

## Examination of the kinetics of $Zr_{1.02}Ni_{0.98}$ alloy hydriding

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The hydriding kinetics of  $Zr_{1.02}Ni_{0.98}$  alloy was examined in dependence on the number of hydriding/dehydriding cycles. The rate constants relating to three subsequent hydriding procedures of an alloy sample, at five temperatures: 423, 448, 473, 498 and 523 K, were determined. The rate constant increases, and the activation energy decreases on each repetition of the hydriding/dehydriding cycle at a given temperature. This behavior was explained by sample crushing, leading to an increase in the surface area accessible to hydrogen.

*Keywords:* hydriding/dehydriding, zirconium-nickel alloy, hydriding rate constant, activation energy.

Some metals and alloys are able to absorb large amounts of hydrogen, and thereby undergo transformation into new chemical compounds – hydrides. The equilibrium hydrogen pressure of a hydride is a characteristic of each material. The possibility of hydrides to be applied as hydrogen storage materials<sup>1</sup> provoked extensive investigation of these topics. Besides pure metals and simple binary alloys, a large number of different multicomponent alloys were also studied. The alloy called "mishmetal", which presents a complex rare metal alloy, including La, Ce, Pr, Nd and Sm, stabilized by the addition of other metals, such as Co, Ni, Al *etc.*, is already being used as a hydrogen electrode<sup>2</sup> to replace the ecologically inconvenient cadmium anode in Cd-Ni secondary power sources.

A hydrogen storage material should satisfy some particular requirements relating to hydriding/dehydriding cycles. Namely, reversibility of cycling, and the closeness of the hydrogen equilibrium pressure to the atmospheric one, are both required. It is also important that, during cycling, the alloy maintains its basic characteristics (phase composition, particle size, hydriding capacity, hydriding rate, *etc.*). Up to date, no metal or alloy has been found which satisfy all these requirements. The most promising seems to be some "mishmetal" based alloys.

The kinetics of the hydriding reactions of different metals and alloys has been studied elsewhere.<sup>3-7</sup> Some recent results were presented at the International

Symposium on Metal-Hydrogen Systems, Fundamentals and Applications, Stuttgart, Deutschland, September 4–9 (1988).<sup>3</sup> The hydriding rates of pure metals, such as U, Th, Y, La, Ce, Nd, and Gd, were investigated at 21 °C, and 10 kPa hydrogen pressure, during a time period of several ks.<sup>4</sup> Josephy and Ron<sup>5</sup> determined the activation energy, rate constant and pre-exponential factor for LaNi<sub>5</sub> and MmNi<sub>4.5</sub>Fe<sub>0.85</sub> (Mm = "mishmetal") hydriding. Xianglong and Suda<sup>6</sup> measured the kinetic parameters for LaNi<sub>4.7</sub>Al<sub>0.3</sub> hydriding under constant volume at variable hydrogen pressures. Watanble *et al.*<sup>7</sup> examined the activation process and absorption/desorption of hydrogen and their isotopes for Zr-Ni alloys by XPS-SIMS (X-ray Photoelectron Spectrometry - Secondary Ion Mass Spectrometry).

Previously,<sup>8</sup> we stated that the multiple repetition of hydriding/dehydriding cycles of a sample of Zr<sub>1.02</sub>Ni<sub>0.98</sub> alloy leads to both a progressive increase in the hydriding rate and a progressive decrease in the maximal hydriding capacity. In this work, these properties of Zr<sub>1.02</sub>Ni<sub>0.98</sub> alloy are reconsidered in a more quantitative manner.

#### EXPERIMENTAL

The subject of examination was a Zr<sub>1.02</sub>Ni<sub>0.98</sub> alloy, synthesized at Baykov Institute, Moscow, Russia. After grinding, the fraction of 4 mm mean particle diameter was used to examine the hydriding kinetics.

The hydriding/dehydriding cycles were performed in a typical volumetric apparatus. A quartz tube with a weighed quantity of Zr<sub>1.02</sub>Ni<sub>0.98</sub> alloy, typical value being 0.1 g, was inserted into a tube-like furnace. The sample tube was connected by a set of valves to other compartments of the apparatus, permitting either evacuation (up to  $5 \cdot 10^{-3}$  mm Hg) or introduction of gaseous hydrogen at atmospheric pressure (760 mm Hg). XRPD (X-Ray Powder Diffraction) measurements were carried out with a Philips PW-1710 diffractometer, using a Cu tube operated at 40 kV and 30 mA.

