LETTER

Refining the formation of nanocrystals in soft magnetic amorphous alloy via EXAFS spectroscopic analyses

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Introduction

The amorphous metallic alloy with the composition $Fe_{73.5}Nb_3Cu_1Si_{13.5}B_9$ is now quite well known as FINEMET, mainly owing to its excellent magnetic properties that are supposed to be due to the formation of small nanocrystals consisting of Fe and Si, i.e., DO_3 phases, during simple heat treatment [1–3]. The evolution of such nanocrystals and their effects on the magnetic properties were comprehensively described in previous reports [4–6]. With using mainly the Fe K-edge and Cu K-edge EXAFS spectra, Ayers et al. carefully studied nucleation kinetics of samples that were heat-treated at various durations [7, 8]. In particular, the role of Cu on nucleation processes in this noncrystalline metal was largely proven by experimental observations of a series of Fourier-transformed EXAFS spectra taken at the Cu K-edge of differently heat-treated samples. A key point in their nucleation model for this amorphous metal is that Cu clusters act as nucleation sites of the DO_3 nanocrystallites [8]. It is noteworthy that not all Cu atoms are involved in the generation of the DO_3 nanocrystals. Nonetheless, Ayers et al.'s analyses were generally qualitative since they explained the local structural evolution of Cu based on the fingerprint comparison between the partial radial distribution functions of the samples. Thus, though successful, their analyses did not give a quantitative fraction of Cu participating in the nucleation processes of DO_3 nanocrystals in their samples.

This study sought to come up with a quantitative refinement of the local structures of copper atoms in the amorphous metals. Specifically, the Cu K-edge EXAFS spectra of three representative specimens, i.e., single crystalline Cu (designated SC hereafter), as-quenched $Fe_{73.5}Nb_3Cu_1Si_{13.5}B_9$ (AQ) and the other one heat-treated for 1 h (HT), were recorded. The fraction of the Cu atoms that remained amorphous without playing a role in the nucleation of the Fe-rich DO_3 precipitates was then determined.

Experimental

Alloys with atomic mass composition $Fe_{73.5}Nb_3Cu_1Si_{13.5}B_9$ were prepared from metals with 99.99% purity or better through vacuum arc melting on a chilled Cu hearth. Ribbon samples of amorphous metal were prepared in Argon using the single roll melt spinning technique. The ribbons were generally 2-mm wide and about $20 \sim 25$-μm thick. Part of the parent ribbon was detached and heat-treated at 580 °C for 1 h, a duration assumed to be long enough to exclude any further change in the local structures of Cu inside the sample. The local structural rearrangements around Cu were verified to end within the duration of 8 min. The heat treatment temperature chosen in this study was in-between the first and second crystallization temperatures of the amorphous alloy. As such our heat treatment condition was also appropriate to obtain an optimised nanocrystal-dispersed microstructure as previously reported [1].

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X-ray absorption measurements were carried out at the EXAFS beamline BL3C1 of Pohang Light Source, Republic of Korea. Photon energies below and above the Cu K-edge were resolved using a pair of Si (111) crystals, with detuning applied to reject third-order harmonic noises. All spectra were measured in transmission mode at room temperature. Energy was calibrated using a Cu metal foil, with energy resolution ($\Delta E/E$) estimated to be $\sim 10^{-4}$ around the Cu K-edge. In each edge and EXAFS region, data were recorded in steps of 0.1 eV and 0.01 Å^{-1}, respectively. Finely pulverized samples whose particle size distribution was made narrow through careful sieving were used for the X-ray absorption measurements.

Data reduction processes, i.e., background removal, Fourier transforms into K- or R-space, and nonlinear least-squares fits, were carried out using the UWXAFS package [9]. Theoretical amplitude envelop functions and phase shift functions of several single and multiple scattering paths were calculated using the FEFF8 code [10]. Detailed data reduction and fitting procedures can be found in other reports [11,12].

