Nanocrystallization in a Cu-doped Fe-based metallic glass

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Abstract

Evolution of microstructure and magnetic properties during annealing of a Cu-doped $\text{Fe}_{75.3}\text{C}_{7.0}\text{Si}_{3.3}\text{B}_{5.0}\text{P}_{8.7}\text{Cu}_{0.7}$ metallic glass were investigated via atom probe tomography. Cu segregation, which contains a rapid nucleation stage and a sluggish growth stage, was found to precede and may trigger the segregation of other elements and promote the following nanocrystallization. The nano-sized α -Fe precipitates have a composition close to that of the grain-orientated high-silicon steel, giving rise to the enhancement in the magnetization.

Keywords: amorphous materials; clusters; nanostructures; magnetic measurements

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1. Introduction

In recent years, Fe-based metallic glasses (MGs) have been widely utilized as high efficiency transformer materials due to their high permeability, low coercive force, and low core losses [1-6]. To further improve energy efficiency, two critical challenges regarding these glassy alloys, however, must be addressed urgently, i.e., the low glass-forming ability (GFA) which results in low packing density (due to the adhesive needed to laminate the thin ribbons together) and increases Joule heat losses, and the relatively low magnetization (M_s) as compared to that of grain-orientated high-silicon steels [7,8]. Recently, it was reported that with minor additions of the Cu element which has positive heat of mixing with Fe, both the GFA and soft magnetic and mechanical properties of Fe-based BMGs were dramatically enhanced [9-12]. Furthermore, an appropriate annealing below the glass transition temperature (T_g) was verified to further improve the M_s value of these Cu-doped Fe-based BMGs, whereas over-aging was found to deteriorate the soft magnetic properties [13-15]. As pointed out by Hono et al. [14, 15], Cu atomic clusters were present in the amorphous state after annealing below the crystallization temperature and gave rise to formation of a high density of tiny α -Fe particles, which might be responsible for the M_s enhancement [13-15]. Even though effects of Cu additions on heterogeneous nanocrystallization and dependence of magnetic properties on annealing conditions have been investigated in several Fe-based metallic glasses, limited studies regarding the entire dynamic crystallization process were conducted [16, 17], especially in those which have a complex atomic structure and nanocrystallization process [18]. Clearly, detailed evidences on evolution of local chemistry around the primary phases during de-vitrification are still missing[19]. As a result, the kinetics and elemental

partitioning related to the transformation of the first Cu atomic clusters from an initial amorphous state into precipitates with an observable crystalline structure are far from being well understood [16]. This situation is due to the fact that the Cu clusters formed at the very early stages of clustering are very small in size with relatively a low volume fraction [17]. Visualizing them in three-dimensions is challenging [20], which results in difficulties in optimizing annealing treatment and processing conditions.

Atom probe tomography (APT) is capable of providing spatial coordinates and elemental identities of the atoms so that their distribution within small volumes of the specimen can be reconstructed in three-dimensions [21,22]. In recent years, APT has been widely used in the field of MGs to examine local atomic packing structure and elemental distribution [14-15]. In this study, the APT technique to investigate elemental redistribution during nanocrystallization process of a Fe-based BMG doped with Cu, and attempted to reveal possible mechanisms responsible for the enhancement in the soft magnetic properties. These results will shed new insights into understanding alloying effects on the soft magnetic properties in general, and particularly those alloyed with the elements having positive heat of mixing with the main constituent.

2. Experimental

Alloy ingots with a nominal composition of $\text{Fe}_{75.3}\text{C}_{7.0}\text{Si}_{3.3}\text{B}_{5.0}\text{P}_{8.7}\text{Cu}_{0.7}$ (at. %) [13], hereafter designated as Cu0.7, were prepared by arc-melting a mixture of pure elements (99.9 %) and the Fe-P alloys (P: 26.28, Si:0.01, C:0.02, Mn:0.69, Ti:0.35, Ca:0.01, S: 0.01 wt%) under an argon atmosphere. Ribbon samples with a width of 1–2 mm and a