Prior to each hydriding procedure, the sample was pre-treated at 773 K under a vacuum of  $5 \cdot 10^{-3}$  mm Hg for 20 h. The duration of pre-treatment was double that needed to achieve complete dehydriding. The completeness of dehydriding was shown by the absence of hydride phase patterns in the XRPD spectrum. After this pre-treatment, the sample was heated up to the required temperature, in the range 423–523 K (150–250 °C). After a constant temperature had been obtained, hydriding was undertaken, starting with a hydrogen pressure of 103.4 kPa (760 mm Hg). The hydrogen pressure decreased during hydriding. The pressure decrease, typically amounting to 1–5 % of its initial value, was monitored by a closed mercury manometer, as a function of time. The hydrogen/alloy mole ratio, as a time dependent variable, was calculated on the basis of the pressure drop.

On completion of the hydriding reaction, when a final equilibrium pressure was achieved, dehydriding was undertaken. The next, second hydriding, as well as the third one, were repeated under identical conditions to those used for the first hydriding.

The multiple hydriding was carried out isothermally at five constant temperatures, *i.e.*, 423 K, 448 K, 473 K, 498 K and 523 K.

#### RESULTS AND DISCUSSION

In a previously published paper,<sup>8</sup> in which cyclic hydriding/dehydriding of a Zr<sub>1.02</sub>Ni<sub>0.98</sub> alloy sample was examined, it was observed that each subsequent hydriding of the same sample proceeded remarkably faster than the previous one.

In the present work, the initial parts of hydriding isotherms were used for a detailed kinetic study.

Assuming the hydriding reaction to be reversible, one can apply the following equation:



where A represents the Zr<sub>1.02</sub>Ni<sub>0.98</sub> alloy, and AH<sub>n</sub> is the corresponding hydride.

The dependence of the hydriding rate on the hydrogen pressure has been derived elsewhere<sup>5</sup>:

$$\frac{dn}{dt} = k \frac{p^a}{p_e^a} \left[ 1 - \frac{p_f}{p} \frac{n}{n_f} \right] \quad (2)$$

where  $p$ ,  $p_e$  and  $p_f$  are the hydrogen pressures at a given time, the plateau pressure (if one is dealing with a two-step isotherm), and the final equilibrium pressure, respectively;  $n$  and  $n_f$  are the mole ratios of atomic hydrogen/alloy, at a certain time, and in the equilibrium state, respectively. The rate constant is designated by  $k$  and the reaction order with respect to hydrogen is designated by  $a$ .

Typical curves depicting the time change of the mole ratio atomic hydrogen/Zr<sub>1.02</sub>Ni<sub>0.98</sub> alloy, relating to the first hydriding at various temperatures, are presented in Fig. 1.

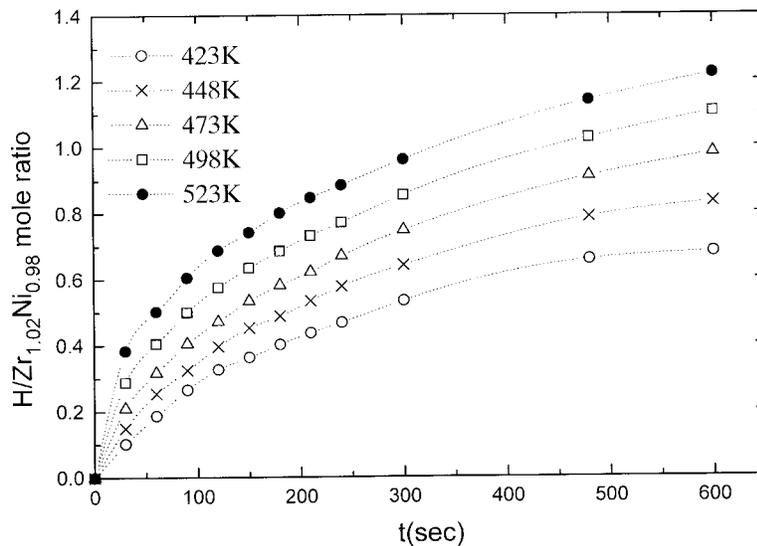


Fig. 1. The initial parts of the hydriding isotherms of Zr<sub>1.02</sub>Ni<sub>0.98</sub> alloy, relating to the first hydriding, at the following temperatures 423, 448, 473, 498 and 523 K.

