XANES study in the solid state reaction of Zr-Ni system

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We have measured x-ray absorption near edge structure (XANES) spectra of mechanically alloyed ZrNi near Ni and Zr K edges as a function of milling time. The x-ray diffraction shows that the system is transformed into an amorphous phase by milling for about 60 h. With increasing the milling time, a small absorption near the Ni threshold rises and finally forms a peak in the amorphous phase, while an absorption near the Zr threshold shows a gradual decrease. The peak of the Ni K edge reflects $3d$ character strongly hybridized with $4p$ states, while the absorption of the Zr K edge comes from states having a $4d$ orbital character.

Keywords: XANES, mechanical alloying, ZrNi, amorphous, $1s{\rightarrow}4p$ transition, $1s{\rightarrow}5p$ transition, *p-d* hybridization

1. Introduction

It has been confirmed that mechanical alloying is a powerful technique of synthesizing amorphous materials (Weeber & Bakker, 1988; McCormick, 1997). It is a high energy ball milling using a solid state interdiffusion reaction at interfaces between elemental metals in the mixture (Koch *et al*., 1983; Schwarz & Koch, 1986). It is completely different in a solid state phase transformation from conventional techniques such as deposition from a gas phase and quenching from a liquid phase.

Amorphization range of Zr-Ni system by mechanical alloying has been successfully extended to be about between 30 at%Ni and 80 at%Ni with different apparatuses such as a planetary ball mill and a vibrating frame milling (Weeber & Bakker, 1988; Eckert *et al*., 1988). Such a wide concentration range of glass formation means that amorphization by mechanical alloying has no need of deep eutectics in the phase diagram, although it plays an essential role in amorphization by the melt spinning technique. The reaction from crystalline to amorphous phases in the system has been investigated from the viewpoint of structural and thermal properties by means of x-ray diffraction and differential scanning calorimetry (Lee *et al*., 1990; Mizutani *et al*., 1990; Chen *et al*.,1993). However, few investigations have been carried out on changes in the electronic state during the mechanical alloying. From the measurements of x-ray absorption near edge structure (XANES) and x-ray diffraction, in the paper, we show how the structure and the electronic states of constituent elements transform from crystalline mixtures of Zr and Ni to an amorphous alloy during the milling.

2. Experimental

The starting material was the mixture of Zr and Ni powder in the purity of 3N5 in the nominal atomic ratio of 1:1, the particle sizes of which were about 50 μm. The total amount of the mixture was 15 g. It was milled in a stainless steel (SUS304) vial on a vibratory apparatus in an argon atmosphere. The ratio of the mixture to the stainless steel balls was 1:7 in weight. An energy dispersive electron probe microanalysis in a scanning electron microscope detected that the concentration of the powder was 55 at%Ni after milling for 200 h. Contamination of the specimen came mainly from the stainless steel vial and balls. The impurity of iron less than 1 at% was observed in the alloy after 200 h milling. The specimens for x-ray diffraction and XANES measurements were the powder fixed homogeneously on an adhesive tape.

The x-ray diffraction measurement was made using Cu Kα radiation in a conventional θ-2θ scan mode. The XANES measurement was carried out at the BL-10B station (Nomura & Koyama, 1989) of the 2.5 GeV storage ring with the beam current of about 350 mA in the Photon Factory. A channel-cut Si(311) crystal monochromatized the synchrotron radiation beam from a bending magnet. We measured XANES spectra near the Ni K (8328 eV) and Zr K (17987 eV) edges at 295 K in the transmission mode using a couple of ionization chambers. The energy of photons from the monochromator was calibrated with that of a well known pre-edge peak of a Cu foil of 5 μm thick in the purity of 5N (8978.78 eV).

