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The effect of annealing time on the electronic structure of the Fe–Cu–Nb–Si–B alloys

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Abstract

Three nanocrystalline (nc-) Fe_{73.5}Cu₁Nb₃Si_{13.5}B₉ (nc-FCNSB) samples were obtained from amorphous (a-) Fe_{73.5}Cu₁Nb₃Si_{13.5}B₉ (a-FCNSB) samples by annealing for 30, 60, and 120 min at a temperature of 550°C. X-ray absorption near-edge-structure (XANES) spectra of these samples were measured at the Fe L_{3,2}-edge using the sample drain current mode at room temperature. The intensities in the Fe L_{3,2}-edge XANES spectra of nc-FCNSBs are significantly different from that of the Fe–Si–B alloy, indicating that Cu and Nb strongly influence the Fe 3d local electronic structure. Crystallization of the FCNSB alloy under the optimum annealing condition improves the magnetic properties of the nc-FCNSB alloys. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: X-ray absorption near-edge-structure (XANES); Extended X-ray absorption fine structure (EXAFS); Fe–Si-based nanocrystal; Amorphous

1. Introduction

The nanocrystalline (nc-) Fe_{73.5}Cu₁Nb₃Si_{13.5}B₉ (denoted as nc-FCNSB) alloy is among a new class of Fe–Si-based soft magnetic alloys which have received considerable interest. Yoshizawa et al. [1] reported that attractive soft magnetic properties were observable only when ~1% Cu and 3% Nb were added to the Fe–Si–B alloy under the optimum annealing condition with a temperature of 550°C for

60 min. A bcc Fe–Si solid solution and a B and Nb enriched amorphous phase with a smaller Si content were also found to coexist in the amorphous matrix [2,3]. The measurement of the Fe and Cu K-edge extended X-ray absorption fine structure (EXAFS) spectra of FCNSB suggested that the modification of the microstructure by Cu in this alloy is due to the cluster-catalyzed nucleation of Fe-rich nanocrystals [4,5]. Our recent analysis of the Fe and Cu L_{3,2}-edge, Nb L₃-edge, and Si K-edge X-ray absorption near-edge-structure (XANES) measurements for the FCNSB alloy showed that Cu and Nb strongly influence the Fe 3d local electronic states and improve the magnetic property of the nc-FCNSB

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alloy [6]. In this work, we focus on the influence of the annealing time on the structural and electronic properties of the nc-FCNSB alloy.

2. Experiments

As-quenched amorphous (a-) $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ (denoted as a-FCNSB) alloy ribbon was prepared by the single roller method. The nc-FCNSB samples were obtained by heating at 550°C for 30, 60 and 120 min, denoted as FCNSB30, FCNSB60, and FCNSB120, respectively, as described elsewhere [7]. The X-ray diffraction (XRD) spectra of the Fe–Si and bcc Fe phases exhibited four diffraction lines as shown in Fig. 1. For the samples prepared with the annealing times of 60 and

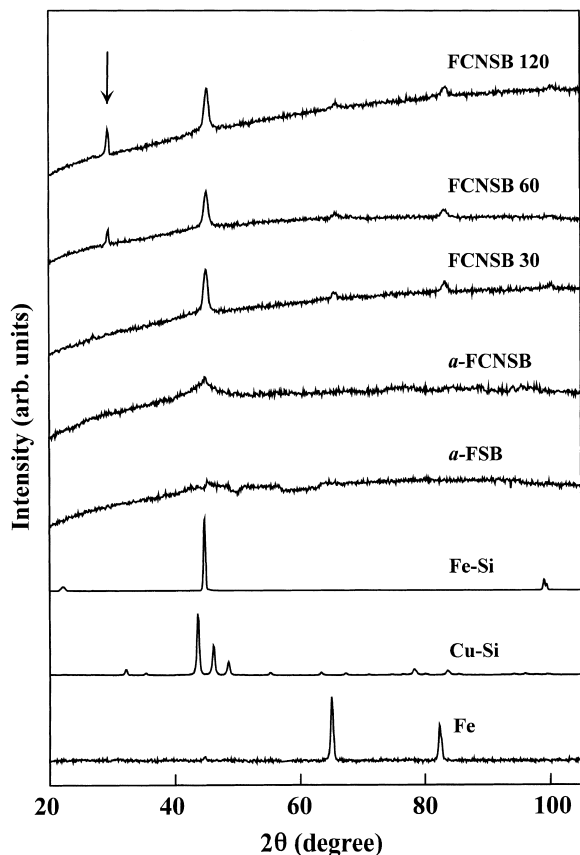


Fig. 1. Representative X-ray-diffraction spectra of nc-FCNSBs, a-FCNSB, a-FSB, Fe–Si, Cu–Si, and the Fe metal.

