

Hydrogenation properties and structural change of $\text{Hf}_x\text{Zr}_{7-x}\text{Ni}_{10}$ ($x = 0-7$)

H.T. Takeshita^{a,*}, N. Fujiwara^a, N. Takeichi^b, H. Senoh^b, T. Oishi^b

^a Faculty of Engineering, Kansai University, 3-3-35 Yamate-cho, Suita, Osaka 564-8680, Japan

^b National Institute of Advanced Industrial Science and Technology, 1-8-31 Midorigaoka, Ikeda, Osaka 567-8580, Japan

Received 6 September 2004; received in revised form 25 January 2005; accepted 1 February 2005

Available online 10 August 2005

Abstract

$\text{Hf}_7\text{Ni}_{10}$ has the same crystal structure as $\text{Zr}_7\text{Ni}_{10}$, which shows several unusual hydrogenation properties such as reversible hydrogenation by irreversible phase transformation and structural change caused by hydrogenation followed by dehydrogenation, and its hydrogenation properties have been unknown. The phase relation and hydrogenation properties of $\text{Hf}_x\text{Zr}_{7-x}\text{Ni}_{10}$ alloys were investigated in the compositional range from $\text{Zr}_7\text{Ni}_{10}$ ($x = 0$) to $\text{Hf}_7\text{Ni}_{10}$ ($x = 7$). All the samples were obtained by arc melting followed by heat treatment in vacuum. The constituent phase was identified by the combination of X-ray diffraction and microscopic analysis and hydrogenation properties were examined by differential scanning calorimetry and Sieverts' method. No structural change from orthorhombic *Cmca* type to another one such as tetragonal *I4/mmm* type and orthorhombic *Pbca* type was observed for the addition of Hf and Hf was substituted for Zr in $\text{Zr}_7\text{Ni}_{10}$ in all the compositional range we examined. The lattice constant of the aimed phase decreased with an increase in Hf content. The measurements using differential scanning calorimetry indicated that the Hf-substituted alloys showed the same phase transformation as $\text{Zr}_7\text{Ni}_{10}$ in hydrogenation, that is the unusual phase transformation that an intermediate hydride phase appears only in dehydrogenation but not in hydrogenation. The transformation temperature decreased with an increase in Hf content.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Hydrogen storage materials; Casting; X-ray diffraction; Thermal analysis

1. Introduction

We have reported unusual and interesting properties for phase transformation of $\text{Zr}_7\text{Ni}_{10}$ in hydrogenation. The compound reversibly absorbs and desorbs hydrogen accompanied by phase transformation caused by three hydrogen occlusion phases, alpha which is a continuous hydrogen solid solution, beta which is a hydride with lower hydrogen content, and gamma which is a hydride with higher hydrogen content. In this phase transformation, the beta phase appears only in hydrogen desorption but not in hydrogen absorption, so the hydrogen absorption is achieved through the phase transformation from alpha to gamma, whereas the hydrogen desorption is achieved through the phase transformation from

gamma to beta and beta to alpha [1]. In addition, the hydrogen solubility of the alpha phase is quite larger in hydrogen absorption than in hydrogen desorption [1]. Moreover, the metal and hydrogen solid solution phases of $\text{Zr}_7\text{Ni}_{10}$ changes from an orthorhombic structure which was reported by Kirkpatrick et al. [2] first and corrected by Joubert et al. [3] recently to a tetragonal structure through the hydrogenation to form its corresponding hydride followed by dehydrogenation [4]. Interestingly this structural change does not occur unless the compound absorbs enough hydrogen to form the hydride [4].

One may think that the properties described above are related to the crystal structure of $\text{Zr}_7\text{Ni}_{10}$. In the previous paper, we investigated the hydrogenation properties of the $\text{Zr}_7\text{Ni}_{10}$ compound with *Pbca* symmetry and found that the tetragonal structure can be obtained by rapid cooling from melt of $\text{Zr}_7\text{Ni}_{10}$ [5]. Thus the fact that this compound

* Corresponding author. Tel.: +81 6 6368 0553; fax +81 6 6388 8797.

E-mail address: h-take@ipc.ku.kansai-u.ac.jp (H.T. Takeshita).

can possess several different structures may affect the interesting hydrogenation properties mentioned above. There are several compounds with the same crystal structure as Zr_7Ni_{10} . Hf_7Ni_{10} is one of these isomorphous compounds and its hydrogenation properties have been investigated. In the present study, the phase relation in the compositional range between Zr_7Ni_{10} and Hf_7Ni_{10} , including structural change, and the hydrogenation properties of the alloys were examined in order to obtain the information about the relation between the above-mentioned characteristic hydrogenation properties observed for Zr_7Ni_{10} and crystal structure.

