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Improvement of hydriding properties of a Zr_1Ni_1 alloy by adding third transition metals for tritium recovery

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Abstract

For tritium handling, application of a Zr_1Ni_1 alloy was attempted. In order to decrease the equilibrium hydrogen pressure in hydriding the Zr_1Ni_1 alloy, substitutions of Ni in Zr_1Ni_1 alloy by either Fe, Co or Cr were conducted. The equilibrium hydriding pressure of the Zr_1Ni_1 alloy was decreased by the substitution and the contribution of the Fe substitution on the decrease of the equilibrium hydrogen pressure of the Zr_1Ni_1 was greatest. Moreover, the equilibrium hydrogen pressures of these alloys showed a close relationship with lattice parameters of the alloys. Therefore, design of the alloy with a desired equilibrium pressure became possible by controlling the lattice parameters of the alloys. Furthermore, it was confirmed that the $Zr_1Ni_{0.8}Fe_{0.2}$ alloy showed faster reaction kinetics than the Zr_1Ni_1 alloy, where the reaction rate of the alloy was twice that in Zr_1Ni_1. Though pulverizing during hydriding was observed in both the Zr_1Ni_1 and the $Zr_1Ni_{0.8}Fe_{0.2}$ alloys, the powdering of these alloys was smaller compared with a generally used hydrogen-absorbing alloy. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

An in situ irradiation test of a fusion blanket mock-up was planned in the JMTR (Japan Material Testing Reactor) using lithium-containing ceramics as the tritium breeder and beryllium as the neutron multiplier [1]. In this regard, it is necessary to develop a getter for recovery of the tritium gas. So far, uranium [2] and titanium [3] have been widely used as the tritium getter. However, uranium is easily pulverized into fine powders by hydride formation, and the powders are inflammable on air exposure [4]. Although the titanium is not pulverized to fine powders by metal hydride formation, tritium permeation through the container materials becomes a serious problem because it is operated at a high temperature [5]. Accordingly, there is a need to develop a more convenient and reliable getter with good characteristics, i.e., low equilibrium pressure same as uranium at room temperature, rapid absorption and desorption rates, non-flammability on air exposure and insusceptibility to impurity gases (O_2, H_2O, N_2, etc.) [6].

In the present study, a Zr_1Ni_1 alloy with the CrB structure was selected for the tritium gettering material because of its high hydrogen-absorption capacity, moderate hydriding stability for tritium absorption [7] and small pulverization in hydriding. However, the equilibrium hydrogen pressure of the alloy at room temperature was about 10^{-1} Pa [7], which is about three figures higher than the equilibrium hydrogen pressure of the alloy required for a tritium gettering material. Thus, improvement of the equilibrium hydrogen pressure of the Zr_1Ni_1 alloy was attempted by partial substitution of Ni by a third transition metal. For this purpose, $Zr_1Ni_{1-x}A_x$ ($x = 0 \sim 0.4$, A = Fe, Co, Cr, V) alloys were prepared and the precipitation phase in the matrix, lattice parameters of the CrB structure and the equilibrium hydrogen pressure of the alloys were examined by measuring X-ray diffraction patterns and equilibrium pressure–composition–isotherms (P–C–T curves). Furthermore, hydrogen absorption kinetics and pulverization of the alloys were also studied.