120 min a new phase appears at $2\theta \approx 29.6^\circ$, indicating the existence of the Fe–B phase [7,8] in FCNSB60 and FCNSB120. This also suggests that the presence of the Fe–B phase in nc-FCNSBs depends on the annealing time of this alloy. The Fe and Cu $L_{3,2}$ -edge, and Si K-edge absorption spectra of nc-FCNSBs prepared at the temperature of 550°C for three different annealing times and the a-FCNSB alloy were measured with the amorphous $\text{Fe}_{78}\text{Si}_{13}\text{B}_9$ (a-FSB) alloy, bulk Fe–Si and Cu–Si alloys, Cu and Fe foils, and the crystalline (c-) Si(100) (c-Si) film as references. These spectra were measured with high-energy spherical grating monochromator and InSb(111) double crystal monochromator beamlines with an electron-beam energy of 1.5 GeV and a maximum stored current of 200 mA at the Synchrotron Radiation Research Center in Hsinchu, Taiwan. The spectra of the Fe $L_{3,2}$ -edge were measured using the sample drain current mode. The fluorescence measurements for the Cu $L_{3,2}$ -edge and Si K-edge spectra were taken at room temperature.

3. Results and discussion

Figs. 2 and 3 show, respectively, the normalized Fe and Cu $L_{3,2}$ -edge XANES spectra of nc-FCNSBs, a-FCNSB, a-FSB, Fe–Si, Cu–Si, and Cu and Fe metals. According to the dipole-transition selection rule, the dominant transition is from Fe (Cu) $2p_{3/2}$ and $2p_{1/2}$ to the unoccupied Fe (Cu) 3d electron states. The area beneath the white-line feature in the Fe (Cu) $L_{3,2}$ -edge XANES spectra is predominately a convolution of the absolute square of the transition matrix element and the unoccupied densities of states of d character. In Fig. 2 the shapes of the Fe $L_{3,2}$ -edge XANES of nc-FCNSBs differ significantly from those of a-FCNSB, reference c-FSB, Fe–Si and the pure Fe metal. The Fe $L_{3,2}$ -edge XANES spectra of nc-FCNSBs, a-FCNSB, a-FSB, and Fe–Si are primarily composed of features a_1 and b_1 . Feature b_1 is more prominent for all three nc-FCNSB than for a-FCNSB. The lineshapes of the Fe $L_{3,2}$ -edge XANES spectra of FCNSBs and a-FSB differ substantially, which suggest that the alloying with Cu and Nb strongly influences the Fe 3d electronic structure in nc-FCNSBs/a-FCNSB. Thole and van der Lann [9] pointed out that the 3d transition-metal ions with