2. Experimental details

Starting materials were Zr (99.6%) and Hf (99.9%) and granular Ni (99.9%). The granules of Ni were polished to remove oxide on the surface. They were weighed to obtain the samples with target compositions and alloyed in an Ar atmosphere of 0.1 MPa in an arc melting furnace. The Ar gas in the furnace was purified by melting Zr getter before melting of each sample. Each ingot was turned over three times to improve its homogeneity. The ingots with the bulk compositions of $Zr_xHf_{7-x}Ni_{10}$ were homogenized by heating at 1273 K in a high vacuum furnace for 86.4 ks ($x = 0$), 172.8 ks ($x = 1-3$) and 345.6 ks ($x = 4-7$). The constituent phases were confirmed by the combination of X-ray diffraction and microscopic analysis.

The hydrogenation properties of the samples were examined by differential scanning calorimetry and Sieverts' method. In the case of thermal analysis, sample ingot was pulverized to pass through sieve of 100 meshes and 30 mg of the powder was supplied to the analysis. The measurement was performed at 3 MPa in hydrogen pressure, from room temperature to 773 K in temperature range, and at 20 K/min in heating and cooling rate. Some of the samples for which reversible hydrogenation and dehydrogenation were confirmed by thermal analysis were supplied to the measurements of pressure–composition isotherms based on Sieverts' method. The experimental conditions such as initial activation, degassing and measurement temperature were determined based on the results of thermal analysis.

3. Results and discussion

According to Glimois et al. [6], Cu can be substituted for Ni in Zr_7Ni_{10} in all the compositional ratio of Cu to Ni. Hf is very similar to Zr for chemical characteristics, and therefore it is expected that Hf can be substituted for Zr in Zr_7Ni_{10} in wide compositional range. Figs. 1 and 2 show the X-ray diffraction profile and metallographic structure of $Hf_3Zr_4Ni_{10}$ sample, respectively, where Fig. 1(b) is the profile calculated with the Rietan 97 beta program based on the assumption that the alloy has the *Cmca* symmetry [4] as the binary Zr_7Ni_{10} compound and Hf atoms can randomly occupy Zr sites and,

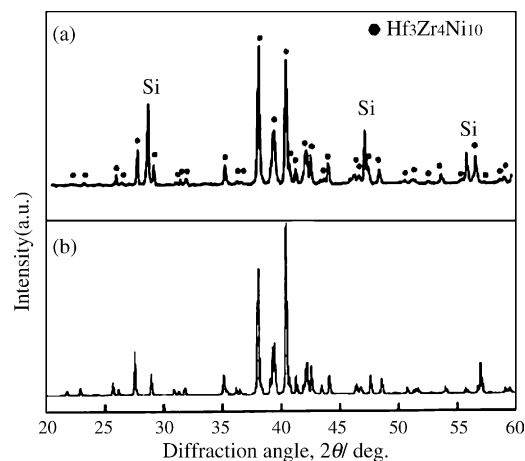


Fig. 1. X-ray diffraction profiles measured for $Hf_3Zr_4Ni_{10}$ sample (a) and calculated based on the assumption that $Hf_3Zr_4Ni_{10}$ compound has the same orthorhombic structure as Zr_7Ni_{10} and Hf atoms can randomly occupy Zr sites (b).

in Fig. 1(a), the diffraction peaks from Si powder which was mixed with the sample powder as internal standard are shown with those from the sample. As expected, the alloy sample had a single phase structure composed of the phase with the orthorhombic *Cmca* symmetry but no other phase or structure such as orthorhombic *Pbca* [2] and tetragonal *I4/mmm* [7] was observed under the present experimental conditions. All the samples annealed for a sufficient time showed the single phase structure composed of the aimed phase. In the case of the Hf-containing samples, the single phase structure was not obtained without heat treatment after alloying and longer heating time was necessary for the sample with higher Hf content. Fig. 3 shows the change in lattice constant with nominal Hf content in the sample. All the lattice constants monotonously decreased with an increase in Hf content, consistent with that the Goldschmidt radius of Hf (0.160 nm) is smaller than that of Zr (0.162 nm), supporting the substitution of Hf for Zr in Zr_7Ni_{10} .

