Local Structure Analysis of Fe$_{83.3}$Si$_4$B$_8$P$_4$Cu$_{0.7}$ Nanocrystalline Alloy by XAFS*

Akimi Oono and Takafumi Miyanaga
Department of Advanced Physics, Hirosaki University, Hirosaki, Aomori 036-8561, Japan

Takeshi Kubota
NJRISE, Hirosaki University, Aomori 030-0813, Japan

We investigated the local structure changes of Fe$_{83.3}$Si$_4$B$_8$P$_4$Cu$_{0.7}$ nanocrystalline alloy prepared by arc melting with various annealing conditions by XAFS. It was found that individual structural changes occur around each element (Fe, Si, P, Cu) by several annealing steps. The as-spun sample shows amorphous like structure. The Fe and Si phase crystallize by annealing at first transition temperature (693 K). On the other hand the local structure around Cu and P atoms changed by two steps at 693 K and 823 K. In order to examine the structure more detail, by the transmission mode and that of Cu was by the fluorescence mode with 19-element SSD (Solid State Detector) at BL12C using InSb(111) monochromator. All X-ray absorption spectra were measured at room temperature. EXAFS data analysis was performed by XANADU code [3] and FEFF8.10 code [4]. The EXAFS oscillation curves $\chi(k)$ were obtained by subtraction of the smooth X-ray absorption background and normalization. The function $k^3\chi(k)$ was Fourier transformed over the range $2.0 \leq k \leq 18.5$ Å$^{-1}$ for Fe and Cu K-edge, $2.0 \leq k \leq 17.2$ Å$^{-1}$ for P K-edge, $2.0 \leq k \leq 8.1$ Å$^{-1}$ for Si K-edge.

I. INTRODUCTION

Nanocrystalline soft-magnetic alloys have been attracting a great attention. The FeSiBPCu nanocrystalline alloy has a characteristic feature of a high saturation magnetic flux density and a super-low core loss as a soft-magnetic material. Over the last two decades, nanocrystalline alloys of FeSiB, FeSiBNbCu, FeZrBCu and FeCoZrBCu have been industrially developed [1]. A drastic reduction of the amount of carbon dioxides can be expected from the use of the advantage of the super-low core loss property as a transformer or a motor core in the future. The structure of FeSiBPCu nanocrystalline alloy prepared by arc melting just after preparation of the sample. The Fe and Si phase crystallize by annealing at first transition temperature (693 K). On the other hand the local structure around Cu and P atoms changed by two steps at 693 K and 823 K. It was suggested that the Fe phase including the isolated Cu atoms can be easily crystallized and shows the high magnetic performance.

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II. EXPERIMENTAL AND DATA ANALYSIS

The ribbon sample of Fe$_{83.3}$Si$_4$B$_8$P$_4$Cu$_{0.7}$ alloy was prepared by the arc melting method in Ar gas and cooled rapidly in the atmosphere using a single-roller melt-spinning. The sample thickness was about 20 μm. The samples were annealed at 693 K and 823 K for 60 min to produce the nanocrystalline phase. The rate of rising temperature was 40 K/min. X-ray absorption measurements were carried out at Photon Factory, KEK, Japan. The K-edge X-ray absorption spectra of Fe was measured by the transmission mode and that of Cu was by the fluorescence mode with 19-element SSD (Solid State Detector) at BL12C using Si(111) crystal monochromator. The K-edge X-ray absorption spectra of Si and P were measured by the fluorescence mode with SSD (Silicon Drift Detector) at BL11B using InSb(111) monochromator. All X-ray absorption spectra were measured at room temperature. EXAFS data analysis was performed by XANADU code [3] and FEFF8.10 code [4]. The EXAFS oscillation curves $\chi(k)$ were obtained by subtraction of the smooth X-ray absorption background and normalization. The function $k^3\chi(k)$ was Fourier transformed over the range $2.0 \leq k \leq 18.5$ Å$^{-1}$ for Fe and Cu K-edge, $2.0 \leq k \leq 17.2$ Å$^{-1}$ for P K-edge, $2.0 \leq k \leq 8.1$ Å$^{-1}$ for Si K-edge.
III. RESULTS AND DISCUSSION

