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Thermal dependence of structural and magnetic properties in an amorphous Fe-Si-B-Cu alloy HPSTAR



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ABSTRACT

Amorphous $Fe_{80}Si_9B_{10}Cu_1$ ribbons were annealed at various temperatures below the crystallization temperature. The structural change was investigated by the synchrotron radiation X-ray diffraction and reverse Monte Carlo method. Intensities of the first peaks on partial pair distribution functions $g_{Fe-Fe}(r)$ and $g_{Fe-Cu}(r)$ rise up with the increase of annealing temperature, which implies the Cu clustering and concomitant Fe aggregation. Employing the Voronoi tessellation method, the enhanced phase separation during annealing was revealed by the variation in population of Fe-centered clusters. These findings are then corroborated by Fe^{57} Mössbauer spectroscopy. Moreover, annealing enhances the average hyperfine field of the alloy ribbons and induces the rotation of easy axis to the ribbon plane.

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1. Introduction

Fe-based nanocrystalline alloys, crystallization products of amorphous precursors, exhibit great application prospects in power industry owing to their excellent magnetic softness such as high saturation magnetic flux density (B_s) , low coercivity (H_c) , and low magnetic core loss, etc. [1-5]. Cu addition proves to be useful for enhancing nanocrystallization and improving the soft magnetic properties in Fe-based amorphous alloys. In this case, Cu clusters form before the onset of crystallization and act as heterogeneous nucleation sites for the precipitation of α -Fe during annealing. With a combination of wide-angle X-ray scattering, small angle X-ray scattering, Mössbauer spectroscopy and X-ray absorption near edge spectroscopy, Gupta et al. [6] have found that Cu clustering initiates and Cu clusters gradually grow in a diffusion controlled manner upon annealing in Fe73.9Cu0.9Nb3.1Si13.2B8.9 amorphous alloy. Employing three-dimensional atom probe, the Cu clusters in Fe₈₉Zr₇B₃Cu₁ are observed in direct contact with α -Fe nanocrystals and serve as heterogeneous nucleation sites [7]. Lately, atom probe tomography studies of Fe_{73 5}Si_{15 5}Cu₁Nb₃B₇ by Pradeep et al. [8] revealed that the Cu clusters act as indirect heterogeneous nucleation sites by inducing chemical inhomogeneities in amorphous matrix.

Extensive research work has been done to study the structural evolution of Cu clusters in commercial Fe-based nanocrystalline alloys, while other Cu-contained Fe-based nanocrystalline alloys such as Fe-Si-B-Cu soft magnetic alloys seem to lag behind. Previous results [8,9] imply that local chemical heterogeneities, owing to the clustering of Cu, are responsible for initial primary crystallization. It has been suggested that Cu has a similar effect on nanocrystallization in Fe-Si-B-Cu soft magnetic alloys and Cu clustering may also result in a concentration fluctuation of Fe. Cu clustering behaviors of Cu-containing Fe-based nanocrystalline alloys have been widely investigated by three-dimensional atom probe, X-ray absorption fine structure and atom probe tomography but there are few reports about changes of local structures around Fe and Cu using reverse Monte Carlo method (RMC) during annealing. Thus, the objective of this work is to study variations in local environment of Fe and Cu from the stage of structural relaxation to the early stage of crystallization. Our results suggest that Cu clustering and Fe aggregation proceed with increasing annealing temperature in Fe-Si-B-Cu amorphous alloys. The Mössbauer spectroscopy study also corroborates the evolution of local structures of Fe and Cu during annealing. This work provides insight into the structural changes upon annealing in Cu-contained Fe-based metallic glasses.

