amorphous, glass and liquids

XANES spectra of mechanical alloyed Y-Cu system

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We report changes in the structure and the electronic states of YCu$_2$ during mechanical alloying. The x-ray diffraction shows that milling for about 60 h transforms mixture of elemental powders of Y and Cu into an amorphous alloy. We have measured the x-ray absorption near edge structure (XANES) spectra of mechanically alloyed YCu$_2$ at Cu K and Y K edges at various milling time. The pre-edge peak near the Cu K threshold grows remarkably and its central energy decreases with increasing the milling time. The absorption near the Y K threshold, on the other hand, decreases with milling time. We discuss these features of XANES spectra in connection with the phase transformation from the crystalline to amorphous states.

1. Introduction

The structure and the electronic states of amorphous materials have been an issue of great interest not only in condensed matter physics but also in industrial applications. Amorphous metallic alloys have been synthesized by rapid cooling techniques such as vapor deposition, sputtering and melt spinning. They are based on the idea that a high cooling rate prevents any crystalline phase from nucleating and growing.

Recently mechanical alloying was developed as a new method for amorphization (Koch *et al.*, 1983; Weeber & Bakker, 1988; McCormick, 1997). It is quite different from the conventional methods because amorphous alloys can be prepared by phase transformation using the solid state interdiffusion reaction on the interface between constituent elements. In the method we need not deep eutectics in a phase diagram to synthesize amorphous materials, although it is of great importance in amorphization by the melt spinning technique. A negative heat of mixing plays an essential part in amorphization by the mechanical alloying (Schwarz & Koch, 1986). According to the phase diagram of Y-Cu system, YCu$_2$ corresponds to an intermetallic composition. This means that it is hard to prepare amorphous YCu$_2$ by melt spinning. In the work we investigate how mixture of Cu and Y transforms into an amorphous alloy YCu$_2$ during mechanical alloying from the viewpoint of the structure and the electronic states of the constituents Cu and Y using x-ray absorption near edge structure (XANES) and x-ray diffraction.

2. Experimental procedures

The starting material in our mechanical alloying was the powder of elemental Cu and Y in the purity of 99.95%. The particle size of Cu powder was about 50 μm, while that of Y was about 800 μm much larger than the former. The powder of a total of 15 g was mixed in the nominal atomic ratio of Cu:Y=2:1 and sealed under argon atmosphere in a stainless steel (SUS304) vial with stainless steel balls. The mechanical alloying was carried out in a ball mill on a vibrating frame with a ball to powder ratio of 7:1 in weight. In an energy dispersive electron probe microanalysis the powder after milling for 200 h showed the concentration of 66 at%Cu with impurity of iron less than 1 at%, which came from the stainless steel vial and balls, and did not contain any oxides. The specimen for x-ray diffraction and XANES measurements was the powder dusted onto Scotch tape homogeneously.

X-ray diffraction patterns were taken in a conventional θ-2θ scan mode using Cu Kα radiation. The XANES measurement was made using synchrotron radiation at the BL-10B station (Nomura & Koyama, 1989) of the Photon Factory, Institute of Materials Structure Science, Tsukuba, Japan. A channel-cut Si(311) crystal monochromator provided a beam between 7 keV and 30 keV with a energy resolution of ΔE/E≈10^{-4}. The storage ring was operated at 2.5 GeV with a beam current of 400 mA in maximum. The XANES spectra were recorded at the K edges of Cu and Y in the transmission mode at room temperature using a couple of ionization chambers. The energy of a monochromatized beam was calibrated using a pre-edge peak of a metallic Cu foil of 5μm thick in the purity of 5N (8978.78 eV).