First, we have checked the XRD of the as-spun sample of the Fe$_{83.3}$Si$_4$B$_8$P$_4$Cu$_{0.7}$ alloy to show the amorphous character. Fourier transform (FT) of the EXAFS of Fe K-edge is shown in Fig. 1. The peak intensity in FT of the as-spun sample is quite small because of its amorphous character. By annealing at 693 K the peak intensities increase compared with the as-spun sample and become close to that of fcc Fe structure. This indicates that the local structure around Fe atom is crystallized by the annealing at 693 K and it shows no more change by further annealing with high temperature (823 K).

Figure 2 shows the FT for Si K-edge for Fe$_{83.3}$Si$_4$B$_8$P$_4$Cu$_{0.7}$ alloy. Analogously to the result of Fe K-edge, the as-spun sample shows the amorphous character but the first nearest peak intensity increases and second nearest peak appears by annealing at 693 K. This result suggests that the structure around Si atoms were also crystallized by annealing at 693 K. In the case of Si, a little more crystallization proceeded by the annealing at 823 K.

Figure 3 shows FT for P K-edge EXAFS. The peak intensities once decrease by annealing at 693 K from the as-spun sample, but they increase greatly by annealing at 823 K. The result suggests that the local structure of P atoms is expected to be distorted after the first annealing (693 K) and crystallize higher annealing temperature (823 K).

Figure 4 shows (a) $k\chi(k)$ spectra and (b) FT for Cu K-edge EXAFS, respectively. FT spectrum (b) for the as-spun sample shows the amorphous like character and it changes to crystalline state by annealing at 693 K, which behavior is similar to that of Fe and Si K-edge. In addition, by annealing at 823 K, the peak intensity further increased. Therefore, it can be supposed that the local structure around Cu atom changes by two steps at these two phase transition temperatures. Judging from the $k\chi(k)$ spectra (a), the structure around Cu atoms in Fe$_{83.3}$Si$_4$B$_8$P$_4$Cu$_{0.7}$ annealed at 823 K is close to that for fcc Cu.

In order to discuss the detail local structure around Cu atom, we compared the XANES of Cu K-edge of Fe$_{83.3}$Si$_4$B$_8$P$_4$Cu$_{0.7}$ alloy annealed at 693 K with that for Fe K-edge of bcc Fe (Fig. 5(a)). And the XANES of Cu K-edge annealed at 823 K with fcc Cu (Fig. 5(b)). From Fig. 5(a), the XANES of the Fe$_{83.3}$Si$_4$B$_8$P$_4$Cu$_{0.7}$ alloy annealed at 693 K may have a similar structure to that of
TABLE I: Interatomic distance (r), coordination number (N) and root mean square displacement (σ) of the Fe₈₃.₃Si₄B₈P₄Cu₀.₇ for the as-spun sample, annealed at 693 K, and 823 K and fcc Cu obtained by the curve fitting method of Cu K-edge EXAFS.

<table>
<thead>
<tr>
<th>sample</th>
<th>atomic type</th>
<th>r (Å)</th>
<th>N</th>
<th>σ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-spun</td>
<td>Cu-Cu</td>
<td>2.53</td>
<td>7.0</td>
<td>0.12</td>
</tr>
<tr>
<td>annealed at 693 K</td>
<td>Cu-Fe</td>
<td>2.49</td>
<td>4.6</td>
<td>0.07</td>
</tr>
<tr>
<td>annealed at 823 K</td>
<td>Cu-Cu</td>
<td>2.55</td>
<td>11.6</td>
<td>0.10</td>
</tr>
<tr>
<td>fcc Cu</td>
<td>Cu-Cu</td>
<td>2.55</td>
<td>12.0</td>
<td>0.09</td>
</tr>
</tbody>
</table>

bcc Fe, so Cu atoms are expected to be incorporated into the bcc Fe site. On the other hand, the XANES for the Fe₈₃.₃Si₄B₈P₄Cu₀.₇ alloy annealed at 823 K shows the same as that for fcc Cu (Fig. 5 (b)). Therefore, it can be considered that the dispersed Cu atoms in the bcc Fe phase aggregates and crystallizes as the fcc Cu phase by annealed at 823 K.