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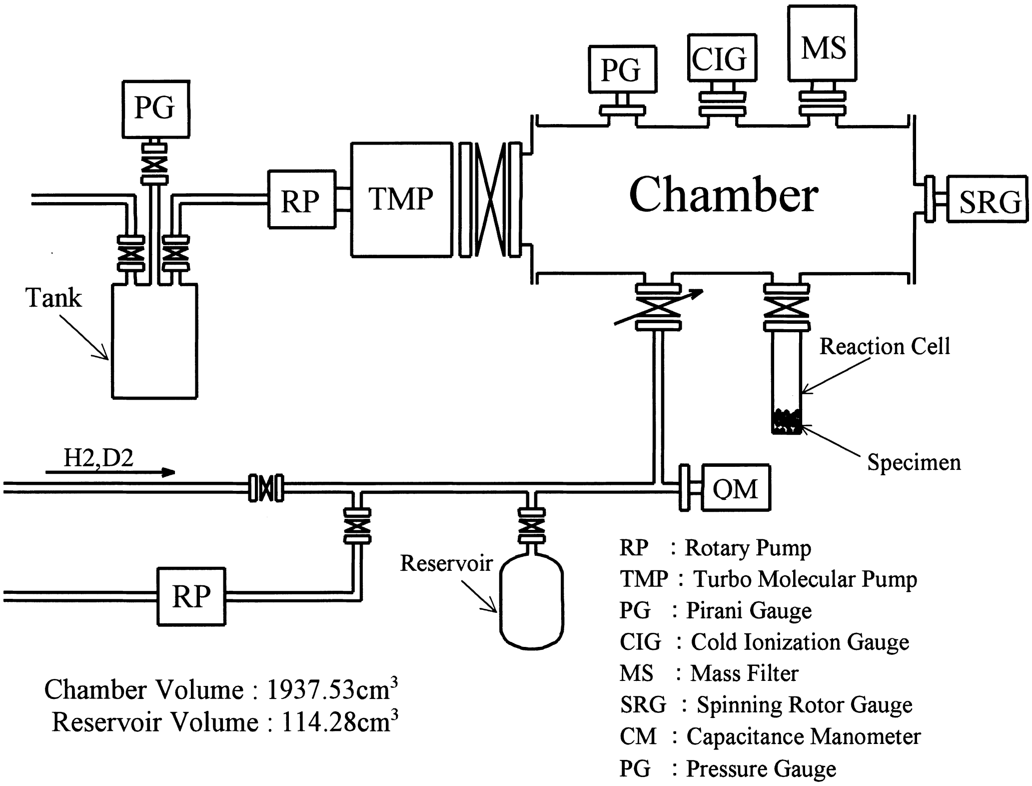

Fig. 1. Schematic diagram of the test apparatus.

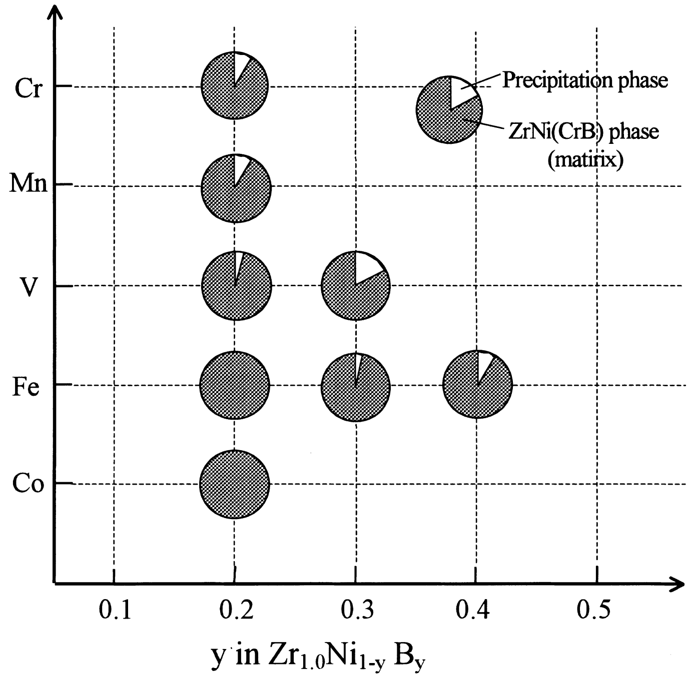

Fig. 2. Volume of precipitation phase in the alloys with various metals substituted for Ni in Zr_1Ni_1 alloy.

2. Experimental procedure

The samples were prepared by melting a Zr_1Ni_1 alloy with an arc furnace under an argon gas atmosphere. Melting was repeated three times by turning the ingot upside down in order to obtain a homogeneous sample. After the melting, the alloys were annealed at 1100°C for 24 h in an argon atmosphere. Finally, the ingots were ground to particles with diameters ranging from 210 to 300 μm in air.