thickness of 30–50 μm were prepared by the melt-spinning technique. Glass transition temperature T_g and onset crystallization temperature T_x are 760 and 774 K, respectively [13]. The as-spun ribbons were annealed at temperatures lower than T_g , i.e., 729 and 749 K for different times under vacuum. Structures of the as-spun and annealed ribbons were characterized by x-ray diffraction (XRD) with Cu-K α radiation. Saturation magnetization (M_s) and coercive force (H_c) were measured with a vibrating sample magnetometer (VSM) under an applied field of 800 kA/m. Needle-shaped specimens for APT characterization were fabricated by a lift-out method in a FEI Nova™ 200 Nanolab™ focused ion beam (FIB) instrument [14,15]. The APT analyses were performed in a Cameca Instruments LEAP 4000X HR in either voltage or laser ($\lambda=400$ nm, 100 kHz pulse repetition rate) modes. The data were binned and the concentration isosurfaces were generated according to a standard method detailed in reference 16. A voxel size of $1 \times 1 \times 1$ nm³ and a delocalization parameter $D=2$ nm were used to depict the elemental concentration isosurfaces. To eliminate possible effects from Ga damage during the sample preparation, only data of the inner part of the needle were chosen for analysis.

3. Results and discussion

X-ray diffraction (XRD) patterns of the as-spun and annealed Cu_{0.7} samples at 729 K and 749K are shown in Fig. 1a. Both the as-spun and the specimen annealed at 729 K for 15 min show only a hump with no crystalline peaks, suggesting an amorphous structure without obvious crystalline phase. Nevertheless, the sample annealed for 30 min shows sharp peaks superposed on the hump, and these crystalline peaks were indexed as α -Fe, suggesting that this sample was partially crystallized. Magnetization curves of the

as-spun and annealed samples are shown in Fig. 1b. The M_s value of the as-cast sample is 1.61 T. The M_s value increased to 1.68 and 1.79 T for specimens annealed at 729 K for 15 and 30 min, respectively. With the further increase of the annealing temperature to 749 K for 30 min, the M_s value decreased to 1.55 T. The as-cast sample has a coercivity of 6.7 A/m and slightly decreases when annealed at 729 K for 15 min, whilst increases when the annealing time or/and temperature is increased (Fig. 1c). It can be seen that a proper annealing treatment appreciably enhanced M_s , whereas excessive annealing deteriorated both M_s and H_c of this Cu_{0.7} glassy alloy. Therefore, it is necessary to investigate the structure evolution during annealing so that the underlying mechanism can be well understood.

Representative 3D reconstructions of the atomic positions of Fe, B, C, P, Si in the sample containing approximately 45 million atoms annealed at 729 K for 15 min. is shown in Fig. 2a, and clearly shows a homogeneous distribution of these five elemental constituents throughout the sample. For the Cu atoms, however, the atom map in Fig. 2a and the corresponding 5% iso-concentration surfaces, shown in Fig. 2b, indicated phase separation of Cu. Note that this 5% threshold is much higher than the nominal composition of 0.7% Cu and cannot be due to random local fluctuations of the Cu atoms. Therefore, numerous Cu-enriched nano-precipitates have been formed in this stage. Based on the compositional line scanning across the amorphous matrix and the Cu-enriched nano-precipitates, shown in Fig. 2c, the nano-precipitates are enriched with up to 15% Cu and consequentially contain lower amounts of the other elements. It has been reported that the well-grown Cu particles in Fe-based BMGs usually have a high Cu content near 100% due to the positive heat of mixing between Cu and Fe [23, 24]. It can

thus be reasonably induced that diffusion and agglomeration of Cu atoms might be gradually taking place, but did not yet reach the fully-segregated equilibrium state at this early annealing stage of 15 min.

As the annealing time was extended to 30 min, elemental segregation occurred not only for Cu, but also for all the other elements. Representative spatial distribution of Fe, C and Cu atoms are shown in Fig. 3a-3c, respectively. The spatial distribution of Fe, C or Cu is not uniform even at the atomic scale, and numerous nano-sized particles with elemental segregation can be observed, which is consistent with the TEM observation [13]. The nano-sized α -Fe phase was found to be isolated by the amorphous matrix or/and small-sized iron-based compounds. With the increase of the nano-sized α -Fe, saturation magnetization was enhanced [25-27]. Segregation process of Cu can be further studied from the evolution of the size and density of the Cu nano-precipitates during annealing. The size and number density of the Cu precipitates are listed in Table 1. During the early annealing stage (0-15min), the number density of the Cu precipitates burst into $1.6 \times 10^{24} \text{ m}^{-3}$ with an average Guinier radius of $0.8 \pm 0.2 \text{ nm}$. During the extended annealing stage, i.e., 30 min, the number density of Cu precipitates decreased to $1.1 \times 10^{24} \text{ m}^{-3}$, while the size of the Cu particles increased to $1.3 \pm 0.3 \text{ nm}$, indicating occurrence of coarsening of the Cu precipitates by dissolution of some small Cu particles. Although Cu precipitation is the first to occur among the precipitation of all the constituent elements, the Cu precipitates have a slower growing rate during annealing compared with those of other precipitates.