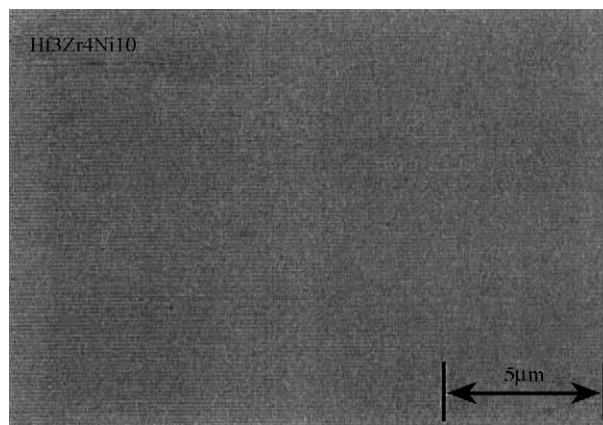


Fig. 2. Metallographic structure of $Hf_3Zr_4Ni_{10}$ sample obtained as backscattering electron image.

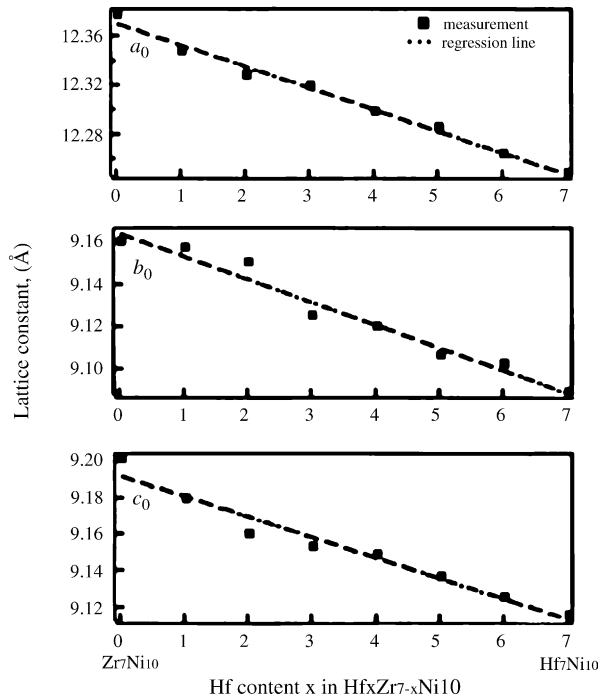


Fig. 3. Change in lattice constant of orthorhombic $Cmca$ structure of $Hf_xZr_{7-x}Ni_{10}$ with nominal Hf content.

Fig. 4 shows the change in heat flow with temperature for the samples, where the heat flow profile of Zr_7Ni_{10} is shown for comparison. In the case of Zr_7Ni_{10} , two endothermic peaks corresponding to the phase transformation from gamma to beta and beta to alpha in heating and one exothermic peak corresponding to the phase transformation from alpha to gamma in cooling were observed. For the samples of $x = 1-3$, two endothermic and one exothermic peaks as observed for Zr_7Ni_{10} were observed in the second cycle, implying that the phase transformation of these alloys occurs in the same manner as the binary Zr_7Ni_{10} compound. In the case of the $x = 4$ sample, endothermic peaks were observed in heating of the second cycle, whereas there was no exothermic peak in cooling. For the other samples ($x = 5-7$), no significant peak was observed.

The results for heat flow profile include both thermodynamic and reaction rate effects. If reaction rate is independent of the sample composition, the change in peaks observed in heat flow profile with Hf content implies the change in stability of the hydride of the alloy with Hf content. Fig. 5 shows the change in the endothermic and exothermic peaks observed in heat flow profile for each sample with nominal Hf content in the sample. The temperatures of these three peaks monotonously decrease with an increase in Hf content, implying that the stability of the corresponding hydride decreases with increasing Hf content on the assumption described above. Judging from the extrapolation line for the hydrogen absorption corresponding to the alpha to gamma transformation, the alloy with higher Hf content ($x = 5-7$) did not absorb enough hydrogen to form the