Results and discussion

Figure 1 shows the measured EXAFS spectra of the three samples. As expected, in addition to the main oscillation associated with the interatomic distance between a central Cu atom and its nearest neighboring atoms, well-resolved higher frequency oscillations appeared in the case of SC. Such higher frequency oscillations were evident in the measured EXAFS spectrum of HT as well, although they were absent in AQ. This implied that the EXAFS spectrum of HT probably included structural information on coordinating atomic shells beyond the nearest neighboring atoms. Indeed, clearly defined higher shell peaks were observed in its Fourier transform spectrum as shown in Fig. 2. The amplitude of the nearest neighbor peak of the sample HT was significantly small compared to SC, although the second and third shell peaks of HT had more or less similar amplitude as that of SC. On the other hand, the amplitude of the first shell peak of AQ was quite smaller than that of SC and HT. Moreover, its peak position shifted to the smaller distance side. In addition, the presence of the second and third shell peaks was doubtful, since their amplitude was quite smaller compared to SC and HT. A decrease in amplitude of the first shell peak, together with the absence of higher shell peaks, was typically observed from the EXAFS spectra of noncrystalline materials [13, 14]. Almost all of the Cu atoms in the sample AQ were thus presumed to have amorphous atomic surroundings in its local structures. Meanwhile, the higher shell peaks in the sample HT, which were definitely
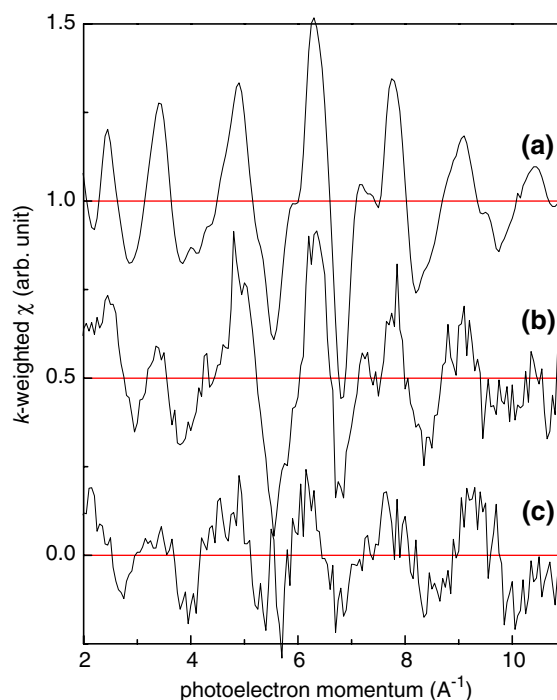

Fig. 1 K-weighted EXAFS spectra taken at the Cu K-edge of the samples: (**a**) Single crystalline Cu standard reference; (**b**) $Fe_{73.5}Nb_3Cu_1Si_{13.5}B_9$ heat-treated for 1 h; (**c**) As-quenched $Fe_{73.5}Nb_3Cu_1Si_{13.5}B_9$

resolved and quite similar in shape as well as position to those of SC, suggested the presence of Cu nanocrystals with FCC atomic arrangements. As a result, the difference in the first shell peaks of the two spectra implied that not all of the Cu atoms formed their nanocrystals but some of them remained amorphous. A quantitative analysis of the fraction is described below in more detail, together with a simple local structural model of Cu inside the $Fe_{73.5}Nb_3Cu_1Si_{13.5}B_9$ alloy before and after heat treatment.

Ayers et al. reported that some of the Cu atoms existed as clusters in their as-melt-spun alloy, based on the presence of two small peaks between 3 and 4 Å in the Fourier-transformed spectra [8]. For the alloy in this study, however, only a peak was resolved in the range of radial coordinates. As shown in Fig. 2, its amplitude was also quite small, i.e., somewhat similar to other peaks beyond the range which might indicate no physical meaning. The spectrum in this study was consistent with the data of Kim et al., who observed only a single small peak in the range of radial coordinates [15]. Thus, this study presumed again that almost all of the Cu atoms inside the sample in its as-quenched state were located in amorphous atomic surroundings with only a negligible portion clustered, if any. As a result, the first shell peak of AQ possibly came in first from the nearest neighboring atoms that were randomly distributed around the Cu atoms. As stated before, the
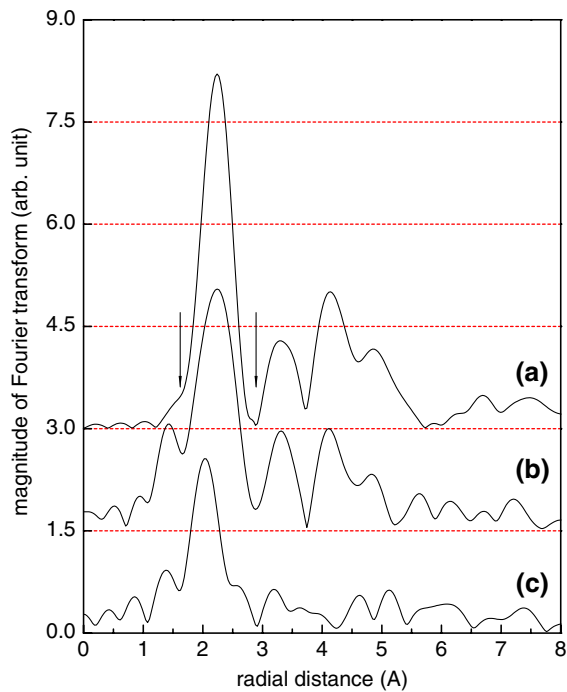
Fig. 2 Fourier-transformed EXAFS spectra of the samples: (**a**) Single crystalline Cu standard reference; (**b**) $Fe_{73.5}Nb_3Cu_1Si_{13.5}B_9$ heat-treated for 1 h; (**c**) As-quenched $Fe_{73.5}Nb_3Cu_1Si_{13.5}B_9$. Fourier transforms were carried out in the range of $2.5 \sim 11$ Å^{-1} with weighting factor k. Two downward arrows indicate the lower and upper limits of Fourier filtering to isolate the nearest neighboring peak. Note that the phase shifts were not corrected