When the sample was annealed at 749 K for 30 min, significant devitrification and strong elemental fluctuation at tens of nanometers were observed (Fig. 4a). In

addition to the amorphous matrix, an α -Fe phase tens of nanometers in extent, ultrafine spheroidal Cu-rich precipitates, and silicon-depleted $\text{Fe}_3(\text{P,B,C})$ and Fe_3C phases were also observed under this annealing condition. The Cu precipitates are at the scale of several to tens of nanometer, which is slightly larger than that in the sample annealed at 729 K for 30 min. Elemental concentration distribution across the interface between the Cu precipitates and the surrounding phases is shown in Fig. 4b. The Cu content is gradually increases from the interface and reaches near 100% in the center of Cu precipitates. The high copper level estimated from the compositional line scanning in the spheroidal Cu precipitates suggests that they are ϵ -Cu with fcc structure, rather than bcc-Cu. The Cu concentration inside the Cu precipitates in this annealed sample (i.e., 30 min. at 749 K) was much higher than that in the sample annealed at 729 K, implying that distinct elemental diffusion took place during the longer annealing process. Nevertheless, it is to be noted that even after annealing at a higher temperature for a longer time, the Cu precipitates were still at the length scale of less than 5 nm. Therefore, evolution of Cu precipitates during annealing can be rationalized as a fast nucleation stage, followed by the slow growth and coarsening stages mediated by elemental redistribution at the nanometer scale. Clearly, phase separation consumes copper atoms in a very small volume around the Cu precipitate, whereas the growth of these precipitates requires the long-range diffusion of Cu in the surrounding media. Note that the elemental diffusion should first be in the metallic glassy matrix, but soon becomes transporting in crystallized phases.

In addition to the observed segregation of Cu, distinct redistribution of the other constituent elements was also found during the long annealing. Elemental concentration

distribution profile across the interface between α -Fe and the surrounding crystals is shown in Fig. 4c. The isolated α -Fe phase is significantly enriched in silicon and has a composition close to that of the grain-oriented silicon steel (i.e., $\text{Fe}_{14}\text{Si}_2$). No other solutes were present in a significant amount in the α -Fe phase. Owing to its composition character and isolated nature, the nano-sized α -Fe phase was believed to contribute to the enhanced M_s value of the annealed samples. The Cu precipitates were also observed on the surface of the α -Fe phase, implying that the precipitation of Cu during the early annealing stage may trigger the segregation of the other elements.

In addition, redistribution of the metalloid elements was also found to be highly inhomogeneous. As shown in Fig. 4a, the 3D elemental distribution map of the metalloids shows distinct segregation characteristics. Nano-sized Fe_3C and $\text{Fe}_3(\text{P},\text{B},\text{C})$ can be clearly seen. Elemental concentration distribution profile across the interface between the Fe_3C and $\text{Fe}_3(\text{P},\text{B},\text{C})$ phases is shown in Fig. 4d. The irregularly-shaped C-enriched phase, Fe_3C , is also enriched in P and Si and contains some B. The irregularly-shaped P-enriched phase, $\text{Fe}_3(\text{P},\text{B},\text{C})$, is highly enriched in B but contains only a small amount of C. Formation and growth of these iron-based compounds consumed part of α -Fe, which eventually deteriorates the soft magnetic properties of the current alloy.