To determine whether there was a precipitation phase or a crystal structure change in the alloys, they were examined by an X-ray diffraction measurement. A schematic diagram of the apparatus used for the P–C–T measurements of the samples is shown in Fig. 1 [8]. It is composed of three elements; namely evacuation equipment using a turbo-molecular pump, hydrogen gas inlet equipment with a reservoir tank and a reaction chamber with various pressure gauges attached. Initial activation processes of the samples were as follows. Sample weights of 20 g were set in reaction bed. After evacuating the reaction chamber at 500°C for 14 h, the samples were allowed to react with hydrogen at a pressure of 0.1 MPa at room temperature. The processes of the degassing and pressurizing of hydrogen were repeated several times, and after that the P–C–T curve and kinetics were measured at various temperatures. Furthermore, the pulverization characteristics of the sample according to hydriding reaction were also examined.

3. Results and discussion

Whether there was a precipitation phase and the ratio of the phase, if present, to the matrix one are shown in Fig. 2. The main precipitation phase in all alloys was the

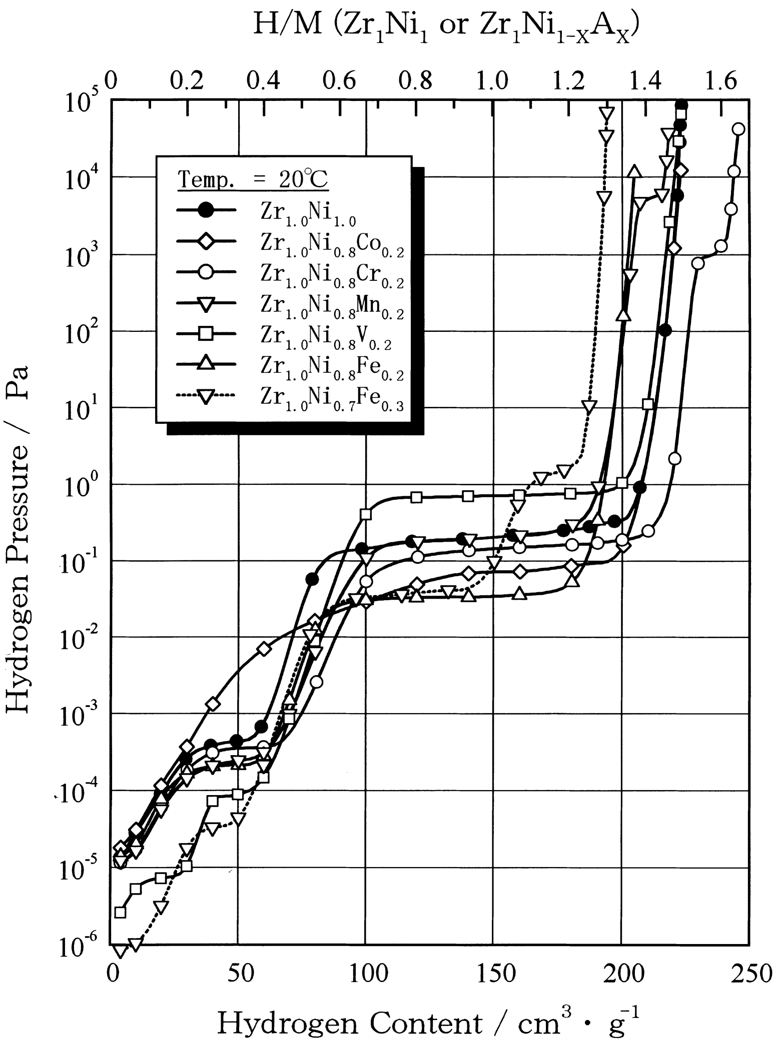

Fig. 3. The P–C–T curves of the alloys with various metals substituted for Ni in Zr_1Ni_1 alloy.

phase with a C14 crystal structure like $ZrCr_2$. In those alloys in which 20% of Ni in Zr_1Ni_1 alloy substituted by Cr, Mn or V, the precipitation phase was recognized. On the other hand, there was no precipitation phase in the alloys with substitution of Fe or Co for 20% Ni. However, the C14 phase appeared with Fe substitution for over 30% Ni in Zr_1Ni_1, and increased with increased Fe substitution.