3. Results and Discussion

Figure 1 shows x-ray reflections from mechanically alloyed YCu$_2$ at various milling time. Some patterns in the upper part are drawn to scale by a half of observed intensity for convenience sake. As indexed in the figure, all the reflections of fcc Cu and hcp Y elements are detected in the pattern after milling for 4 h. Intensity of the reflections shows a rapid decrease by milling till 20 h. In the specimen of 30 h milling we can observe only a small reflection from Y and four peaks from Cu. At 50 h all the reflections from the lattice planes of fcc Cu and hcp Y disappear and a broad maximum around 40 degrees appears. This shows that the powder
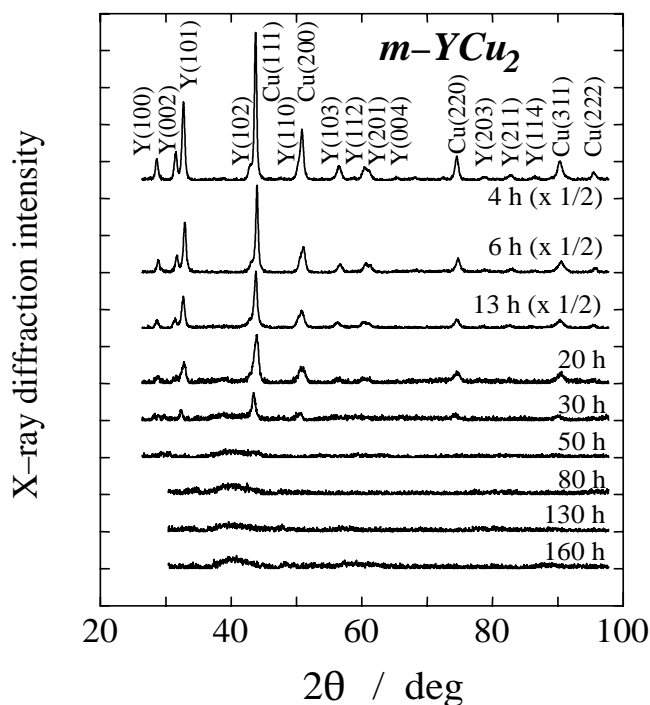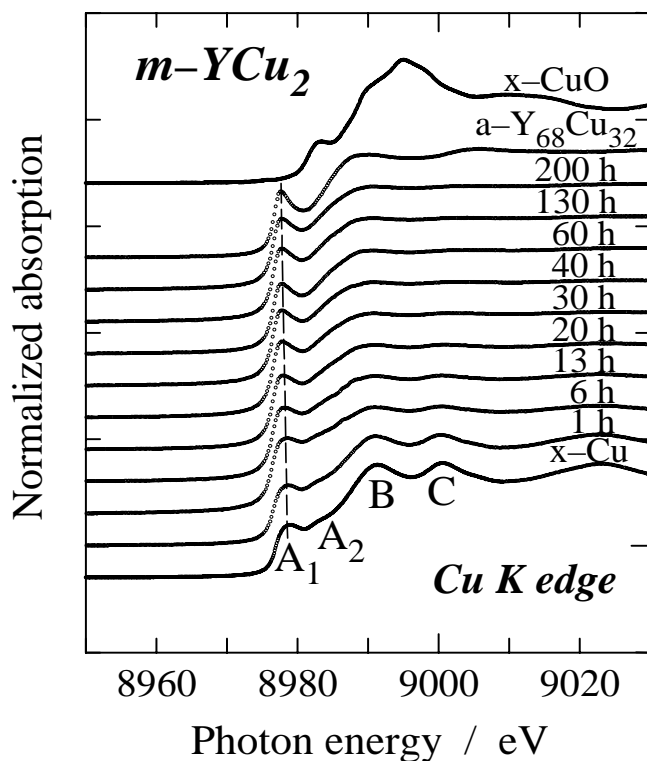

Figure 1
The x-ray reflections from mechanically alloyed YCu$_2$ after various milling time. Intensity of some upper curves is reduced by a half. The reflections from fcc Cu and hcp Y are indexed.

of the intermetallic composition of YCu_2 is almost in an amorphous phase by milling for about 50 h. We have milled the specimen till 200 h. The x-ray diffraction pattern does not show any change with milling from 50 h till 200 h.

We expect a drastic change in electronic states of Cu and Y atoms in the solid state reaction of amorphization. This motivates our investigation of XANES which reflects an unoccupied density of states directly (Grunes, 1983). Normalized XANES spectra near the Cu K and Y K edges of mechanically alloyed YCu_2 are shown in Figs. 2 and 3. Normalization of XANES is of great importance in comparing each spectrum with the other without knowing the difference in absorption due to thickness of the specimen. We normalize the observed spectra as follows. We regard the energy at the first inflection point of the spectrum as the threshold E_0. For the background absorption due to all but the $1s$ electrons, we obtain the exponent n in the functional form of $a+bE^n$ to be –2.85 from the best fit to both our collected absorption data and the compiled tables (McMaster *et al.*, 1969). Subsequently the constants a and b of each spectrum are estimated from the least squares fit of the observed absorption within the energy range between E_0–500 eV and E_0–40 eV to the functional form. The cubic spline method is applied for estimating the absorption due to an isolated absorbing atom. An edge jump is the difference between these calculated curves at the threshold. We subtract the background from the raw data, scale the result by the edge jump and finally obtain the normalized spectrum.
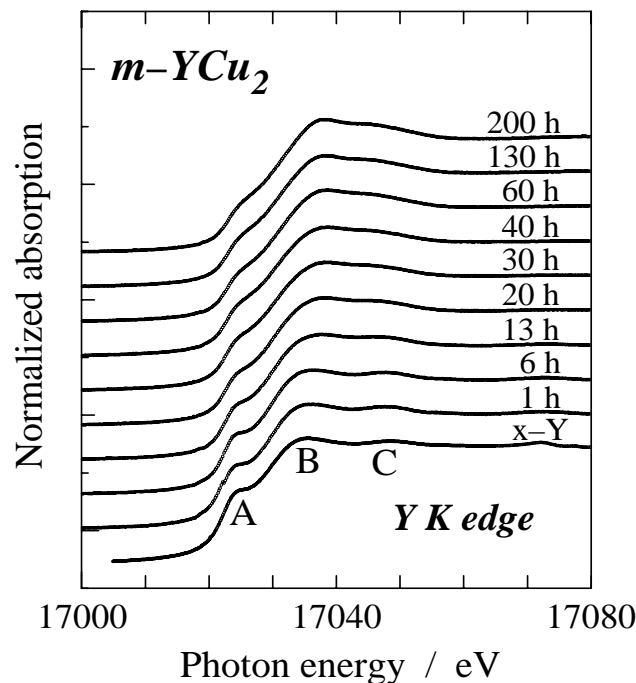
In Fig. 2 the spectra of an amorphous $Y_{68}Cu_{32}$ ribbon made by the melt spinning technique, an oxide CuO and a Cu metallic foil are also shown for comparison. The normalized XANES spectrum