376-2017

2. Experimental details

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The master alloy ingots with the nominal composition of



Fe₈₀Si₉B₁₀Cu₁ were prepared by arc-melting a mixture of industry raw materials: Fe (99.9%), Si-Fe (Si: 99.586%, Fe: 0.27%), B-Fe (B:17.0%, Fe:83.0%) and Cu(99.99%) in an argon atmosphere. With electromagnetic stirring, the alloy ingots were remelted at least four times in a Ti-gettered argon atmosphere. Amorphous ribbons with about 1.5 mm in width and 25 um in thickness were produced by single-roller melt spinning method in an argon atmosphere onto a copper wheel with a surface velocity of 40 m/s. Thermal properties of melt-spun ribbons were measured by differential scanning calorimeter (DSC) at a heating rate of 20 K/min. The as-quenched amorphous ribbons B₀ were isothermally annealed at 563, 583 K for 480s to get two independent glassy samples B₁, B₂, respectively, under the Ar flow and then cooled to room temperature in the furnace. The structure of melt-spun and annealed ribbons was identified by X-ray diffraction (XRD) with Cu-Ka radiation $(\lambda = 1.54056 \text{ Å})$ and a transmission electron microscope (TEM). We performed the synchrotron radiation-based X-ray diffraction with a wavelength of 0.117418 Å by using beam line 11-IDC in the Advanced Photon Source of USA. The two dimensional diffraction data were recorded using a Mar345 image plate and integrated to Q-space by programme Fit2D [10]. Subsequently, the output data were normalized to get structure factor S(Q) through software PDFgetX [11].

The structure factors *S*(*Q*) were determined from the normalized elastically scattered intensities as:

$$S(\mathbf{Q}) = \frac{I(\mathbf{Q}) - \left(\langle f^2 \rangle - \langle f \rangle^2\right)}{\langle f \rangle^2},\tag{1}$$

$$\left\langle f^{2}\right\rangle =\sum_{i=1}^{n}c_{i}f_{i}^{2},\left\langle f\right\rangle =\sum_{i=1}^{n}c_{i}f_{i},\tag{2}$$

where I(Q) indicates the normalized and corrected intensity, Q is the magnitude of scattering vector, c_i denotes the atomic concentration of the *i*-th kind element, f_i is the atomic scattering factor and n is the number of the atomic species [12].

The Fourier transformation of S(Q) yields the pair distribution function g(r):

$$g(r) = 1 + 1/2\pi^2 \rho_0 \int_0^\infty Q[S(Q) - 1]\sin(Qr)d(Q),$$
(3)

where ρ_0 is the number density [13].

The S(Q) data were simulated under the framework of RMC [14,15]. Cubic boxes that we used in the reverse Monte Carlo (RMC) simulation contained 32000 atoms, matching the Fe₈₀Si₉B₁₀Cu₁ composition. The simulation data were obtained by comparing to experimental data through the least square iterative calculation

$$\delta^2 = \frac{1}{\varepsilon_s^2} \sum_n \left(S_m(Q_n) - S_{\exp}(Q_n) \right)^2, \tag{4}$$

where δ^2 denotes the deviation between the experimental $S_{\exp}(Q_n)$ and simulation $S_m(Q_n)$ data. ε_s is the experimental error. In RMC procedure, atoms move randomly within a determined time interval. If $\delta_n^2 < \delta_0^2$, the move is accepted and the old configuration is replaced by a new one. If $\delta_n^2 > \delta_0^2$, the move is still accepted with a probability of $\exp(-(\delta_n^2 - \delta_0^2)/2)$. In our fitting processes, the cut-off distances between Fe-Fe, Fe-Si, Fe-B, Fe-Cu, Si-Si, Si-B, Si-Cu, B-B, B-Cu and Cu-Cu atomic pairs are set as 2.2, 2.1, 1.95, 2.25, 2.0, 1.85, 2.15, 1.7, 2.0 and 2.3 Å, respectively, which enables the movement of atoms while avoids strong overlap between neighbor atoms. δ^2 decreases gradually until it reaches a certain value. The result obtained from RMC is an atomic structural model available for further analysis through the Voronoi tessellation method [16]. Finally, the Mössbauer spectroscopy measurements were performed in transmission geometry at room temperature using standard constant acceleration spectrometer with a ⁵⁷Co(Rh) source. The NORMOS program was used to fit experimental spectra.