amorphous state of the Cu atoms in the sample AQ was further reinforced by the decreased amplitude, together with the shift of the peak toward the shorter distance side. Ayers et al. also noted that both the amplitude of the nearest neighboring peak and position of the peak in the radial coordinates were smaller in those alloy samples subjected to various heat treatments compared to pure Cu metal [7]. Based on this observation, they concluded that the crystallization of Cu atoms occurred very fast and ended within duration of a few minutes. As such, this study inferred that only some of the Cu atoms crystallized into FCC Cu nanocrytals, with the other Cu atoms remaining amorphous even in fully heat-treated samples. The sample HT in this study, which was heat-treated for 60 min, also showed a decrease in the magnitude of the first shell peak. Therefore, this study assumed that not all of the Cu atoms in the samples formed their own nanocrystals but instead some of them still remained amorphous. Accordingly, the EXAFS spectrum of HT should consist of structural information from both Cu atoms that formed Cu nanocrystals and that remained amorphous. As such, the EXAFS spectra in this study were simplified. Specifically, the EXAFS spectrum of HT ($\chi(k)$) was written as:

$$\chi(k) = f\chi_{crys}(k) + (1-f)\chi_{amor}(k),$$

where $\chi_{amor}(k)$ and $\chi_{crys}(k)$ represent the EXAFS oscillation triggered by Cu atoms in amorphous phase and those forming Cu nanocrystals, respectively. Here, f denotes the Cu atoms that crystallized. The differences in backscattering amplitude functions and atomic radii between constituent atoms possibly playing a part in the nearest neighboring shell of Cu in amorphous phase and Cu atoms forming Cu nanocrystals would give rise to a clear distinction between $\chi_{amor}(k)$ and $\chi_{crys}(k)$. In this respect, $\chi(k)$ may be written as a combination of the EXAFS spectra of SC and AQ. The first shell peak was isolated from the entire Fourier-transformed spectra, with both ends for the inverse Fourier transforms marked with arrows in Fig. 2. Fig. 3 shows the resulting Fourier-filtered EXAFS spectra of the samples that were supposed to possess only information on the nearest neighboring atoms. Then, the first-shell EXAFS spectrum of sample HT could be modeled well with the equation above as shown in Fig. 4. The least squares fit of the spectra of SC and AQ to the spectrum of HT yielded a best value of $f = 0.65 \pm 0.05$.

Such fitting procedure could also be applied to higher shell peaks. However, the huge Debye-Waller factors involved in the higher-order shells of AQ resulted in the
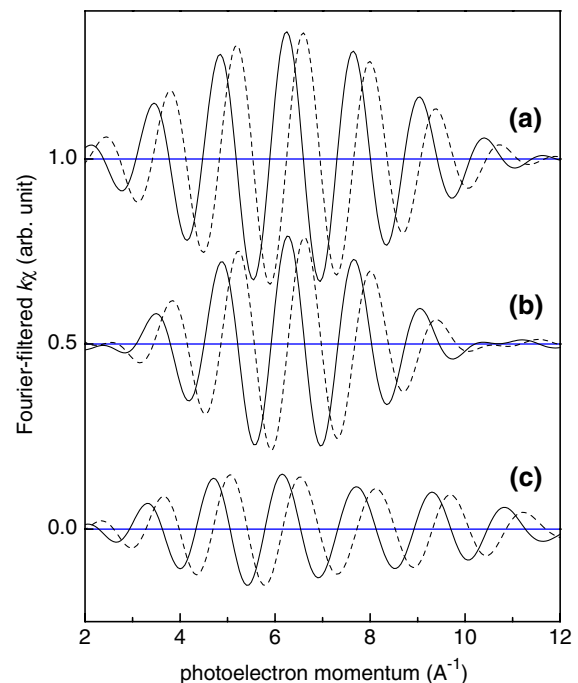