Fig. 3 shows the P–C–T curves of the alloys. The P–C–T curve of the Zr_1Ni_1 shows two plateaus; the first plateau of 5×10^{-4} Pa in equilibrium pressure is of the coexistence of Zr_1Ni_1 metal phase and $Zr_1Ni_1H_1$ monohydride phase, and the second plateau of 2×10^{-1} Pa is of the coexistence of $Zr_1Ni_1H_1$ monohydride phase and $Zr_1Ni_1H_3$ trihydride phase. The second plateau pressures of these alloys were lower than that of pure Zr_1Ni_1 except V substitution. Furthermore, the alloy with Fe substitution showed the lowest equilibrium pressure in the case of the same amount of substitution. Accordingly, in order to lower the equilibrium plateau pressure of the second plateau in the hydriding of Zr_1Ni_1, Fe substitution for Ni showed the best effect. However, the alloys with 30% Fe substituted for Ni show the same plateau pressure as $Zr_1Ni_{0.8}Fe_{0.2}$ at the point of 0.8 in the hydrogen to metal atom ratio (H/M), moreover a third plateau appeared in H/M = 1.1. The reason that the plateau pressure was not decreased in $Zr_1Ni_{0.7}Fe_{0.3}$ is the precipitation of the C14 phase, that is, excess Fe was used for the precipitation phase. In order for the substitution of Fe for Ni to progress and then to lower the equilibrium second plateau pressure, it is necessary to suppress the precipitation of the C14 phase.

To control the equilibrium plateau pressure of Zr_1Ni_1, the effects of physical parameters of the alloys on the plateau pressure were investigated. Fig. 4 shows the relationship between the second plateau pressure and unit cell volume of the CrB structure in each alloy. Close relationships between them are recognized. The log-scale equilibrium pressure of Zr_1Ni_1 decreased linearly with increasing cell volume of the Zr_1Ni_1 structure. Using this correlation, design of an alloy with a desired equilibrium pressure of the Zr_1Ni_1 alloy becomes possible by controlling the lattice parameters of the alloys. The reason for the decrease in equilibrium pressures with increasing cell volume was seen as follows. The space of the interstitial site that will be occupied by hydrogen becomes wide with increasing cell volume. Thus, the hydrides become more stable and then the equilibrium pressure becomes lower.

The reactions of the Zr_1Ni_1 and the $Zr_1Ni_{0.8}Fe_{0.2}$ alloys with hydrogen under various hydrogen pressures at room temperature are shown in Fig. 5. The reaction rate became faster as the hydrogen pressure was larger in both alloys. As for the reason why the reaction rate slowed when H/M was over about 0.4, it is thought that the pressure difference between the hydrogen pressure and the equilibrium pressure became small over 0.4 H/M. This is because the reaction rate is supposed to be governed by this pressure difference. The reaction rate of