The experimental data from Fig. 1 were fitted to Eq. (2) by plotting the hydriding rate ( $dn/dt$ ) vs.  $(p/p_e)^a [1 - (p_f/p) n/n_f]$ . A series of straight lines was

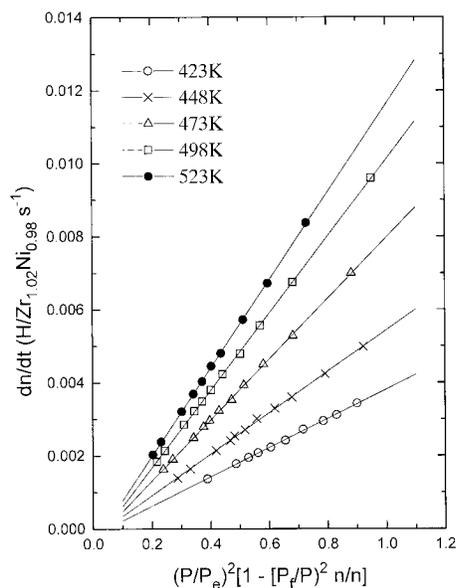


Fig. 2. The hydriding rate *vs.*  $(p/p_e)^2 [1 - (p/p_e)^2 n/n_f]$  for the first hydriding of a  $Zr_{1.02}Ni_{0.98}$  alloy at 423, 448, 473, 498 and 523 K.

obtained, which are presented in Fig. 2. Using Eq. (2), a reaction order of 2 was found to be the best fitting parameter.

The time dependence of the  $H/Zr_{1.02}Ni_{0.98}$  mole ratio at 423 K, for three subsequent hydriding procedures, is presented in Fig. 3, illustrating the increase in hydriding rate at each repetition of hydriding/dehydriding cycle. Similar plots were obtained also at temperatures 448, 473, 498 and 523 K. The data relating to the second hydriding were used to draw linear plots of hydriding rate *vs.*  $(p/p_e)^2$

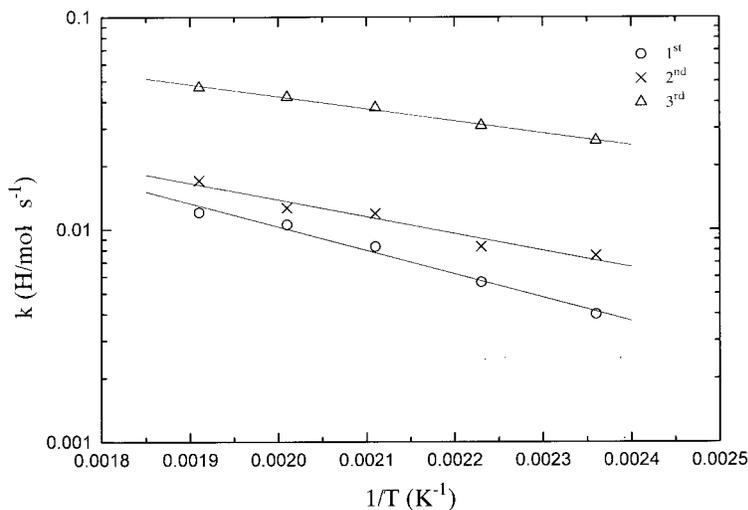


Fig. 3. The initial parts of the hydriding isotherms of a  $Zr_{1.02}Ni_{0.98}$  alloy sample, for the first, second and third subsequent hydriding at 423 K.

