Electronic structure of the Fe–Cu–Nb–Si–B alloys by x-ray absorption spectroscopy

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We measured x-ray absorption near-edge-structure (XANES) spectra of nanocrystalline- (nc-) and amorphous- (a-) Fe$_{73.5}$Cu$_{1}$Nb$_{3}$Si$_{13.5}$B$_{9}$ (nc-FCNSB and a-FCNSB) and Fe$_{78}$Si$_{13}$B$_{9}$ (a-FeSiB) alloys at the Fe $L_{3,2}$ edge using the sample drain current mode and at the Cu $L_{3,2}$ and Nb $L_{3}$ edge and Si $K$ edge using the fluorescence mode. The features in the Fe $L_{3}$-edge XANES spectrum of nc-FCNSB changed shape significantly with the addition of Cu and Nb to the Fe–Si–B alloy under the optimum annealing conditions, indicating that Cu and Nb strongly influence the Fe 3d local electronic structure. Closely examining the Cu $L_{3,2}$-edge XANES spectrum of nc-FCNSB reveals that the Cu clusters essentially have a body-centered-cubic structure. The white-line features at the Nb $L_{3}$ edge suggest a slight increase in delocalization of Nb 4d orbits when a-FCNSB is crystallized into nc-FCNSB. The Si $K$-edge XANES spectrum demonstrates the dominance of Fe–Si bonds around the Si atom in nc-FCNSB. © 2000 American Institute of Physics.

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Recently a new class of soft magnetic alloys made by optimally crystallizing metallic glasses, for example, Fe–Si-based nanocrystalline alloys, has received considerable interest. The Fe$_{73.5}$Cu$_{1}$Nb$_{3}$Si$_{13.5}$B$_{9}$ alloy is among the soft magnetic materials of interest. Yoshizawa et al. reported that attractive soft magnetic properties were observable only when approximately 1% Cu and 3% Nb were added to the Fe–Si–B alloys with an annealing temperature of 550 °C for 60 min. A body-centered-cubic (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. The measurement of the Fe and Cu $K$ edges extended x-ray absorption fine structure spectra of Fe$_{73.5}$Cu$_{1}$Nb$_{3}$Si$_{13.5}$B$_{9}$ suggested that the modification of the microstructure by Cu in this alloy is due to the cluster-catalyzed nucleation of Fe-rich nanocrystals. Here we carry out Fe and Cu $L_{3,2}$-edge, Nb $L_{3}$-edge, and Si $K$-edge x-ray absorption near-edge-structure (XANES) measurements for the Fe$_{73.5}$Cu$_{1}$Nb$_{3}$Si$_{13.5}$B$_{9}$ alloy.

As-quenched amorphous (a) Fe$_{73.5}$Cu$_{1}$Nb$_{3}$Si$_{13.5}$B$_{9}$ (denoted a-FCNSB) alloy ribbon was prepared by the single roller method. The nanocrystalline (nc) Fe$_{73.5}$Cu$_{1}$Nb$_{3}$Si$_{13.5}$B$_{9}$ (nc-FCNSB) was obtained by heating at 550 °C for 60 min as described elsewhere. The x-ray diffraction (XRD) spectra of nc-FCNSB exhibits four diffraction lines of those of Fe–Si and bcc Fe phases as shown in Fig. 1. The sharp peak at $2\theta$=29.6° indicated that the Fe–B phase also made some contribution. The Fe and Cu $L_{3,2}$-edge, Nb $L_{3}$-edge, and Si $K$-edge XANES spectra of nc-FCNSB and a-FCNSB alloys were measured with the samples of amorphous (a) Fe$_{78}$Si$_{13}$B$_{9}$ (a-FeSiB) alloy, bulk Fe–Si and Cu–Si alloys, Cu, Fe, Nb foils, and 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, Nb $L_{3}$-edge, and Si $K$-edge spectra were taken at room temperature.

Figures 2 and 3 show, respectively, the normalized Fe and Cu $L_{3,2}$-edge XANES spectra of nc-FCNSB, a-FCNSB, a-FeSiB, Fe–Si, Cu–Si, and Cu and Fe metals. According to dipole-transition selection rules, the dominant transition is from Fe (Cu) 2$p_{3/2}$ and 2$p_{1/2}$ to the unoccupied Fe (Cu) 3$d$ electron states. The area beneath the white line in the Fe (Cu) $L_{3,2}$-edge XANES 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-FCNSB differ significantly from those of a-FCNSB, reference c-FeSiB, Fe–Si, and pure Fe metal. The Fe $L_{3,2}$-edge XANES spectra of nc-FCNSB, a-FCNSB, a-FeSiB, and Fe–Si are primarily composed of features $a_1$ and $b_1$. Feature $b_1$ is more prominent for nc-FCNSB than for a-FCNSB. The line shapes of the Fe $L_{3}$-edge XANES of nc-FCNSB/a-FCNSB and a-FeSiB differ
substantially, which suggests that the alloying with Cu and Nb strongly influences the Fe 3d electronic structure in nc-FCNSB/a-FCNSB. Our Fe L₃,₂-edge spectra reflect that the 3d electronic structure of first-row transition-metal ions depend strongly on the crystal-field symmetry and ligand-field splitting parameter 10Dq.8 Thole and van der Lann9 pointed out that the 3d transition-metal ions with a high-spin states have a relatively large branching ratio of the white-line intensity I(L₃)/(I(L₃) + I(L₂)). In a high-spin state these ions have close to or nearly saturated occupation of majority-spin 3d orbitals and highly depleted minority-spin 3d orbitals. The latter corresponds to a large number of unoccupied minority-spin 3d-derived states and appears as the L₃ feature in Fig. 2. Thus a larger branching ratio means a larger number of unoccupied minority-spin 3d-derived states and a higher-spin state. I(L₃) and I(L₂) obtained are, respectively, 18.8 ± 0.5 and 7.7 ± 0.3 for nc-FCNSB and 10.0 ± 0.5 and 6.4 ± 0.3 for a-FCNSB. The branching ratio is 0.71 for nc-FCNSB 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 Cu and Nb enhances the spin state of Fe ions and improves the magnetic property of the nc-FCNSB alloy.