3. Results and discussion

Fig. 1 shows the DSC curve of as-quenched Fe₈₀Si₉B₁₀Cu₁ amorphous ribbons. There are two distinct exothermic peaks, indicating that two stages are involved in the crystallization. The primary and secondary exothermic peaks can be ascribed to the production of α-Fe(Si) and Fe-B compounds, respectively. The XRD patterns of the as-quenched and annealed samples are shown in Fig. 2. The amorphous nature with typical halo peak of samples B₀ and B₁ was verified by XRD. However, a very weak peak corresponding to α-Fe(Si) can be noted for sample B₂, which indicates the initiation of nanocrystallization at 583 K. It can be noted that the samples tend to lose their amorphicity upon temperature rise. The TEM bright field images shown in Fig. 3 reveal that as-spun ribbons annealed at 563 K (B₁) consist only amorphous phase. while ribbons annealed at 583 K (B₂) are composed of many fine patches dispersed in amorphous matrix. This effect may originate from the Cu clustering-induced heterogeneous nucleation at 583 K. It can thus be concluded that annealing probably induces the Cu clustering and Fe aggregation, and annealing up to 583 K leads to the onset of heterogeneous crystallization. Previous investigations [8,9] have indicated that Cu enrichment causes significant reduction in Fe concentration, and that Fe and Cu constitute the so called Cu clusters. Results from XRD and TEM imply that annealing in the investigated temperature range contributes to the occurrence of phase separation. Thus, it is worthwhile to study the atomic rearrangements of Fe and Cu upon annealing in more detail.

It is well known that the pair distribution function g(r) describes the distribution of atoms relative to a given atom, and can reflect the degree of order [17]. The reverse Monte Carlo method (RMC) enlightens one to seek possible changes in local environment of Fe thorough partial pair distribution functions (PPDF). The average coordination numbers for a centered atom and their corresponding inter-atomic distances have been calculated from peaks of PPDF by Babilas et al. [12]. Structure factors S(Q) for B₀, B₁ and B₂ were







Fig. 2. XRD patterns of $Fe_{80}Si_{9}B_{10}Cu_{1}$ alloy melt-spun (B_{0}) and annealed $(B_{1}\&B_{2})$ ribbons.

collected and stimulated under the framework of RMC. Profiles of the structure factors S(Q) of all the Fe₈₀Si₉B₁₀Cu₁ amorphous ribbons along with the corresponding simulated curves are shown in Fig. 4. All the samples are amorphous and no sharp peaks can be seen on S(Q) patterns. Because the number of α -Fe(Si) is rather limited in B₂, the S(Q) patterns of α -Fe(Si) may be obscured by that of the amorphous phase. We believe that the amorphous phase dominates the patterns of S(Q) and very tiny α -Fe(Si) can't be distinguished from the amorphous matrix in this case. The excellent match between the experiment and simulation data ensures the reliability of the RMC simulation. The partial distribution functions $g_{\text{Fe-Fe}}(r)$ and $g_{\text{Fe-Cu}}(r)$ are illustrated in Fig. 5(a) and (b), respectively. One can note that both the amplitudes of $g_{\text{Fe-Fe}}(r)$ and $g_{\text{Fe-Cu}}(r)$ around the first peak rise up with an increase in annealing temperature, which indicates the increase in the coordination numbers of Fe and Cu around Fe. This effect agrees well with related work [8]. With the depletion of Fe neighbors at short-range length scale, Cu clustering initiates and rapidly develops in amorphous matrix before primary crystallization. The formation and subsequent increase in number density of Cu clusters may interpretate the behavior of $g_{\text{Fe-Cu}}(r)$ around the first peak. Meanwhile, Cu clustering induces the aggregation of Fe atoms and results in the amplitude increase in $g_{\text{Fe-Fe}}(r)$ around the first peak. Recently, Huang et al. [18] observed that the formation of the nucleus precursor of nanocrystals formed by atom aggregation in the early stage of crystallization. We believe that Cu clustering and concomitant Fe aggregation are in progress with an increase in annealing temperature.