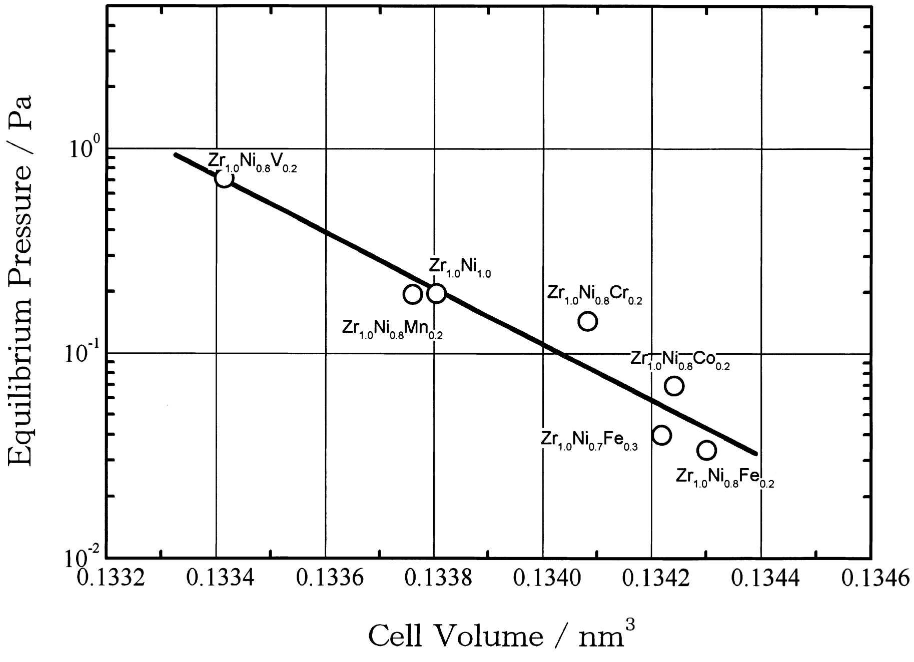

Fig. 4. Relationship between cell volume and equilibrium hydrogen pressure of Zr_1Ni_1 and $Zr_1Ni_{1-x}A_x$ alloys.

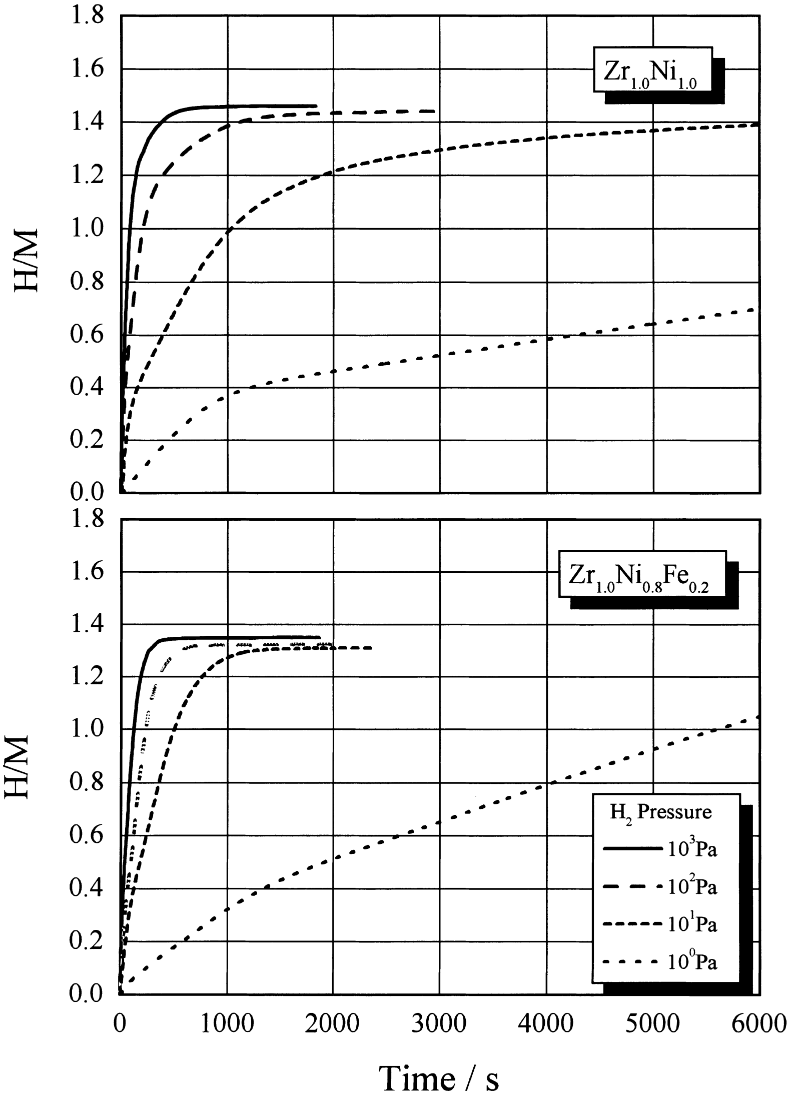

Fig. 5. Hydriding reactions of Zr_1Ni_1 and $Zr_1Ni_{0.8}Fe_{0.2}$ alloys under various hydrogen pressures.

the $Zr_1Ni_{0.8}Fe_{0.2}$ alloy is larger compared with the Zr_1Ni_1 alloy. For example, the reaction of $Zr_1Ni_{0.8}Fe_{0.2}$ under the hydrogen pressure of 10^1 Pa finished in about 1 000 s though the time was about 6 000 s in the Zr_1Ni_1 alloy.

