing the composition, it is necessary to study in very detail the behavior of the starting composition, especially the thermal stability and the crystallization way, in order to choose the best procedure to follow. In this paper, \([\text{Fe}_{0.5}\text{Co}_{0.5}\text{Si}_{0.05}\text{B}_{0.25}\text{Nb}_{0.05}]\) glassy alloys were chosen for investigation. The GFA and the thermal stability of these alloys were evaluated. The phase evolution, the kinetics parameter and the magnetic properties, including \(M_s\), \(H_c\) and \(T_c\) were investigated. These results can give more details to understand the relationship between the decomposition of the metastable glassy phase and the magnetic properties and they will be discussed in comparison with other published data.
Thermal stability and magnetic properties of partially Co-substituted (Fe$_{71.2}$B$_{24}$Y$_{4.8}$)$_{96}$Nb$_4$ bulk metallic glasses

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The influence of partial replacement of Fe with Co in the quaternary (Fe$_{71.2}$B$_{24}$Y$_{4.8}$)$_{96}$Nb$_4$ bulk metallic glasses on their structure, thermal stability and magnetic properties was studied. It was found that Co increases the thermal stability, as well as the Curie temperature, which monotonously increases as the Co content increases. The saturation magnetization shows a maximum of 1.01 $\mu_B$ per magnetic atom for $x = 0.1$, followed by a perfectly linear decrease for higher Co contents. The extension of the supercooled liquid region may reach even 98 K and the glass transition temperatures approach the theoretical value of 2/3 of the melting temperature. The mean field theory allows to calculate the magnetic exchange stiffness constant and to correlate its variation with the variation of the magnetic saturation.


I. INTRODUCTION

Metallic glasses have a unique combination of properties that makes them superior to their crystalline counterparts, such as high strength, high corrosion resistance and good soft magnetic properties. Fe- and Co-based amorphous alloys have been the subject of considerable research interest and activities for the last two decades due to applications related to their outstanding soft magnetic properties. During the past years, new bulk metallic glasses (BMGs) such as Ln-, Mg-, Zr-, Ti-, Fe-, or Co-based glasses, have been developed (overviews are given in Refs. 8, 9). Most of these BMGs have a rather wide supercooled liquid region between the glass transition and the onset of crystallization, and a high resistance against crystallization, which enables the production of bulk glassy samples at low cooling rates. Based on their attractive properties, such as good soft magnetism as well as mechanical behavior (high yield strength, high hardness, good wear resistance) or excellent corrosion resistance, many bulk metallic glasses have potential technological applications in various areas: machinery structural materials, die materials, tool materials, hydrogen storage materials, sporting goods materials, zero magnetostrictive materials, ornamental materials, etc. Fe-based BMGs typically exhibit a wide supercooled liquid region of almost 40 K, and good soft magnetic properties, such as 1.2 T for saturation magnetization and less than 2 A/m coercivity. In most of cases, Fe-based BMGs with very good glass-forming ability (GFA) contain many elements, for example (Fe$_{44.3}$Cr$_{13.8}$Co$_{5}$Mo$_{12.8}$Mn$_{11.2}$C$_{15.8}$B$_{5.9}$)$_{98.5}$Y$_{1.5}$ or (Fe$_{44.3}$Cr$_{10}$ Mo$_{13.8}$Mn$_{11.2}$C$_{15.8}$B$_{5.9}$)$_{98.5}$Y$_{1.5}$ (Ref. 13). A few years ago, a new Fe-based BMG alloy system with high GFA but consisting of a small number of constituting elements was developed by Kim et al. As a starting alloy composition, they selected Fe$_{71.2}$B$_{24}$Y$_{4.8}$ since high GFA (a maximum diameter for glass formation of 1 mm) has been reported by Zhang et al. Further, Nb was chosen as a candidate for the fourth alloying element based on the empirical rules for achieving high GFA. The Goldschmidt atomic radius of Nb is 0.146 nm, which is significantly larger than those of Fe and B (0.126 and 0.098 nm, respectively), and smaller than that of Y (0.178 nm). Nb exhibits a significant atomic size mismatch (>12%) with the main three constituent elements. The mixing enthalpy between the main constituents reaches large negative values (i.e., for Fe–Nb and B–Nb pairs −16 and −39 kJ/mol, respectively). Furthermore, Nb has been reported to stabilize the liquid against primary crystallization of α-Fe (Refs. 18–20) and within this class of BMGs, (Fe$_{71.2}$B$_{24}$Y$_{4.8}$)$_{96}$Nb$_4$ shows the best GFA, while still keeping very good soft magnetic properties.