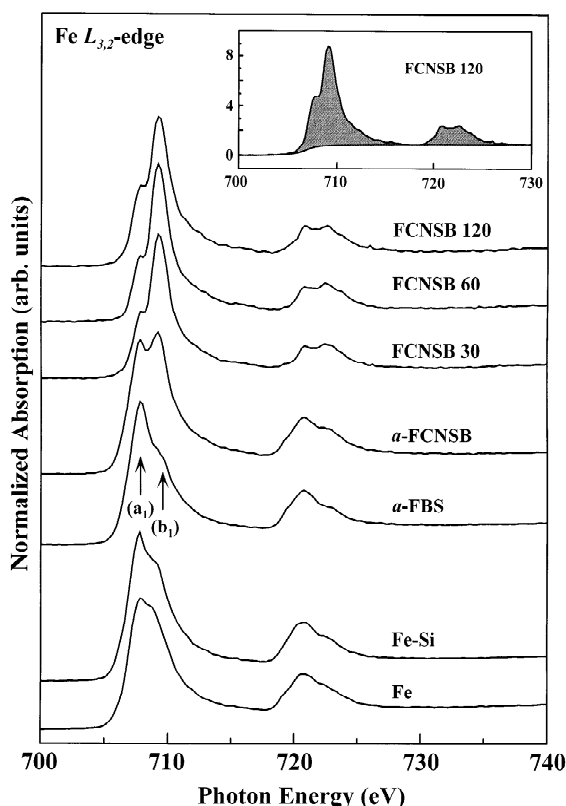


Fig. 2. Normalized Fe $L_{3,2}$ near-edge absorption spectra of nc-FCNSBs, a-FCNSB, a-FSB, Fe–Si, and Fe metal. The integrated area of shaded regions represent the extrapolated background at the Fe L_3 -edge for FCNSB120, as shown in the inset. These areas are used to calculate the $I(L_3)$ and $I(L_2)$. The center of the continuous step of the arctangent function was selected at the inflection point of the threshold.

high-spin states have a relatively large branching ratio of the white-line intensity $I(L_3)/[I(L_3)+I(L_2)]$. Thus a larger branching ratio means a larger number of unoccupied minority-spin 3d-derived states and a higher-spin state. $I(L_3)$ and $I(L_2)$ are determined by subtracting the background intensity described by an arctangent function displayed in the inset of Fig. 2 and are integrated between 705.0 and 718.6 eV and between 718.6 and 727.5 eV, respectively, for the nc-FCNSBs and a-FCNSB spectra. The branching ratio is 0.71–0.79 for nc-FCNSBs and 0.61 for a-FCNSB. This result indicates that the overall number of Fe unoccupied minority-spin 3d-derived states increases with crystallization. The enhanced crystallization of the FCNSB alloy with the addition of

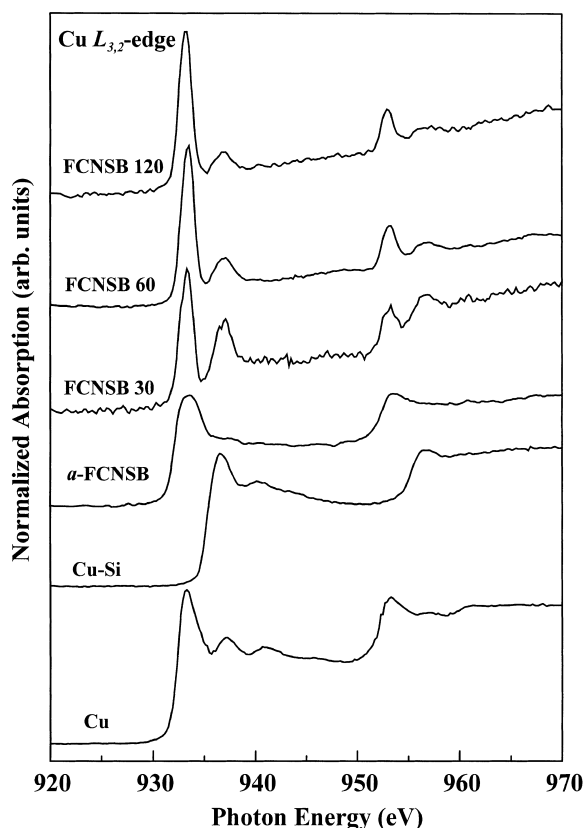


Fig. 3. Normalized Cu $L_{3,2}$ near-edge absorption spectra of nc-FCNSBs, a-FCNSB, Cu–Si, and the Cu metal (the data of Cu metal were measured using the sample drain current mode).

Cu and Nb enhances the spin-state of Fe ions and improves the magnetic property of the nc-FCNSB alloys [6].

In Fig. 3 the general lineshapes in the Cu L_3 -edge XANES spectra of nc-FCNSBs and a-FCNSB differ from those of the Cu–Si and Cu metal. It has been well established that there are characteristic two- and three-peak features in the Cu L_3 -edge XANES spectra of the bcc and fcc Cu-metal and Cu-alloys [8,10,11], respectively. The similarity of the two-peak features shown in Fig. 3 suggests that the local structure of the Cu clusters in nc-FCNSBs generally resembles that of the Cu metal, which indicates that the Cu clusters essentially have an fcc structure. The shapes of the Cu $L_{3,2}$ -edge XANES spectra of nc-FCNSBs differ significantly from those of a-FCNSB, reference Cu–Si and the pure Cu metal. The second

feature at the Cu L_3 -edge is more prominent for FCNSB30 than for FCNSB60 and FCNSB120, which implies that the electronic structure of the Cu cluster in nc-FCNSBs is also affected by the annealing time.