of the Cu metal has a well known pre-edge peak A_1 and other peaks B and C. A mark A_2 represents another absorption, which will appear explicitly in the deconvolution below. They are ascribed to the electric dipole transitions from $1s$ to $4p$ states. The peaks B and C slightly reduce by milling for 1 h. They flatten rapidly with milling till 60 h and show no change in the form from 60 h till 200 h. It is usual for the spectrum to become flat in the amorphous state. The absorption A_1 grows even by the milling for 1 h and transforms into a sharp peak at 60 h. It does not change shape after 60 h till 200 h at all and is as sharp as that of the amorphous $Y_{68}Cu_{32}$ alloy. It should be noted that the central energy of the peak A_1 moves to lower energy with the milling as shown by the broken line. The threshold of CuO occurs at a higher energy than that of the Cu metal, which is a common feature in $3d$ transition metals and their oxides (Grunes, 1983). On the contrary, the threshold of YCu_2 milled for 200 h moves to a lower energy. This supports that oxygen does not contaminate the powder milled till 200 h. As shown in Fig. 3, crystalline Y has three absorptions A, B and C. The electric dipole allowed $1s \rightarrow 5p$ transition is responsible for them. They decrease in amplitude gradually during milling from 1 h till 60 h and have no change after 60h till 200 h. They exist even at 200 h. The observation of the Cu K and Y K XANES spectra gives the rather important results as follows: the amorphous state has been already achieved at 60 h which is consistent with the result from x-ray diffraction mentioned above; the subsequent milling after 60 h makes no change in the electronic states of Cu and Y atoms in the amorphous phase.

One of the most important part of the work is to detail changes in configuration of the electronic states by the mechanical alloying, especially the peaks near the thresholds of both Cu and Y. This is because we decompose the spectra according the following procedure. In our deconvolution procedure the transition into continuum states at the threshold is represented by an arctangent function in the form,

Figure 2
Normalized XANES spectra near the Cu K edge for mechanically alloyed YCu_2 at various milling time. The labels A_1, A_2, B and C are attributed to the dominant $1s \rightarrow 4p$ transitions. Amorphous $Y_{68}Cu_{32}$ prepared by liquid quenching, crystalline CuO and metallic Cu are presented. The broken line shows that the well known pre-edge peak shifts to lower energy with increasing the milling time.
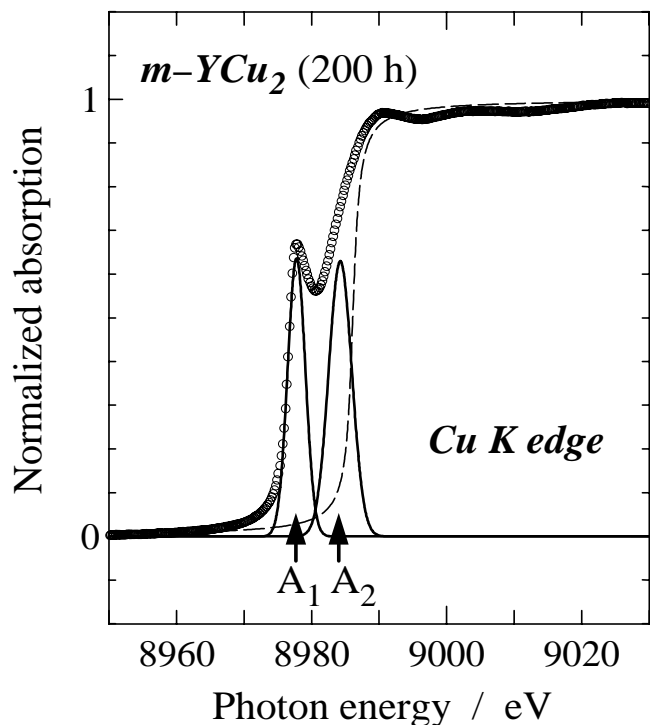