In several cases it was observed that partial substitution of Fe with other magnetic elements (as Co or Co/Ni) may enhance the GFA. At the same time, the soft magnetic properties are changed, basically due to the fact that such compositional variation may change the magnetostriction of the amorphous samples. In the present work, the structural, thermal and magnetic property changes induced by partial substitution of Fe with Co in [(Fe$_{1−x}$Co$_{x}$)$_{71.2}$B$_{24}$Y$_{4.8}$]$_{96}$Nb$_4$ alloys ($x = 0, 0.1, 0.3,$ and 0.5) are studied. It was found that upon substitution, the thermal stability becomes better, with glass transition temperatures exceeding 835 K and with a maximum extension of the supercooled liquid region (SCL) of almost 100 K for $x = 0.3$. This is unusual for Fe-based
FeCoSiBNbCu bulk metallic glass with large compressive deformability studied by time-resolved synchrotron X-ray diffraction

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By adding 0.5 at. % Cu to the strong but brittle [(Fe0.5Co0.5)0.75Si0.05B0.20]96Nb4 bulk metallic glass, fully amorphous rods with diameters up to 2 mm were obtained. The monolithic samples with a 1 mm diameter revealed a fracture strain of 3.80% and a maximum stress of 4143 MPa upon compression, together with a slight work-hardening behavior. SEM micrographs of fractured samples did neither reveal any shear bands on the lateral surface nor the typical vein patterns which characterize ductile fracture. However, some layers appear to have flowed and this phenomenon took place before the brittle final fracture. An estimate of the temperature rise ΔT in the shear plane gives 1039 K, which is large enough to melt a layer of 120 nm. The overall performance and the macroscopic plastic strain depend on the interaction between cleavage-like and viscous flow-like features. Mechanical tests performed in-situ under synchrotron radiation allowed the calculation of the strain tensor components, using the reciprocal-space data and analyzing the shift of the first (the main) and the second broad peak positions in the X-ray diffraction patterns. The results revealed that each atomic shell may have a different stiffness, which may explain the macroscopic compressive plastic deformation. Also, there were no signs of (nano) crystallization induced by the applied stress, but the samples preserve a monolithic amorphous structure until catastrophic failure occurs. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4864671]