In Fig. 3 the general line shapes in the Cu L₃,₂-edge XANES spectra of nc-FCNSB and a-FCNSB differ from those of the Cu–Si and Cu metal. It has been well established10 that there are characteristic two- and three-peak features in the Cu L₃-edge XANES spectra of bcc and face-centered-cubic (fcc) Cu metal and Cu alloys, respectively. The Cu clusters may form a bcc or fcc structure in the nc-FCNSB alloy.2,3 Although Ref. 10 reported some deviations of the relative intensities and peak positions from those of bcc Cu, according to Fig. 3 the local structure of the Cu clusters in nc-FCNSB essentially resembles the two-peak feature of the bcc structure. A comparison between the spectra of nc-FCNSB and Cu–Si shows that no observable Cu–Si chemical bonds occur, although Hono et al. suggested...
that the added Cu may cause a concentration fluctuation of Fe because of partial substitution of Fe (Ref. 2) by Cu and the existence of the Cu–Si bond in nc-FCNSB.

Figure 4 shows the normalized Nb $L_3$-edge XANES for nc-FCNSB, a-FCNSB and the reference Nb metal. Feature $a_2$ in the Nb $L_3$-edge XANES mostly involved transitions from the Nb 2$p_{3/2}$ to unoccupied 4$d$ final states. The general line shapes in the Nb $L_3$-edge XANES spectra of nc-FCNSB, a-FCNSB, and Nb display similar features above the Nb $L_3$ edge, except that the intensity of feature $a_2$ and its higher energy satellite structure $b_2$ are considerably larger in the pure Nb spectrum. Feature $a_2$ for nc-FCNSB is lower than that for pure Nb, while feature $a_2$ for a-FCNSB is only slightly lower than that for nc-FCNSB. A lower feature near the threshold in the XANES spectrum qualitatively means fewer unoccupied Nb 4$d$ states and reduced delocalization of Nb 4$d$ orbitals. This trend reflects a decreasing metallic character in the order of pure Nb, nc-FCNSB, and a-FCNSB.

Figure 5 presents the normalized Si $K$-edge XANES spectra of nc-FCNSB, a-FCNSB, a-FSB, Fe–Si, Cu–Si, and c-Si(100). The Si $K$-edge XANES spectrum reflects a transition from the Si 1$s$ core level to the unoccupied Si 3$p$-derived states. The general line shape of the features in the nc-FCNSB spectra differs from those in a-FCNSB and a-FSB, which indicates that the chemical state of the absorbing Si atom in nc-FCNSB differ significantly from those in a-FCNSB and a-FSB. Figure 5 also shows that the Si $K$-edge XANES spectra have a main feature $a_3$ and a sharp feature $b_3$. Feature $b_3$ in the nc-FCNSB spectrum is more prominent than feature $a_3$ and is split into two fine peaks unlike those of a-FCNSB and a-FSB. Features $a_3$ and $b_3$ in the nc-FCNSB spectrum can be attributed to the crystalline Fe–Si bonds surrounding the Si atom because their line shapes and positions closely resemble those of Fe–Si and differ substantially from those of Cu–Si shown in the inset of Fig. 5. It is also consistent with the report in Ref. 2 that Fe–Si solid solution dominated and that there was no observable Cu–Si chemical bond around the Si atom in nc-FCNSB. Feature $b_3$ is distinctly enhanced and features $a_3$ and $b_3$ appear to be better resolved in the spectrum of nc-FCNSB 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-FCNSB.

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7. Our Fe $L_{3,2}$-edge XANES spectrum of the Fe metal may contain some contribution from oxidized surface Fe atoms. However, the general line shapes in the spectrum of the Fe metal are quite similar to those of the pure Fe thin film reported previously [see M. M. Schwickert, G. Y. Guo, M. A. Tomaz, W. L. O’Brien, and G. R. Harp, Phys. Rev. B 58, R4289 (1998)].