3. Results and Discussion

The x-ray diffraction patterns of mechanically alloyed ZrNi in several milling time are shown in Fig. 1. It is noted that the intensity at 1 h scales down by a half. The pattern after milling for 1 h has all reflections from lattice planes of fcc Ni and hcp Zr elements, which are indexed in the figure. Although they are still observed at 10 h, they reduce the intensity remarkably. Almost all but a few reflections such as Zr(101) and Ni(111) vanish at 30 h. At 50 h the typical broad maximum appears near 40 degrees, which shows that a great part of the specimen is amorphous. In the milling for 90 h sharp reflections have completely disappeared. The specimen has been milled till 200 h. However, we cannot observe any change in the x-ray diffraction pattern after 90 h. This
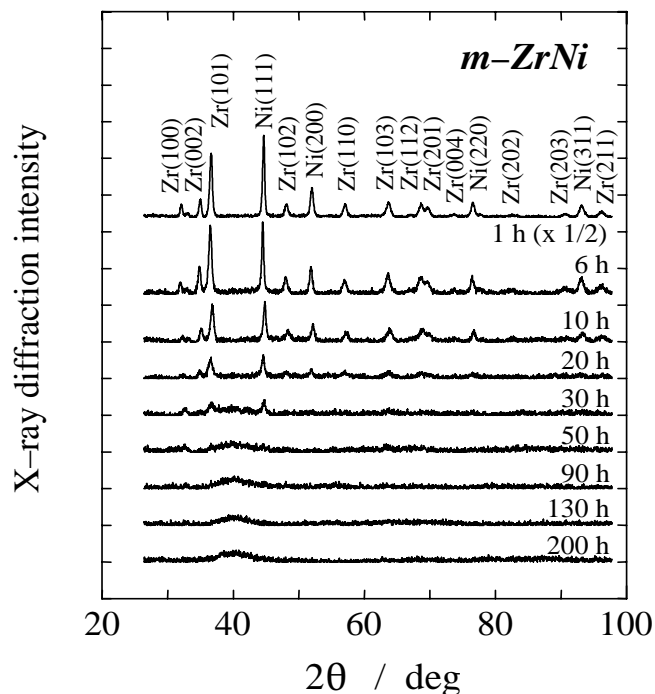
Figure 1
X-ray diffraction patterns of mechanically alloyed ZrNi at typical milling time. Note that the intensity at 1 h is reduced by a half. The reflections from lattice planes of fcc Ni and hcp Zr are indexed.
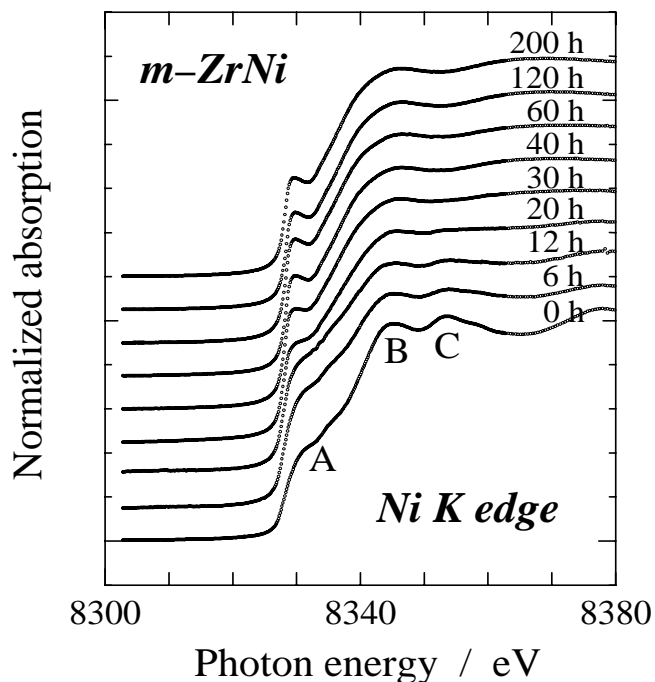
Figure 2
Normalized XANES spectra near the Ni K threshold for mechanically alloyed ZrNi after various milling time. The marks A, B and C show dominant absorptions.
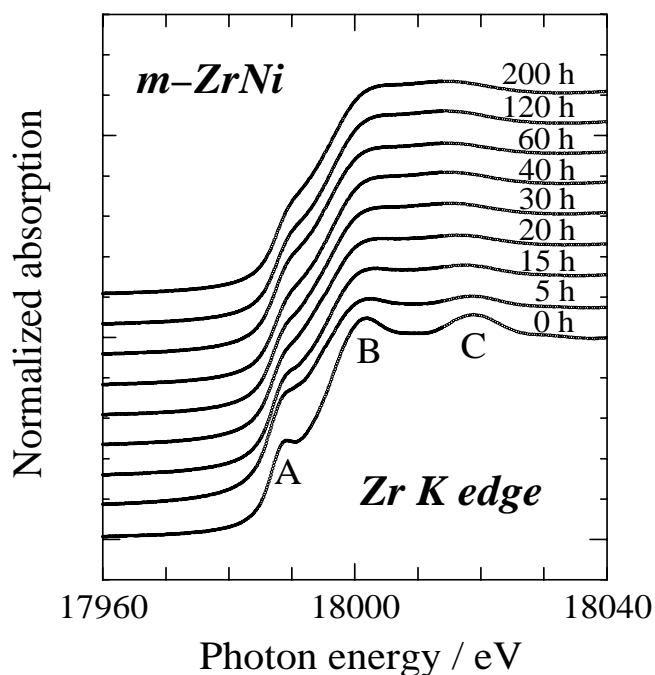
Figure 3
Normalized XANES spectra of ZrNi near the Zr K edge at typical time of mechanical alloying. The dominant peaks are labeled as A, B and C.

means that milling for nearly 60 h makes the specimen amorphous.