Fig. 6 shows the correlation between the reaction rate and the hydrogen pressure plotted log–log scale in Zr_1Ni_1 and $Zr_1Ni_{0.8}Fe_{0.2}$, respectively. The reaction rate in each condition was determined by the gradient at the point of 0.8 H/M in the reaction curves shown in Fig. 5. The reaction rate in each alloy rose linearly as the hydrogen pressure grew up to the pressure of 10^2 Pa. However, over this pressure the reaction rates tended to saturate. The reaction rate of $Zr_1Ni_{0.8}Fe_{0.2}$ was faster than that of the Zr_1Ni_1 alloy by about twice.

Fig. 7 shows scanning electron microscope (SEM) photographs of the sample powders before hydriding and after 20 cycles of hydriding and dehydriding. The powder diameter of the sample before hydriding was about 0.5 mm for both Zr_1Ni_1 and $Zr_1Ni_{0.8}Fe_{0.2}$. After the hydriding and dehydriding cycles, the particle size of the powder became remarkably small, below 0.1 mm, especially for $Zr_1Ni_{0.8}Fe_{0.2}$. One of the reasons that the reaction rate of $Zr_1Ni_{0.8}Fe_{0.2}$ was larger than that of Zr_1Ni_1 is the larger reaction surface area in $Zr_1Ni_{0.8}Fe_{0.2}$ than in Zr_1Ni_1. However, the powdering tendencies of these alloys were small compared with a generally used hydrogen absorbing alloy like $LaNi_5$, of which the particle size becomes about 10–30 μm in diameter after only a few cycles of hydriding and dehydriding.

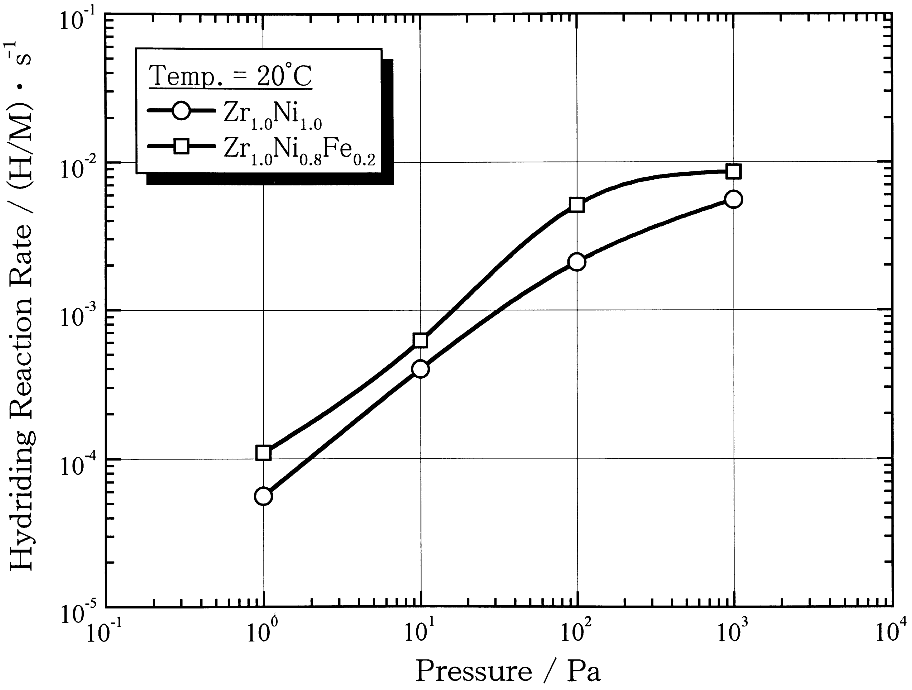

Fig. 6. Correlation between hydrogen pressure and reaction rates of Zr_1Ni_1 and $Zr_1Ni_{0.8}Fe_{0.2}$ alloys.