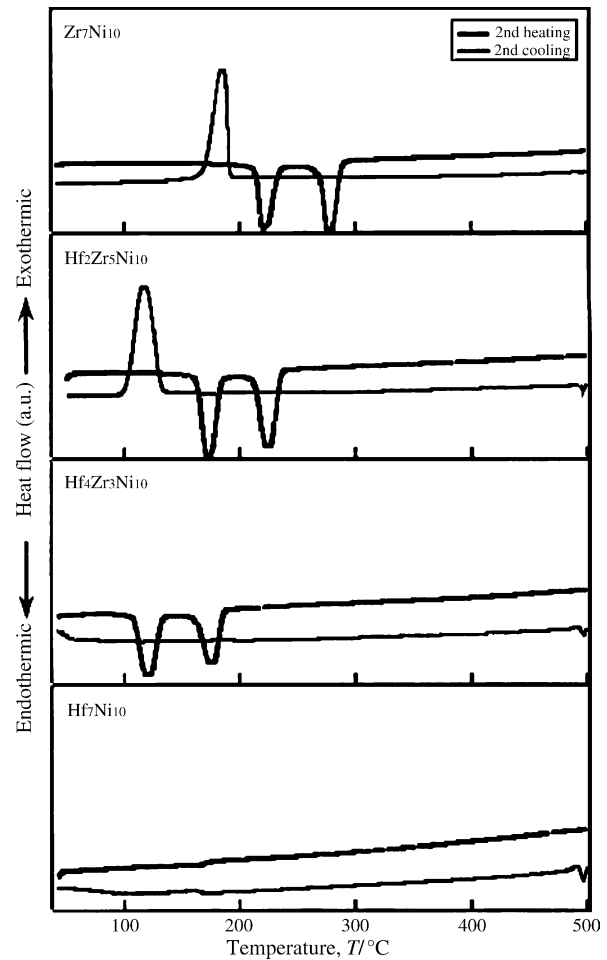


Fig. 4. Change in heat flow with temperature for Zr_7Ni_{10} , $Hf_2Zr_5Ni_{10}$, $Hf_4Zr_3Ni_{10}$ and Hf_7Ni_{10} . All the heat flow profiles were obtained in hydrogen atmosphere of 3 MPa at 20 K/min in heating and cooling rate.

hydride within the measurement temperature range, which can be considered to be the reason that no other peak except the one corresponding to initial hydrogenation was observed in the heat flow profile. In the case of the $x = 4$ sample, it

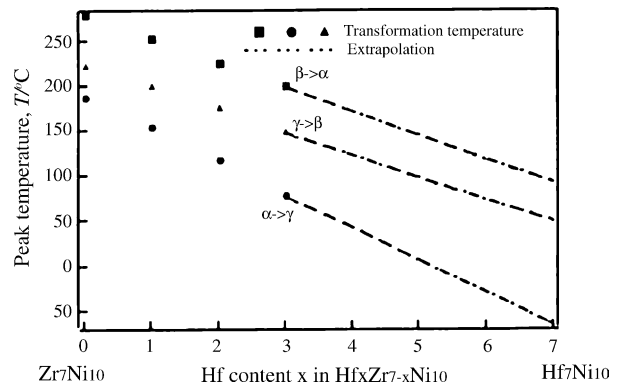


Fig. 5. Change in the temperature of exothermic and endothermic peaks observed in Fig. 4 with nominal Hf content in $Hf_xZr_{7-x}Ni_{10}$ samples. Dashed lines are extrapolation lines obtained by least square method for the three kinds of peaks.