We have measured XANES spectra for mechanically alloyed ZrNi near the Ni and Zr K edges to investigate the electronic states of the constituent atoms in the phase transformation from the mixture of the elements to the amorphous alloy. Normalization of the XANES signals is of much importance to eliminate the difference in the thickness of each specimen. At first the threshold is assumed to be the energy at the maximum of the first derivative of the absorption on energy. In the second step the background due to all but the 1s state is deduced from approximating the observed absorption between -500 eV and -40 eV below the threshold to an equation in the form of $a+bE^{-2.85}$ with a couple of constants a and b where E is the photon energy. The exponent of the form is derived from the best fit to both our observed absorption data and the compiled tables (McMaster *et al.*, 1969). A hypothetical absorption due to an isolated atom is estimated from the cubic spline fit to the observed signal sufficiently above the threshold, that is, +30 eV to +500 eV. We calculate an edge jump from the difference between these extrapolations at the threshold. Finally we subtract the background from the observed data and divide the residual by the edge jump.

Figure 2 shows the normalized XANES spectra thus obtained for mechanically alloyed ZrNi near the Ni K edge for typical milling time. The spectrum at 0 h before milling shows a characteristic structure of fcc Ni, that is, a small absorption A and a couple of peaks B and C. They are attributed to the electric dipole $1s \rightarrow 4p$ transitions. Although the peaks B and C decrease the amplitude rapidly in the early stage of milling, they persist until 20 h. After milling for 30 h the peak C disappears and the peak B becomes rather flat. The shape of B does not change after 60 h till 200 h. It is a common feature of amorphous materials that amplitude of the oscillation above the edge reduces. The absorption A at 0 h consists of a couple of peaks as shown below (Grunes, 1983). It swells gradually with the milling till 12 h, which shapes like a step from 20 h till 30 h. With further milling the left edge of the step grows into a sharp peak in the amorphous phase. Such features have also been observed in XANES of the Ni K edge of mechanically alloyed Y_2Ni (Nakai & Tokuyoshi, 1999).

In Fig. 3 we present the normalized XANES spectra at the Zr K edge of mechanically alloyed ZrNi. Crystalline Zr corresponding to 0 h has three peaks A, B and C. They are assigned as the electric dipole $1s \rightarrow 5p$ transition. In the early stage of milling till 15 h they reduce their amplitude remarkably as well as the peaks B and C in the Ni K edge. From 15 h till 40 h they little by little but still decrease, while they do not change their form at all after 60 h, that is, after the alloy has been amorphous.

To clarify the feature of these transitions in the Ni and Zr K edges, we apply a deconvolution model to the normalized spectra. The model consists of the following functions convoluted with a Gaussian resolution function,

$$f(E) = \sum_i \frac{c_i}{(E - E_i)^2 + \gamma^2} + \left[\frac{1}{\pi} \arctan \left(\frac{E - E_c}{\Gamma/2} \right) + \frac{1}{2} \right]. \tag{1}$$

Here the Lorentzian function describes each transition to bound states with the peak position E_i, the width γ and the constant c_i. The arctangent function represents the transition into the continuum states where E_c is the difference between the core and the continuum levels and Γ is the core-hole lifetime. Examples of deconvolution are shown in Figs. 4 and 5. The broken lines are the arctangent functions of eq. (1) with E_c=8340.10 eV and Γ=1.4 eV

for the Ni K edge and with E_c= 17993.91 eV and Γ=3.8 eV for the Zr K edge. The value of Γ used here is consistent with that of the literature (Müller *et al.*, 1982).