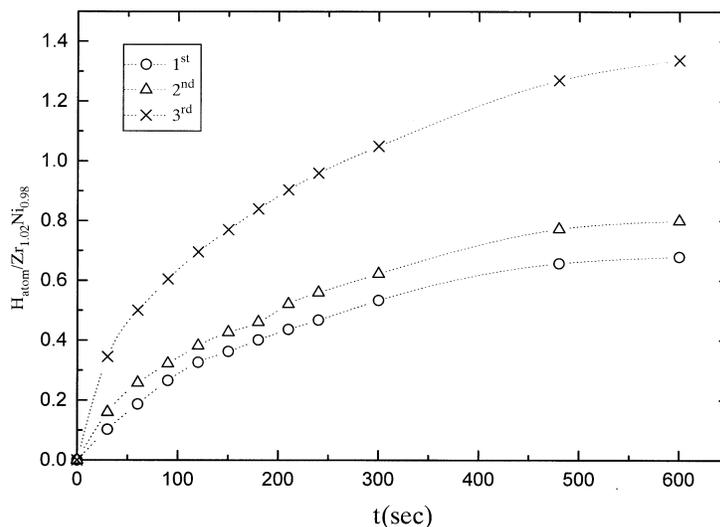


Fig. 4 The hydriding rate vs.  $(p/p_e)^2 [1 - (p/p_e)^2 n/n_f]$  for the second subsequent hydriding of  $Zr_{1.02}Ni_{0.98}$  alloy at the following temperatures: 423, 448, 473, 498 and 523 K.

$[1 - (p/p_e)^2 n/n_f]$ , according to the Eq. (2), using  $a = 2$ . These plots are presented in Fig. 4. The results of the third subsequent hydriding are presented in the same manner in Fig. 5. From Figs. 2, 4 and 5 it is obvious that the hydriding rate, expressed as the time change of the  $H/Zr_{1.02}Ni_{0.98}$  mole ratio, depends strongly on temperature.

The rate constants calculated from the slopes of the straight lines in Figs. 2, 4 and 5, using  $a = 2$ , together with the corresponding temperatures, enabled Arrhenius

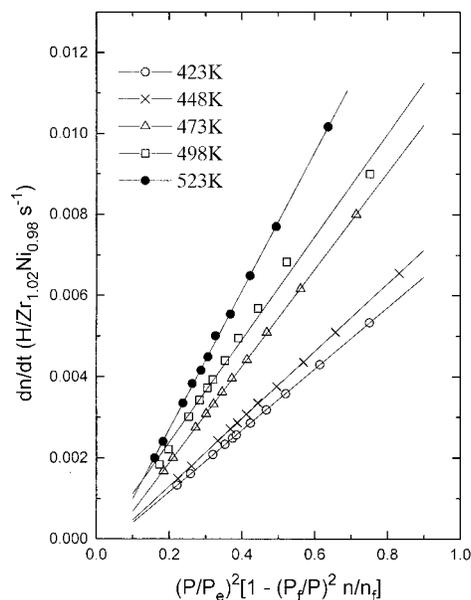


Fig. 5. The hydriding rate vs.  $(p/p_e)^2 [1 - (p/p_e)^2 n/n_f]$  for the third subsequent hydriding reactions of  $Zr_{1.02}Ni_{0.98}$  alloy at the following temperatures: 423, 448, 473, 498 and 523 K.

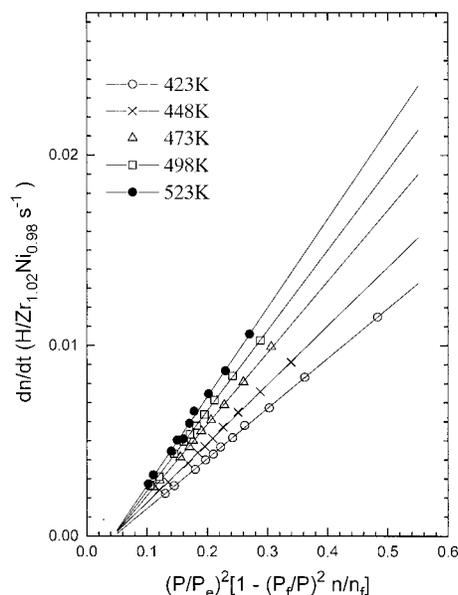


Fig. 6. Arrhenius plots for the first, second and third subsequent hydriding of  $Zr_{1.02}Ni_{0.98}$  alloys.

plots to be drawn (presented in Fig. 6) from which the activation energies for the first, the second and the third hydriding reactions could be determined.

The activation energies calculated from the slopes of Arrhenius plots amount to 9.2 kJ/mol, 7.5 kJ/mol and 4.72 kJ/mol for the first, second and third hydriding, respectively. The decrease in the activation energy upon each repetition of the hydriding is clearly evident.