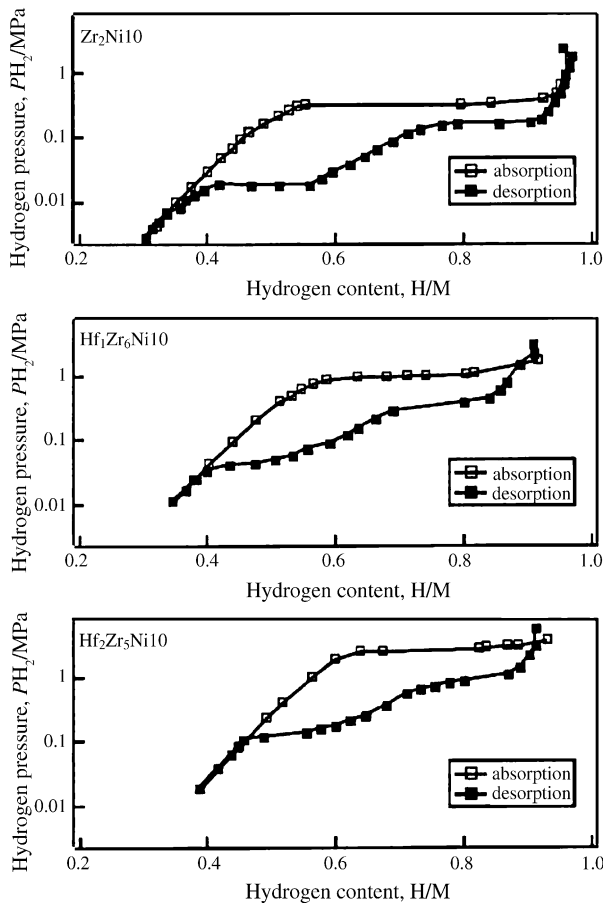


Fig. 6. Hydrogen pressure–composition isotherms of Zr_7Ni_{10} , $Hf_1Zr_6Ni_{10}$ and $Hf_2Zr_5Ni_{10}$ samples. All the measurements were conducted at 403 K.

can be considered that the alloy absorbed hydrogen very slowly around room temperature, which is the reason that no exothermic peak corresponding to the hydrogenation was observed, because it can be expected from Fig. 5 that its exothermic peak is around room temperature.

In order to confirm about the stability of the hydride of the alloy, the hydrogen pressure–composition isotherms of the three samples ($x = 0–2$) were measured at 403 K with a conventional Sieverts' type apparatus. The curves obtained are shown in Fig. 6. Hf-containing samples showed one plateau in hydrogen absorption and two plateaus in hydrogen desorption as well as Zr_7Ni_{10} , indicating the existence of the intermediate hydride phase beta which appears only in hydrogen desorption but not in hydrogen absorption. The three plateau pressures corresponding to the alpha to gamma, gamma to beta and beta to alpha transformation increase with an increase in nominal Hf content, which means that the hydride of the alloy with higher Hf content is less stable. These results are consistent with the expectation from the results obtained by differential scanning calorimetry.

In the present study, the hydrogenation behaviors of the Hf-rich compounds were not observed because their hydrides were very unstable. However, all the alloys whose hydrogenation properties were observed under the present experimental conditions exhibited the phase transformation in the same manner as the binary Zr_7Ni_{10} compound. This fact implies that the unusual phase transformation in hydrogenation of Zr_7Ni_{10} is strongly related to its crystal structure.

4. Conclusions

In order to obtain the information about the relation between the unusual phase transformation in hydrogenation of Zr_7Ni_{10} and its crystal structure, the $Hf_xZr_{7-x}Ni_{10}$ alloys were examined on the compositional range of $x = 0–7$. In the compositional range examined, the orthorhombic *Cmca* type phase can only exist but no other structure is obtained under the conventional melting and annealing conditions. Hf can substitute for Zr in Zr_7Ni_{10} in every compositional ratio of Hf to Zr and the $Hf_xZr_{7-x}Ni_{10}$ compound has the orthorhombic structure with the space group *Cmca*. Since the corresponding hydride becomes unstable with an increase in Hf content, the phase transformation in hydrogenation of Hf-rich compounds was not observed. For the alloys showing the hydrogenation accompanied by phase transformation, however, the same phase transformation as Zr_7Ni_{10} is observed, such as the transformation from alpha to gamma in hydrogen absorption and from gamma to beta and from beta to alpha in hydrogen desorption. Therefore, the unusual phase transformation that the intermediate beta phase does not appear in hydrogen absorption can be strongly related to the crystal structure.

References

- [1] H.T. Takeshita, T. Kiyobayashi, H. Tanaka, N. Kuriyama, M. Haruta, *J. Alloys Compd.* 311 (2000) L1.
- [2] M.E. Kirkpatrick, J.F. Smith, W.L. Larsen, *Acta Crystallogr.* 15 (1962) 894.
- [3] J.-M. Joubert, R. Cerny, K. Yvon, M. Latroche, A.P. Guégan, *Acta Crystallogr. C* 53 (1997) 1536.
- [4] H.T. Takeshita, N. Fujiwara, T. Oishi, D. Noréus, N. Takeichi, N. Kuriyama, *J. Alloys Compd.* 360 (2003) 255.
- [5] H.T. Takeshita, S. Kondo, H. Miyamura, N. Takeichi, N. Kuriyama, T. Oishi, *J. Alloys Compd.* 376 (2004) 268.
- [6] J.L. Glimois, P. Forey, J. Feron, C. Beclé, *J. Less-Common Met.* 78 (1981) 45.
- [7] H.T. Takeshita, D. Noréus, N. Kuriyama, in press.