We concentrate on the transitions A in these edges because they
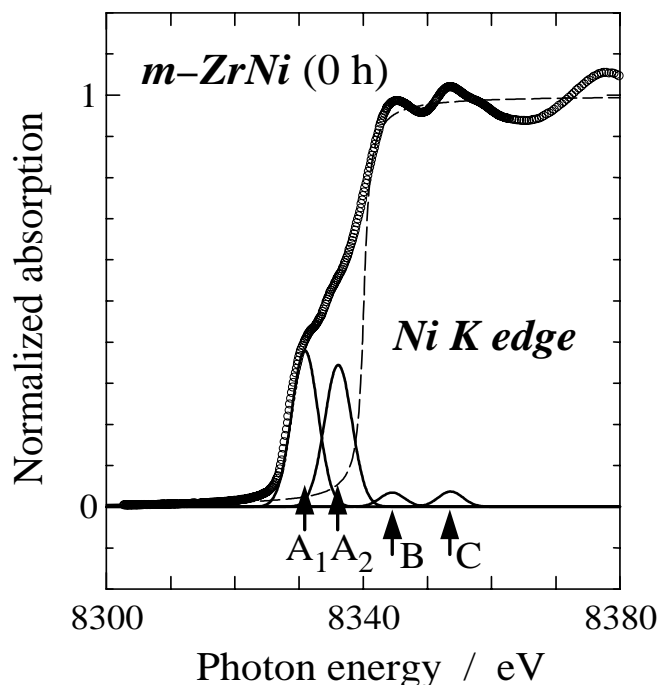
Figure 4
Deconvolution of XANES signals of ZrNi near the Ni K edge before miling. The broken line shows an arctangent function. The solid lines denote four Gaussian broadened Lorentzian functions.
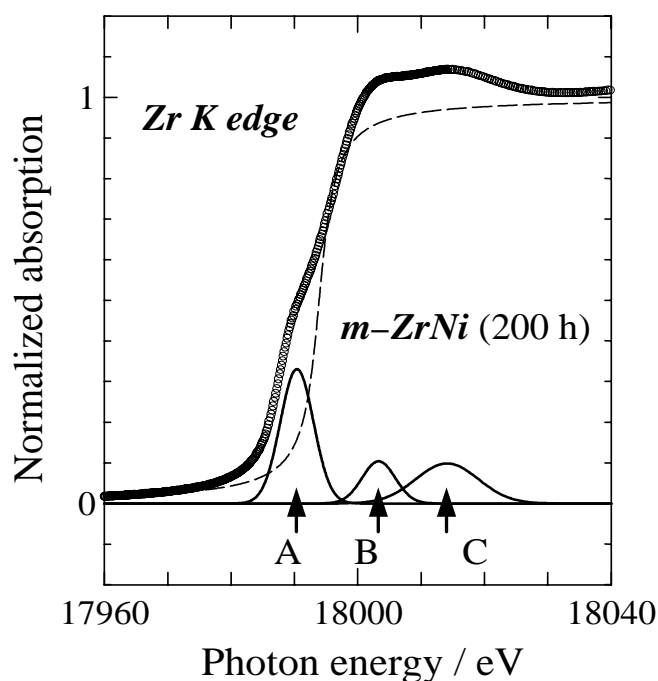
Figure 5
Deconvolution of XANES signals of ZrNi near the Zr K edge after milling for 200 h. The broken line represents the transitions to the continuum. The solid lines are three Gaussian broadened Lorentzians.

show a remarkable change during the milling as mentioned above. It is noted that the small absorption A of the Ni K edge shown in Fig. 2 is separated definitely into two peaks labeled as A_1 and A_2 in Fig. 4. As shown in Fig. 5, on the other hand, the absorption A at the Zr threshold is composed of only one peak. In the Ni K edge the energy position of the peak A_2 is fixed within 0.1 eV during the milling till 200 h. The position of the peak A_1 reduces with the milling time, that is, from 8330.9 eV at 0 h to 8330.0 eV at 60 h, which is unchanged by the subsequent milling till 200 h. In a sharp contrast to the peak A_1, the transition A of the Zr K threshold shows a considerable increase in the energy from 17989.0 eV at 0 h to 17990.4 eV at 60 h and makes no change with milling after 60 h till 200 h. The absorption A_1 is attributed to the 4p states strongly hybridized with the 3d states, while the peak A of the Zr K edge arises from states having a 4d orbital character by the p-d hybridization (Müller, 1978). It is emphasized that both the energy positions of the transition A_1 in the Ni K edge and the peak A of the Zr K threshold make a rapid change in the early stage of milling till 20 h. We have found that both peaks A_1 and A_2 of elemental Ni powder milled for 130 h are as same as those of Ni without milling. This means that only lattice deformation by milling hardly changes the electronic states of Ni atoms. Therefore the rapid change of the transitions A_1 and A of the Ni and Zr K edges suggests that alloying by atomic interdiffusion at the boundary of the elements starts in the early stage of milling.

4. Conclusions

We have observed XANES spectra of ZrNi mechanically alloyed till 200 h and decomposed them according the deconvolution model. It is found that the mechanical alloying remarkably changes both the peak A_1 near the Ni edge and the transition A near the Zr threshold. The feature reflects the 3d and 4d orbital characters through the p-d hybridization.

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