Structural change of Zr₇Ni₁₀ caused by mechanical grinding

T. Kishida and H. T. Takeshita

Faculty of Engineering Kansai University, 3-3-35 Yamate-chou Suita, Osaka 564-8680, E-mail:h-take@ipcku.kansai-u.ac.jp

Structural change of Zr_7Ni_{10} was investigated by using mechanical grinding. Mechanical grinding was conducted in H₂ atmosphere, where the operation was carefully done not to form a hydride phase. The milled samples were heated at 773K for 3.6ks in vacuum. The diffraction peaks of the samples became broader with an increase in milling time and disappeared for the sample milled for 5.4ks. The original orthorhombic structure of Zr_7Ni_{10} was obtained by heating at 773K from the sample which showed the diffraction peaks even after milling and was heated at 773K in vacuum. But the tetragonal structure of Zr_7Ni_{10} was obtained only for the sample which shows no diffraction peaks after milling and was then heated at 773K.

Key words: metal-hydrogen system, structural change, mechanical grinding, X-ray diffraction, Zr-Ni alloys

1. Introduction

Recently, anomalous hydrogenation properties about a Zr_7Ni_{10} intermetallic compound have been reported[1]. Zr_7Ni_{10} undergoes the phase transition from α to γ and from γ to β in hydrogen absorption and β to α in hydrogen desorption, whereas reverse transitions for γ to β and β to α are not observed. Fig. 1 is a hydrogen pressure-composition isotherm during initial hydrogen cycle for Zr_7Ni_{10} . The metal and hydrogen solid solution phases of Zr_7Ni_{10} dehydrogenated after its hydrogenation have a tetragonal structure (D^{17}_{4h} , I4/mmm) as shown in Fig.2 but not an original orthorhombic one (D^{18}_{2h} , *Cmca*) as shown in Fig.3[3].

For this crystal structure change of Zr_7Ni_{10} , Takeshita *et al.* reported that the metal phase and the hydrogen solid solution one absorbing hydrogen within hydrogen solubility (solubility limit 0.56H/M in hydrogen absorption) maintain an original orthorhombic structure, whereas those absorbing hydrogen to form the γ -hydride followed by dehydrogenation have a tetragonal structure. Furthermore, the tetragonal structure of Zr_7Ni_{10} is obtained by quenching from molten alloy [4].

Amount of lattice defects may be introduced into intermetallic compounds when hydride is formed[5]. So the tetragonal structure might be also obtained by increasing internal energy of the intermetallic compounds by introducing the lattice defects, for example, by mechanical grinding (MG).

In this study, mechanical grinding (MG) of orthorhombic Zr_7Ni_{10} phase was applied in order to obtain the information about which structure of Zr_7Ni_{10} is more stable. If tetragonal structure of Zr_7Ni_{10} is obtained by MG, it is more likely that the tetragonal structure is metastable and hydrogenation and dehydrogenation treatments may become a new method to produce a metastable substance.



Fig. 1 Pressure-composition isotherm at 403K of initial hydrogenation cycle for Zr_7Ni_{10} , where measurement was started from hydrogen absorption[2]. Two larger filled and open circles respectively mean the positions of samples with 0.49 and 0.40 H/M (H/M; the molar ration of hydrogen to metal) in hydrogen content.



Fig. 2 X-ray diffraction profile of Zr_7Ni_{10} with 0.40H/M in hydrogen content[2], where its hydrogenation record is shown in Fig. 1.



Fig. 3. X-ray diffraction profile of Zr_7Ni_{10} with 0.49H/M in hydrogen content[2], where its hydrogenation record is shown in Fig. 1. Arrows indicate the diffraction peaks observed only for orthorhombic structure.

2. Experimental details

Zr sponge (99.9% purity) and Ni balls (99.99% purity) were weighed to correspond with stoichiometric compositions of Zr_7Ni_{10} . These metals were melted and alloyed on a water-cooled copper hearth in an arc melting furnace under Ar atmosphere of 0.1MPa. Before melting of the objective sample, Zr ingot was melted to remove residual reactive gases in furnace. The samples after alloying were heated at 1273K for 86.4ks in a high vacuum furnace (about 1.2×10^{-2} Pa) in order to homogenize the composition.

X-ray diffraction (XRD) using Cu-K α radiation and field emission-scanning electron microscope (FE-SEM) were used for the identification of the constituent phases in the samples. Si powder (Aldrich, 99.9995%) was mixed with the sample powder to calibrate the diffraction angles for XRD analysis.

The samples were crushed to powder with the particle size less than 150μ m and were weighed by about 4.5g. The powder was put into a Cr steel container together with Cr steel balls of 10mm in diameter. For effective milling, the MG was conducted in H₂ atmosphere for 1.8ks so that hydrogen content of the sample was 0.35H/M, less than the solubility limit of the continuous hydrogen solid solution phase. Subsequent MG was conducted in Ar atmosphere. Each 0.4g of powder was sampled after milling for 1.8ks, 5.4ks, 12.6ks, 27ks and 55.8ks, and total milling periods for these samples were respectively 1.8ks, 5.4ks,

12.6ks, 27ks and 55.8ks. Compositional analysis of the samples after MG was conducted by energy dispersive X-ray fluorescence analysis.

The samples after MG were heated at 773K in a high vacuum furnace for 3.6ks or supplied to thermal analysis such a differential scanning calorimetry (DSC).

The analysis of crystal structure of samples after heat treatment was conducted by the combination of X-ray diffraction and Rietveld analysis. RIETAN97 β [6][7] was used for the refinement of the XRD profile.