Fe is the principal element in most of Fe-based amorphous alloys. The annealing-dependences of morphology and distribution of α -Fe make it possible for the magnetic softness tuning in the Febased nanocrystalline alloys [19,20]. Similarly, it is worthwhile to investigate the distribution of Fe-centered clusters at different annealing temperatures. In Cu-contained Fe-based amorphous alloys, the distribution of Fe and Cu atoms usually varies greatly compared to that of other elements [7,8]. Cu clusters keep growing through rejecting Fe atoms, which will significantly influence the local structure of Fe. It means that Cu clustering can be indirectly traced by the variation in distribution of Fe-centered clusters. Hence, the Voronoi tessellation method was applied on the RMC structural model to extract the distribution of Fe-centered clusters. In this work, a cut-off distance was set to 3.46 Å to identify the neighboring atoms. The Voronoi index $\langle n_3, n_4, n_5, n_6 \rangle$, was used to



Fig. 3. Bright field TEM micrographs of $Fe_{80}Si_9B_{10}Cu_1$ alloys annealed at 563 K (a) and 583 K (b).

characterize the clusters. The n_j denotes the number of facets of the Voronoi polyhedron with j edges. Fig. 6 shows the top thirteen Fecentered clusters diagram for as-quenched and annealed samples. As can be observed, bcc-like polyhedra such as $\langle 0,3,6,4 \rangle$, $\langle 0,2,8,4 \rangle$ and $\langle 0,3,6,5 \rangle$ and icosahedra-like polyhedra such as $\langle 0,1,10,2 \rangle$, $\langle 0,2,8,2 \rangle$ and $\langle 0,3,6,3 \rangle$ dominate the whole population. Interestingly, one can note that clusters with coordination number no less than 13 gradually aggregate with the increase of annealing temperature. Therefore, the phase separation tendency may be enhanced in this case.

To confirm above findings, Fe^{57} Mössbauer measurements are conducted to investigate the local structure of Fe upon annealing. Fig. 7(a) illustrates room temperature Fe^{57} Mössbauer spectra of all specimens. As can be observed, all the spectra consist of six broadened lines, typical of amorphous phase. As can be observed from XRD, a very small number of α -Fe(Si) was produced in B₂. Since the six-line patterns of the crystalline α -Fe(Si) overlap with



Fig. 4. Structure factors S(Q) of $Fe_{80}Si_9B_{10}Cu_1$ alloy melt-spun (B₀) and annealed (B₁&B₂) ribbons.





Fig. 6. Distributions of Fe-centered clusters for melt-spun (B_0) and annealed $(B_1\&B_2)$ $Fe_{80}Si_9B_{10}Cu_1$ ribbons.



Fig. 5. The partial pair distribution functions $g_{Fe-Fe}(r)$ and $g_{Fe-Cu}(r)$ of melt-spun (B₀) and annealed (B₁&B₂) Fe₈₀Si₉B₁₀Cu₁ ribbons.

(b) of melt-spun (B_0) and annealed ($B_1 \& B_2$) $Fe_{80}Si_9B_{10}Cu_1$ ribbons. re. The trans-

that of the amorphous phase at room temperature. The transmission Mössbauer spectra may not be able to reveal the existence of α -Fe(Si). All the sextet patterns imply the existence of nonequivalent Fe sites. The hyperfine field distribution, *P*(*B*_{hf}), is shown in Fig. 7(b). Two *P*(*B*_{hf}) humps are observed for B₀, B₁ and B₂,

Hyperfine parameters: average hyperfine field (B_{hfa}) , change of isomer shift for each magnetic field (DTI), isomer shift (IS), quadrupole splitting (QS).