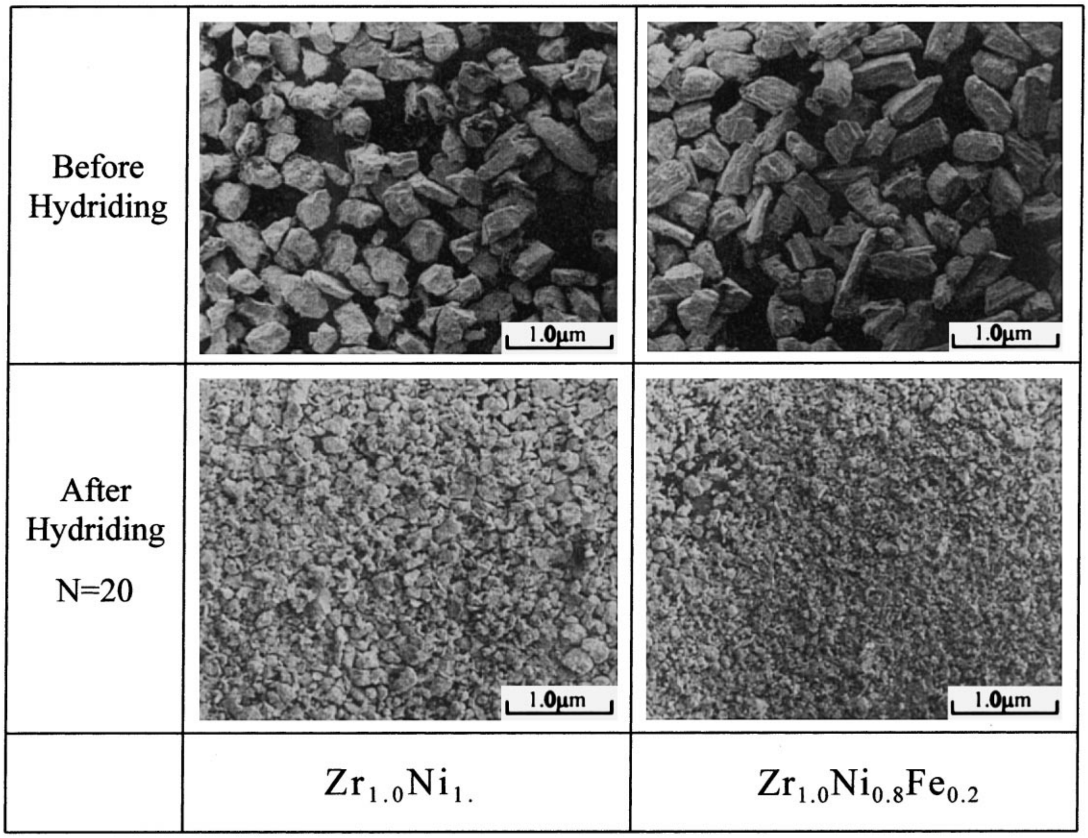

Fig. 7. Pulverization characteristics of the Zr_1Ni_1 and $Zr_1Ni_{0.8}Fe_{0.2}$ alloys.

4. Conclusions

The equilibrium hydriding pressure of the Zr_1Ni_1 alloy was decreased by substitution of Fe, Co or Cr for Ni. The contribution of the Fe substitution on the decrease of the equilibrium pressure of Zr_1Ni_1 was the largest. Moreover, the equilibrium pressures of these alloys showed close relationships with lattice parameters. Therefore, the design of an alloy with a desired equilibrium pressure became possible by controlling the lattice parameters of the alloys. Furthermore, it was confirmed that the $Zr_1Ni_{0.8}Fe_{0.2}$ alloy had twice larger reaction rate than that of Zr_1Ni_1 alloy. Though pulverizing with hydriding was recognized in both the Zr_1Ni_1 and the $Zr_1Ni_{0.8}Fe_{0.2}$ alloys, the powder size of these alloys was not so small compared with a generally used hydrogen absorbing alloy.

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