4. Results

4-1. XRD profiles after mechanical grinding

Fig. 4 shows XRD profiles of the sample before and after MG. The diffraction peaks gradually became broader as milling time increases, and disappeared for the sample milled time for 5.4ks. The diffraction peak of about $2\theta = 45^{\circ}$ of the samples after MG is for Fe and Cr because Cr steel container and balls is used for MG, and the angle of this diffraction peak is Fe and Cr. In addition, another diffraction peak has low angle side of XRD profile for the sample after MG for 55.8ks. This diffraction peak corresponds the maximum diffraction peak of Zr hydride. And so, the diffraction peaks of the samples after MG shifted to a low angle side, and the sample after MG for 55.8ks shifted to a high angle side again. It is considered that two peak shifts respectively occurred for expansion of the lattice by hydrogen absorption and for shrink of the lattice by decrease of hydrogen and Zr concentration.



Fig. 4 X-ray diffraction profiles of the samples before milling (a) and prepared by mechanical grinding for 1.8ks (b), 5.4ks (c), 12.6ks (d), 27ks (e), and 55.8ks (f).

4-2. Determination of the crystal structure after heat treatment

The samples after MG were heated at 773 K for



Fig. 5 The measured and calculated X-ray diffraction profiles for the sample heated at 773K in a high vacuum after mechanical grinding for 1.8ks.

3.6ks since they couldn't determine the crystal structure. Rietveld analysis was conducted with the samples after MG for 1.8ks and 12.8ks for before heat treatment. Fig. 6 shows results of the sample after MG for 1.8ks by Rietveld analysis. For Rwp value, orthorhombic structure is smaller than tetragonal structure, and for S value, it is closer to 1 than in this figure. And so There is nothing to tetragonal structure and a peak peculiar to orthorhombic one exists. For this reason, the crystal structure in Fig. 5 is orthorhombic structure. Fig. 6 shows result of the sample after MG for 12.8ks by Rietveld analysis. In this figure, orthorhombic structure is smaller and is closer to 1 for Rwp (weighted pattern factor) value and S (goodness-of-fit) value, respectively. But the difference between lattice parameter b and c for orthorhombic structure has less than 1σ , and there is no significant difference. In addition a peak peculiar to orthorhombic is unidentified, and also for R_{I} (Intensity factor) and $R_{\rm F}$ (structure factor) value, tetragonal structure is smaller than orthorhombic one. For these reason, this crystal structure is tetragonal structure. From these things, crystal structure of the sample showed no diffraction peaks after MG is tetragonal after heating at 773K for 3.6ks, and the sample showed even diffraction peaks after MG is orthorhombic.

4-3. Thermal analysis

The samples which no diffraction peaks after MG supplied thermal analysis by DSC for the confirmation of whether to be amorphous or nanocrystal. Before DSC measurement, the sample was dehydrogenated at 613K for 3.6ks. Fig. 7 shows heat flow profile of the sample after MG for 12.6ks. When first heating, two exothermic peaks were seen at about 823K and



Fig. 6 The measured and calculated X-ray diffraction profiles for the sample heated at 773K in a high vacuum after mechanical grinding for 12.6ks.



Fig. 7 Heat flow profile obtained by DSC in Ar atmosphere for the sample after mechanical grinding for 12.6ks.



Fig. 8 X-ray diffraction profiles of the samples heated at each temperature under Ar atmosphere after milling for 12.6ks.

Ni Fe Molar Zr /mol% /mol% /mol% ratio of Ni to Zr :N_{Ni}/N_{Zr} Before 44.3 ± Not 1.257 ± 55.7 ± MG detected 0.1 0.1 0.005 After 36.8 ± 44.3 ± 2.90 + 1.634 ± MG for 0.1 0.008 0.2 0.05 12.8ks

Table 1 Composition of the sample before and after MG.

873K. Fig. 8 shows XRD profiles of the samples heated at 773K, 823K, 843K and 873K. TheXRD profile of the sample at 773K was appeared a few diffraction peaks. For the XRD profile of the sample heated at 823K, all diffraction peaks shows Zr₇Ni₁₀. The XRD profile of the sample 843K and appeared heated at 873K unidentification peaks and these peaks grew up. It is proved from these that the exothermic peak at 823K shows crystallization of Zr₇Ni₁₀ and the exothermic peak at 873K shows crystallization of the second phase. Table 1 shows result of energy dispersive X-ray fluorescence analysis. The samples after MG decrease Zr concentration. It is considered that the second phase is Ni rich phase of Zr-Ni system. It is reported that for A-Zr₃₇Ni₆₃ with low Zr concentration from Zr₇Ni₁₀, two crystallization peaks was identified[8].

5. Discussion

Because It is clear by the thermal analysis that the sample after MG for 12.8ks occurs crystallization by heating, the sample before being changing to tetragonal structure after heating isn't nanocrystal but amorphous. In other words, orthorhombic Zr_7Ni_{10} changed tetragonal Zr_7Ni_{10} by heating after amorphism. the tetragonal structure of Zr_7Ni_{10} is metastable, and that the structural change to the tetragonal structure occurs via formation of the third phase. But it can't be clarified which tetragonal and orthorhombic Zr_7Ni_{10} are more stable because the change to tetragonal structure from orthorhombic structure didn't caused directly.

6. Conclusions

By mechanical grinding treatment of Zr_7Ni_{10} , metastable phase was tried and it aimed at clarifying stability of the crystal structure. Consequently, the following things became clear.

(1) Orthorhombic Zr_7Ni_{10} become amorphous by mechanical grinding. And tetragonal Zr_7Ni_{10} is obtained from the amorphous alloy by heating at 773K for 3.6ks.

(2) The structural change of Zr_7Ni_{10} to the tetragonal structure from orthorhombic one occurs via formation of the third phase.

(3)Orthorhombic Zr_7Ni_{10} occurs composition change to Ni rich side by mechanical grinding.

7. References

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