Figure 3
Normalized XANES spectra of mechanically alloyed YCu_2 near the Y K edge at typical milling time. The dominant peaks assigned as the electric dipole $1s \rightarrow 5p$ transition, which are labeled as A, B and C. Crystalline Y is also shown for comparison.
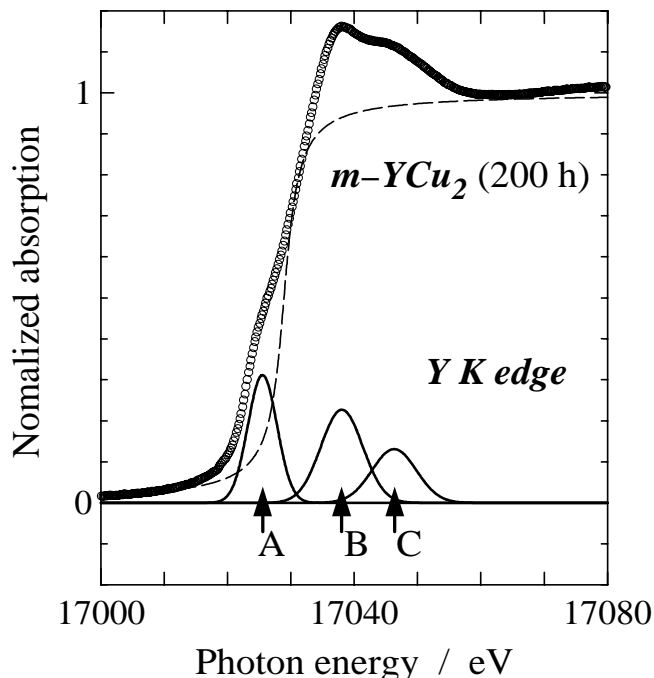
$$f(E) = \frac{1}{\pi} \arctan\left(\frac{E - E_c}{\Gamma / 2}\right) + \frac{1}{2}, \qquad (1)$$

where E_c shows the difference of the core level from the continuum and Γ represents the core-hole width of the $1s$ states. We approximate the transition from $1s$ to p states using the Gaussian function. Figure 4 shows the deconvolution of YCu_2 milled for 200 h at the Cu K edge where the broken line is eq. (1) with E_c=8986.1 eV and Γ=1.5 eV. There appears another peak A_2 above the pre-edge peak A_1. In Fig. 5 that of the Y K edge is presented where the broken line represents the transition into the continuum with E_c= 17028.9 eV and Γ=3.48 eV. Only one peak forms the absorption A of the Y K edge. These values of Γ are consistent with those of the literature (Müller *et al*., 1982).

We here discuss behavior of the peaks A_1 and A_2 at the Cu K edge and the peak A of the Y K edge. The central energy of the peak A_1 shown by an arrow in Fig. 4 decreases with increasing the milling time: the milling for 60 h makes a reduction of 1.0 eV and there is no change in the energy from 60 h till 200 h. The peak A_2 keeps the position from the beginning till 200 h. In the Y K edge the peak A has an increase in the central energy of 1.4 eV during the milling from 0 h till 60 h, while it does not move in energy after 60 h. The behavior up to 60 h forms a striking contrast between them. The peak A_1 of the Cu K edge is attributed to the $4p$ states strongly influenced by the $3d$ states; the peak A of the Y K edge reflects the $5p$ states having a $4d$ orbital character through the p-d hybridization (Müller, 1978).

Figure 5
Deconvolution of the Y K XANES spectrum after milling for 200 h. The broken line shows the transition to the continuum and the solid lines are the $1s \rightarrow 5p$ transitions marked as A, B and C.

4. Conclusions

The mixture of elemental Cu and Y powder transforms into the amorphous alloy having the intermetallic composition of YCu_2 by the solid state interdiffusion reaction for about 60 h. The milling after 60 h till 200 h makes no change in the structure and the electronic states of the amorphous alloy. We find from the deconvolution model that there is a remarkable contrast between the peak A_1 of the Cu K edge and the absorption A of the Y K edge in the early stage of milling till 60 h. This behavior comes from the $3d$ and $4d$ orbital characters through strong p-d hybridization.

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Figure 4
Deconvolution of the Cu K XANES signal of YCu_2 mechanically alloyed for 200 h. The broken line shows the arctangent function for the transition to the continuum states. The solid lines are two Gaussian functions for transitions labeled as A_1 and A_2, which are assigned to the $1s \rightarrow 4p$ transitions. The transition A_1 reflects the $3d$ orbital character through the p-d hybridization.