I. INTRODUCTION

Ferromagnetic Fe- and (Fe,Co)-based amorphous alloys are regarded as attractive industrial alloys due to relative low price and simple routes for fabrication.1 Within several new bulk metallic glasses (BMGs) developed in the last decade, (Fe-Co)-Si-B-Nb glassy alloys play an important role because they combine a high glass-forming ability (GFA) with good soft-magnetic properties and very high compressive strength.2,3 It was shown that the composition with the best combination of properties in this alloy family is [(Fe0.5Co0.5)0.75Si0.05B0.20]96Nb4, which may be cast as amorphous rods with diameters up to 7 mm,2 can reach a compressive strength of 4000 MPa,3 and shows a direct current (DC) saturation polarization of 1.13 T.2 A major drawback, which hinders the application potential, is the absence of any plastic deformation.3 Generally, the routes used to enhance deformability of glassy alloys point towards the creation of a composite structure4–6 or designed heterogeneities, for example, through mechanical indentation or severe plastic deformation.7–9 These methods must be applied eventually with caution to Fe- and (Fe,Co)-based alloys, because the soft magnetic properties can deteriorate in the presence of non-magnetic crystalline phase(s) or due to the stress induced by mechanical treatment. A solution for magnetic BMGs can be fine-tuning the composition by adding element(s) with large Poisson ratio such as, for example, Ni10 or minor additions of Cu.11 In the first case, one deals with a self-toughening mechanism through the control of the atomic bonding. In the second case, the aim is to produce a composite microstructure with small or length-scale modulated heterogeneities in the glassy matrix, because Cu has a large positive enthalpy of mixing with Fe12 and has a miscibility gap with Fe in the solid state.13 For example, Makino et al.11 reported the presence of Fe nanoclusters with less than 10 nm diameter embedded in the amorphous matrix when 0.1 at. % Cu were added to a FeSiBP BMG. It was supposed that these clusters act as nucleation sites for α-Fe crystals during compression testing, which may further interact and hinder shear band propagation, thus enhancing the overall compressive deformability. In the (Fe-Co)-Si-B-Nb bulk amorphous alloy system, several researchers tried to elucidate the influence of minor addition of Cu on GFA, mechanical and magnetic properties of the resulting alloys.14–18 Altogether the results suggest that a deformable glassy alloy of this compositional class should contain less than 1 at. % Cu addition. Furthermore, the mechanism responsible for the enhancement of the plastic deformation is neither fully investigated nor understood.

Over the last years a universal diffraction method employing synchrotron radiation for characterizing bulk stress and strain fields in amorphous materials19 has been established. This method was successfully applied to reveal the effect of hydrostatic stress state on the atomic-scale structural changes in glasses at high pressure,20 the change of free volume during annealing,21 the strain in the crystalline phase in glass-matrix composites,22,23 as well as for calculating the strain tensor in monolithic BMG below the
Title: FE-BASED SOFT MAGNETIC GLASSY ALLOY MATERIAL

Abstract: The invention is related to an Fe based alloy material, suitable for producing a soft magnetic glassy alloy product, a product produced thereof and a method for producing such a product. The product can be a master alloy product obtained after a first melting step starting from suitably selected starting materials, or it can be a final soft magnetic glassy alloy product obtained after a further step of melting the master alloy. The alloy material of the invention comprises: C between 1.4wt% and 2.2wt%; Si between 0.9wt% and 1.35wt%; B between 0.43wt% and 0.65wt%; P between 5wt% and 7.5wt%; Mo between 0.9wt% and 9.2wt%; Mn between 0.05wt% and 0.6wt%; O up to 0.3wt%; Al up to 0.1wt%; S up to 0.05wt%; Ti up to 0.45wt%; Cr up to 0.3wt%; Cu up to 0.25wt% or Cu between 0.25wt% and 0.8wt%, the balance being Fe and incidental impurities. A Fe-based soft magnetic glassy product according to the invention can be produced starting from non-pure starting materials.
Field of the Invention

[0001] The present invention is related to Fe-based amorphous alloy materials, in particular to alloy compositions suitable for producing soft magnetic glassy alloy materials and to products made thereof.

State of the art.

[0002] Fe-based amorphous/glassy alloys comprising C, Si, B, P and Mo are known in the art. For example CN1936059 and CN101148743A describe such alloys. In WO2010/135415, an alloy is described which may further comprise Al. In most of these publications, production processes are described wherein the alloy is produced from pure starting materials, melted into a master alloy which is subsequently further melted and solidified to form a final product. Melting of the starting products and of the master alloy usually takes place under vacuum.

[0003] It is not economically advantageous to start from pure materials, nor is it always technically possible. For example, pure Phosphor is often problematic due to its high reactivity. Non-pure starting materials on the other hand have the disadvantage of containing an undefined number of impurities whose influence on the glass forming ability of the alloy is unknown so that the quality of the final product in terms of glass forming ability may vary between broad limits.

[0004] Also, melting under air is economically advantageous compared to vacuum melting, but again, the