Fig. 3 Inverse Fourier-transformed EXAFS spectra of the samples: (**a**) Single crystalline Cu standard reference and $Fe_{73.5}Nb_3Cu_1Si_{13.5}B_9$ alloy; (**b**) Heat-treated for 1 h; (**c**) As-quenched. The transform range is marked in Fig. 2. Solid and dotted lines represent the real and imaginary parts, respectively, of the Fourier transforms

very small amplitudes, thereby causing difficulty in using such fit for those higher shell peaks (Fig. 2c). On the other hand, only negligible higher-shell EXAFS oscillations would result from a Cu atom embedded in amorphous phase due to the disordered arrangements of coordinating constituent atoms and as a result the EXAFS oscillations indicating higher shells of HT would come from Cu atoms among Cu nanocrystals. As such, the well-resolved higher shell peaks in the measured spectrum of HT could be observed (Fig. 2). In this case, fit with the theoretical EXAFS functions generated from the FCC structure of Cu metal would be possible.

Each individual theoretical EXAFS function was calculated using the FEFF8 code of an FCC Cu crystal within 5 Å. Given a range of $3 \sim 5$ Å, several multiple scattering paths whose effective path lengths were all less than 5 Å coexisted with single scattering paths from the second and third shells [16]. As a result, without knowing the shift of energy origin and Debye–Waller factor of all the involved paths, it was almost impossible to carry out least squares fits with such theoretical EXAFS functions incorporating the multiple scattering paths as well. Therefore, the experimental EXAFS spectra of SC and HT were fitted using only the two single scattering paths. The results of the fits were quite comparable; thus confirming that Cu

atoms in the heat-treated amorphous alloy $Fe_{73.5}Nb_3Cu_1Si_{13.5}B_9$ indeed formed nanocrystals consisting only of Cu in FCC crystalline structure.

Although our Cu K-edge EXAFS spectra were consistent with those of previous studies, the local structures of Cu in this material were refined more quantitatively. Thus, the previous structural model [8] describing the evolution of nanocrystals occurring as a result of heat treatments are still valid. Our EXAFS fitting model may also be applicable to other amorphous metallic systems where local structure of a constituent atom changes from initial fully amorphous surrounding to final well-ordered crystalline as a result of heat treatment.

Summary

The Cu K-edge EXAFS spectra of soft magnetic amorphous alloy $Fe_{73.5}Nb_3Cu_1Si_{13.5}B_9$ were analyzed before and after heat treatment and compared with that of the single crystalline Cu metal. Almost all of the Cu atoms were embedded in amorphous surroundings in our as-quenched alloy. After being heat-treated for 1 h at 580 °C, only some of the Cu atoms formed their own FCC nanocrystals. Based on the consideration that the first-shell Cu EXAFS spectrum of the heat-treated sample could be modeled by combining the corresponding EXAFS spectra of as-quenched sample and single-crystalline Cu metal, fraction of the Cu atoms that participated in the formation of Cu nanocrystals was determined: approximately 65% of the Cu atoms formed their own nanocrystals in FCC structure.
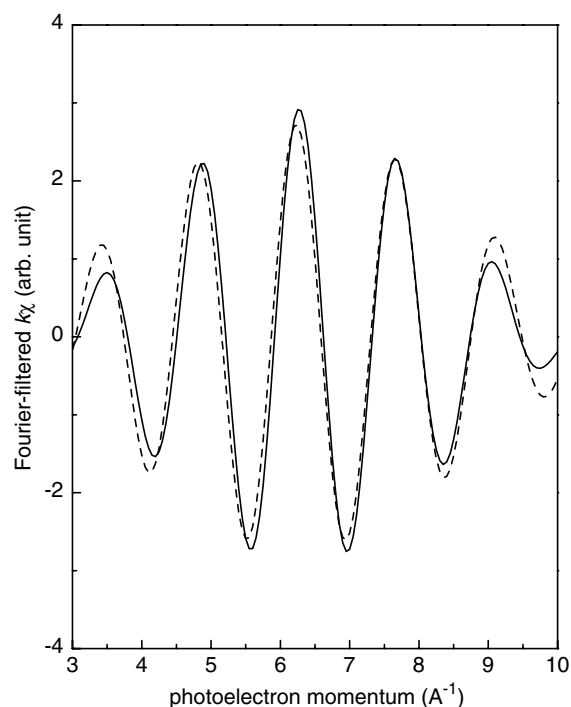
Fig. 4 A representative example of fitting the first-shell EXAFS spectrum of HT with the corresponding EXAFS spectra of SC and AQ. Solid and dotted lines represent the real part of inverse Fourier-transformed EXAFS of HT and modeled EXAFS spectrum with the adjusting parameter, $f = 0.65$, respectively

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