Samples	$B_{\rm hfa}\left({\rm T}\right)$	DTI (mm/s)	IS (mm/s)	QS (mm/s)
B ₀	24.86	0.0056	-0.166	-0.036
B ₁	25.35	0.0105	-0.303	-0.020
B ₂	25.57	0.0038	-0.108	-0.014

movement for Cu from Fe-rich zones to Fe-deficient sites [6]. In this work, as the annealing temperature increases, the intensity of the low field peaks decreases, which implies the Cu enrichment in Fedeficient zones. For the high field component in the hyperfine field distribution, however, the intensity of peaks corresponding to Ferich zones decreases with an increase in annealing temperature, while the high field peak position shifts to large value of $B_{\rm hf}$, which means the gathering of Fe atoms during structural relaxation. Upon annealing at 583 K, the heterogeneous nucleation is likely to set in, accompanied by the reduction of Fe sites in amorphous matrix. Thus, the intensity of the high field peaks gradually decreases until the crystallization occurs. It was previously reported that, upon annealing, Fe atoms are rejected from the Cu-rich regions during cluster formation, whereupon chemical heterogeneity and subsequent primary crystallization initiate in amorphous matrix [8,21], which is also verified in this study. Moreover, hyperfine parameters like average hyperfine field (B_{hfa}) , change of isomer shift for each magnetic field (DTI), isomer shift (IS), quadrupole splitting (QS) for all samples are listed in Table 1. The QS of annealed samples is larger than that of as-quenched samples, where the QS increases from -0.036 mm/s of B₀ to -0.014 mm/s of B₂. On the other hand, the significant increase in B_{hfa} can be seen, which should be ascribed to an enhanced magnetic interaction. This may originate from Cu diffusing out of the amorphous matrix and its local clustering which reduces the shield effect on magnetic interaction among Fe neighbors [22].

The average hyperfine field B_{hfa} and the intensity ratio R of the second to the third line obtained from analysis of Mössbauer spectra as functions of annealing temperature are shown in Fig. 8. The B_{hfa} monotonically increases with the increase of annealing temperature, which can be assigned to an increase in the topological order in the system because the atomic ordering can enhance the exchange-interaction [23]. Meanwhile, one can also note that *R* initially increases and then slightly decreases. The variation in R reflects the rotation of easy axis during annealing, i.e., the increase of R manifests a rotation of easy axis to the ribbon plane [22]. Low-temperature annealing in this work relieves the



Fig. 8. The average hyperfine field B_{hfa} and the intensity ratio R of the second to the third line as functions of annealing temperature.

internal stress in metallic glass, thereby rotating the easy axis to inplane of ribbons and increasing the value of R. The subsequent slight decrease in R may be ascribed to the nucleation in amorphous matrix where stress-induced perpendicular anisotropy was introduced [24].

4. Conclusions

We investigated local structure changes upon annealing in Fe₈₀Si₉B₁₀Cu₁ amorphous ribbons by synchrotron X-ray diffraction and reverse Monte Carlo method. The results reveal that the amplitudes of $g_{\text{Fe-Fe}}(r)$ and $g_{\text{Fe-Cu}}(r)$ around the first peak increase with annealing temperature, implying the Cu clustering and ongoing Fe aggregation during annealing. Moreover, one note that clusters with coordination number no less than 13 aggregate stepwise with the increase of annealing temperature, which indicates the possible phase separation is enhanced during annealing. RMC studies and the Voronoi tessellation method provide an indirect observation of atomic-scale aggregation in the Fe-Si-B-Cu amorphous alloy. Also, the local structure changes of Fe and Cu with an increase in annealing temperature are confirmed by Fe⁵⁷ Mössbauer spectroscopy. Annealing enhances the average hyperfine field of alloy ribbons and induces the rotation of easy axis to the ribbon plane.

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