From these analysis, it can be seen that the Cu clustering played an important role in nanocrystallization of the current Fe-based MG during annealing. To further study role of the minor additions of Cu, the 7.5% P iso-concentration surfaces and 3% Cu iso-concentration surfaces for the sample annealed 30 min. at 749 K were used to identify the positions of the Cu precipitates (Fig. 4e). Most spherical copper precipitates were located preferentially on the interfaces of other phases. A lower number density of intraphase Cu

precipitates, i.e., the ones circled in Fig. 4e, were also observed, and they were slightly smaller.

These results indicate that after 15 min of annealing at 729 K, only copper segregation is present in the amorphous matrix. Meantime, structural relaxation occurred during the early annealing, residual stress and defects such as free volume were reduced or annihilated, which would alleviate magnetic anisotropy and lead to increase of M_s and decrease of H_c [27]. With the longer annealing time of 30 min at the same temperature, there were indications of phase separation of the other elements, particularly Fe and C. It seems that M_s was increased due to formation of more α -Fe, but H_c was also increased due to its increased grain size [27]. During annealing for 30 min at the higher temperature of 749 K, the Cu precipitates were larger and present at lower number densities, and distinct α -Fe, Fe_3C and $Fe_3(P,B,C)$ phases were observed. By combining these results, the precipitation sequence appears to entail the initial phase separation of the Cu precipitates, and when their respective incubation periods were exceeded these Cu precipitates act as preferential nucleation sites for the α -Fe, Fe_3C and $Fe_3(P,B,C)$ phases. The Cu precipitates will also be pinning sites for their respective interfaces during growth of these iron-containing phases. The isolated nano-sized α -Fe precipitates had a composition close to the orientated silicon steel, which improved the magnetization. The increase in the size of the α -Fe phase, and the formation of the other iron-based compounds containing the metalloid elements deteriorated the soft magnetic properties. It is important to point out that for actual applications of Fe-based BMGs as soft magnetic materials, both magnetization and coercivity have to be considered. Proper processes such as rapid

annealing [17] for properly controlling precipitation and nanocrystallization are crucial for achieving desirable overall soft magnetic properties.

4. Conclusions

Nanocrystallization behavior of a Cu-doped iron-based MG during annealing was investigated by APT. Cu segregation was found to precede and may trigger the segregation of other elements. Evolution of the Cu nano-precipitates can be regarded as a process of fast nucleation at the early stage, followed by slow coarsening at the late stage. The α -Fe phase had a composition close to that of the grain-orientated silicon steel and was isolated by the residual amorphous matrix and/or the other crystalline phases enriched in the metalloids, giving rising to the enhanced magnetization. With excessive annealing treatment, extensive precipitation and coarsening of iron-based compounds deteriorated the soft magnetic properties.

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Captions

Table 1 Number density and radius of the Cu precipitates in the as-cast and annealed samples.

Fig. 1 X-ray diffraction patterns (a) and Magnetization curves (b) of the Cu_{0.7} samples annealed at different temperature, and (c) variation of M_s and H_c of the Cu_{0.7} alloy as a function of annealing temperature.

Fig. 2 Elemental distribution of the sample annealed 15 min at 729 K; (a) the elements Fe, Si, B, C, P and Cu, and (b) iso-concentration surface of 5% Cu. (c) Compositional line scanning across the matrix and the Cu-enriched nanoprecipitates. Length unit in the figures is nm.

Fig. 3 Elemental distribution for the sample annealed at 729K for 30 min, Fe (a), C (b), and Cu (c). Length unit in the figures is nm.

Fig. 4 3D reconstruction of elemental distribution for the specimens annealed at 749 K for 30 min (a), the compositional line scanning across the interface between the matrix and Cu particles (b), and the α -Fe particles (c), compositional line scanning across the interface between Fe₃C and Fe₃(P,B,C) (d), and (e) the 7.5% P iso-concentration surface along with the 3% Cu iso-concentration surface to show the location of Cu precipitates.

Table 1

Treatment	Number density	Guinier Radius
As cast	0	n/a
15min @ 729K	$1.6 \times 10^{24} \text{ m}^{-3}$	$0.8 \pm 0.2 \text{ nm}$
30min @ 729K	$1.1 \times 10^{24} \text{ m}^{-3}$	$1.3 \pm 0.3 \text{ nm}$

Fig. 1

(c)

Fig. 2

(a)

(b)

(c)

Fig. 3

(a)

(b)

(c)

Fig. 4

(a)

(b)

(c)

(d)

(e)