![Absorption intensity vs. E(eV) for Cu K-edge XANES](image)

FIG. 5: (a) Cu K-edge XANES of the Fe₈₃.₃Si₄B₈P₄Cu₀.₇ annealed at 693 K (red line) and Fe K-edge XANES of bcc Fe (black line). Each absorption edge is set to 0 eV. (b) Cu K-edge XANES of the Fe₈₃.₃Si₄B₈P₄Cu₀.₇ annealed at 823 K (blue line) and of fcc Cu (black line).

Finally, to discuss the structure more detail we analyzed the Cu K-edge EXAFS of Fe₈₃.₃Si₄B₈P₄Cu₀.₇ alloy by the curve fitting method. In order to analyze in k-space, the first peak including the information about the first nearest neighboring atom (Cu–Cu) of Cu K-edge FT was inversely Fourier transformed. For the curve-fitting process, an intrinsic loss factor (S₀²=0.85 and ΔE₀=1.19 eV were determined from fcc Cu as a standard. The fitting results were summarized in Table I. The as-spun sample shows the character of amorphous Cu because of the small coordination number (N) and large root mean square displacement (σ) for first nearest Cu–Cu in comparison to the fcc Cu. And the structural parameters for the Fe₈₃.₃Si₄B₈P₄Cu₀.₇ alloy annealed at 823 K is quite similar to that for fcc Cu. As expected from the XANES result shown in Fig. 5(b) this curve-fitting result indicates that the local structure around Cu for the Fe₈₃.₃Si₄B₈P₄Cu₀.₇ alloy annealed at 823 K is same as fcc Cu. We analyzed the EXAFS for Fe₈₃.₃Si₄B₈P₄Cu₀.₇ alloy annealed 693 K as a model in which there is Cu–Fe first nearest neighbor as expected from the previous discussion in Fig. 5(a). It is interesting that r for Cu–Fe is close to that of Fe–Fe (2.48 Å) in bcc Fe. This curve fitting result also supports that Cu atom are located in the bcc Fe phase individually in the Fe₈₃.₃Si₄B₈P₄Cu₀.₇ alloy annealed at 693 K as discussed in Fig. 5(a). But the N for Cu–Fe model (N=4.6) is smaller than that for bcc Fe (N=8.0). This means that the local structure around Cu for this intermediate state may not be pure bcc Cu model but any mixture of fcc Cu phase.

It was reported that the addition of Cu promotes the crystallization of α-Fe and then the first transition temperature was lowered [5]. At lower than 693 K Cu is amorphous phase, but the Cu atom is embedded in bcc Fe phase between 693 K and 823 K. The present result means that the dispersion of Cu atoms into Fe phase promotes the crystallization or α-Fe phase including the isolated Cu atoms can be easily crystallized. The magnetic properties of this materials are mainly governed by α-Fe phase. The high magnetic performance such as the high magnetic density and the low core loss can be originated from the Fe phase with dispersion of isolated Cu atoms.

IV. CONCLUSION

Structural change around Fe, Si, P, and Cu atoms in Fe₈₃.₃Si₄B₈P₄Cu₀.₇ nanocrystalline alloy with annealed at 693 K and 823 K was investigated by XAFS. The Fe and Si phase crystallized by annealing at 693 K. On the other hand, the P and Cu phase crystallize by two steps and completely crystallized at 823 K. In the annealing process, Cu K-edge shows interesting behavior. In the intermediate phase between 693 K and 823 K Cu atoms are embedded in bcc Fe phase and this behavior may be related to the characteristically high magnetic performance in this region.

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