Fig. 4 presents the normalized Si K-edge XANES spectra of nc-FCNSBs, a-FCNSB, a-FSB, Fe–Si, Cu–Si, and c-Si. The Si K-edge XANES spectrum reflects transition from the Si 1s core level to the unoccupied Si 3p-derived states. The general lineshape of the features in the nc-FCNSBs spectra differ from those in the a-FCNSB and a-FSB spectra, which indicates that the chemical states of the absorbing Si atom in nc-FCNSBs differ significantly from those in a-FCNSB and a-FSB. Fig. 4 also shows that the Si K-edge XANES spectra have a main feature a_2 and a sharp feature b_2 . Feature b_2 in

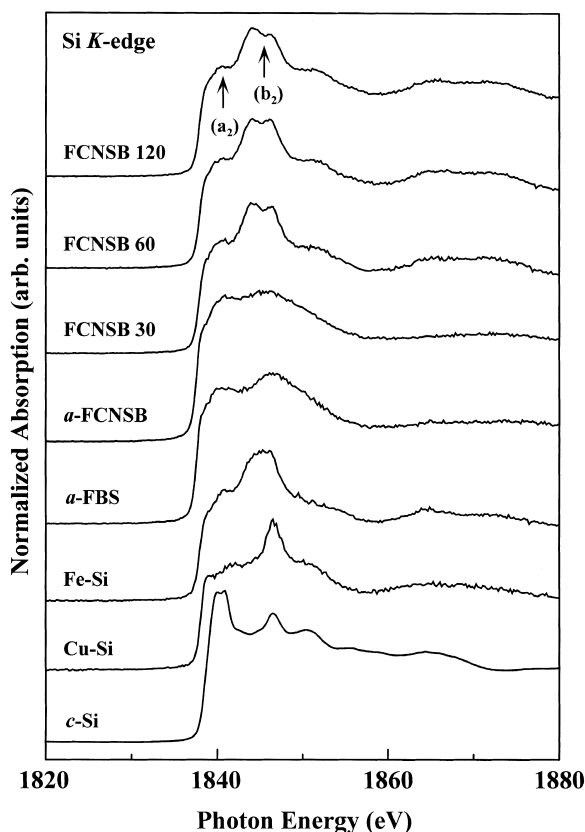


Fig. 4. Normalized Si K near-edge absorption spectra of nc-FCNSBs, a-FCNSB, a-FSB, Fe–Si, Cu–Si, and c-Si (the data of c-Si were measured using the sample drain current mode).

the nc-FCNSB spectra is more prominent than feature a_2 and is split into two fine peaks unlike those in the a-FCNSB and a-FSB spectra. Features a_2 and b_2 in the nc-FCNSB spectra can be attributed to the crystalline Fe–Si bonds surrounding the Si atom because their lineshapes and positions closely resemble those of Fe–Si and differ substantially from those of Cu–Si shown in Fig. 4. This explanation is supported by our X-ray data and the Cu L_3 -edge XANES spectra. It is also consistent with the report of Refs. [2,3] that Fe–Si solid solution dominated and there was no observable Cu–Si chemical bond around the Si atom in nc-FCNSBs. Feature b_2 is distinctly enhanced and features a_2 and b_2 appear to be better resolved in the spectra of nc-FCNSBs relative to those of a-FCNSB and a-FSB. These spectra also illustrate the influence of Cu and/or Nb added under the optimum annealing condition, which is important in enhancing crystallization of the Fe–Si solid solution in nc-FCNSBs.

4. Conclusion

In summary, analyses of X-ray diffraction data and the Fe $L_{3,2}$ -edge XANES spectra reveal chemical inhomogeneity at the Fe sites in nc-FCNSBs. A characteristic two-peak feature above the Cu L_3 -edge of the nc-FCNSB spectra indicates that the Cu clusters essentially have a fcc structure. The chemical bonds around the Si atom in nc-FCNSBs are mainly Fe–Si bonds not Cu–Si bonds.

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