The rate constants calculated for various temperatures for the three subsequent hydriding procedures are summarized in Table I. The increase in the value of the rate constant upon each subsequent hydriding is clearly apparent. As is evident from Table I, the rate constant relating to the second hydriding is about double the one relating to the first hydriding. The rate constant of the third hydriding is even three times higher than that relating to the second hydriding.

TABLE I. Hydriding rate constants for the three subsequent hydriding reactions of the  $Zr_{1.02}Ni_{0.98}$  alloy sample at different temperatures

Temperature/K	Rate constant/s <sup>-1</sup>		
	1st hydriding	2nd hydriding	3rd hydriding
423	0.00399	0.00755	0.02627
448	0.00565	0.00831	0.03088
473	0.00832	0.01190	0.03754
498	0.01055	0.01266	0.04213
523	0.01204	0.01706	0.04672

The increase in the hydriding rate upon each repetition of the hydriding procedure had already been established qualitatively in one of our previously published papers.<sup>8</sup> The results presented in Table I now illustrate this in a quantitative manner.

A possible explanation of the increase in the hydriding rate with increasing number of hydriding/dehydriding cycles can be found in the crushing of the alloy particles, leading to an increase in the surface area accessible to hydrogen.

An alternative explanation of the observed phenomenon might be that the remaining hydride phase serves as some sort of activating substance for hydrogen absorption.

In order to clarify this point the XRPD spectrum of the dehydrided samples were recorded after each dehydriding. The XRPD patterns of the dehydrided alloy samples always indicated the absence of a hydride phase. Based on these results, the explanation based on a hydride phase serving as an activating substance could be rejected.

Evidence of crushing and homogenization of alloy samples as a consequence of hydriding, on the example of nickel alloys has already been published elsewhere.<sup>9,10</sup> Namely, Libowitz *et al.* published that hydride phase formation causes the alloy particles to expand,<sup>9</sup> while Fukai<sup>10</sup> found that the unit cell dimensions can expand by up to  $2 \cdot 10^{-3} \text{ nm}^3$  due to site-occupancy by H atoms in nickel at a mole ratio  $H/Ni = 1$ .

Watanabe *et al.*<sup>7</sup> found that changes in the  $Zr_xNi_y$  alloy composition influences the kinetic and thermodynamic parameters of hydrogen absorption, such as activation energy, heat of absorption, kinetic isotope effect and selective pumping property. Upon heating above 800 °C for 10 min in a vacuum, the samples of various composition were exposed to hydrogen, the pressure of which varied in the range  $10^{-6} - 10^{-2} \text{ Pa}$ , during a period 10–180 min, at temperatures in the range 25–400 °C. The activation energies of hydriding were found to amount to 2.6 kcal/mol for Zr, 2.8 kcal/mol for  $Zr_{85}Ni_{15}$ , 1.1 kcal/mol for  $Zr_{80}Ni_{20}$  and 0.63 kcal/mol for  $Zr_{67}Ni_{33}$ . Based on both literature data and their own results, the authors concluded that the activation energy of hydriding depends on both the nature and the concentration of the alloying element in Zr-based alloys.

The activation energies of hydriding of  $Zr_{1.02}Ni_{0.98}$  alloy determined in the present work are in good agreement with those reported by Watanabe *et al.*, despite the difference in alloy composition, as well as in other experimental conditions. Our results also show that the activation energy evidently depends on the pre-history of the alloy sample, *i. e.* on the number of subsequent hydriding processes the alloy had previously undergone.

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## ИЗВОД

ИСПИТИВАЊЕ РЕАКЦИЈЕ ХИДРИРАЊА ЛЕГУРЕ  $Zr_{1.02}Ni_{0.98}$ БРАНИСЛАВ Р. СИМОНОВИЋ,<sup>\*</sup> СЛАВКО В. МЕНТУС и МИЛЕНКО В. ШУШИЋ

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Испитивна је кинетика хидрирања легуре  $Zr_{1.02}Ni_{0.98}$  у зависности од броја циклуса хидрирања/дехидрирања. Одређене су константе брзина за три узастопне реакције хидрирања на узорку легуре, на пет температура: 423, 448, 473, 498 и 523 К. Понављање циклуса хидрирања/дехидрирања праћено је сталним порастом константе брзине и опадањем активационе енергије. Ова појава је објашњена уситњавањем узорка, што доводи до повећања површине која је доступна водонику.

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