



# Hydrogen extraction by Laves phase alloys in an alkaline solution containing hydrazine

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## Abstract

The behavior of powders and electrodes of Laves phase alloys with C14 and C15-type structures was studied in 6 M KOH solution containing hydrazine monohydrate at 20°C. When these alloy powders were immersed in the solution, they extracted hydrogen from hydrazine and absorbed until the absorbing hydrogen reached the maximum value (about  $H/M=1$ , 410–429 mAh/g) after about 30 h. The initial rate of hydrogen absorption of these alloy powders was in the range of 26.2 to 37.0 mA/g when the rate was converted into the current density. On the other hand, as the electrode made from alloy powder was immersed in 6 M KOH solution containing 10 vol.% hydrazine monohydrate and was discharged, the electrode potential was linearly shifted to the cathodic side with the increase in current density. The current density reached 550–664 mA/g at  $-0.9$  V versus Ag/AgCl which was shifted about 300 mV from the rest potential to the cathodic side. © 1999 Published by Elsevier Science S.A. All rights reserved.

**Keywords:** Hydrogen storage alloy electrode; Laves phase; Treatment; Electrochemical properties

## 1. Introduction

No study with respect to the interaction between a hydrogen-absorbing alloy and hydrazine has been performed except for our previous works [1,2]. We have studied the interaction with hydrazine of a variety of AB<sub>5</sub> system alloys such as LaNi<sub>5</sub>, CaNi<sub>5</sub>, Ti–ZrNi, Ti<sub>2</sub>Ni, TiNi, Zr<sub>7</sub>Ni<sub>10</sub> and so on. These alloy electrodes were found to extract hydrogen from hydrazine and to absorb it. The initial rate of hydrogen absorption was in the range of 20 mA/g(LaNi<sub>5</sub>) to 167 mA/g(TiNi<sub>0.7</sub>), calculated in terms of current density in an alkaline solution containing 5 vol.% hydrazine monohydrate [1].

In this study, the rates of hydrazine decomposition and hydrogen absorption by the powders of the Laves phase alloys of Ti–Zr–Ni–V–Mn system with C14(hexagonal) or C15(cubic) type structures and by the electrochemical decomposition of hydrazine and hydrogen absorption with the electrodes made of the same alloys in an alkaline solution were studied. The properties of these alloys were also compared with those of AB<sub>5</sub> and Mg<sub>1.85</sub>Ni alloys.

## 2. Experimental details

In this study, four kinds of alloy were used as shown in Table 1. The alloy Mg<sub>1.85</sub>Ni (No. 4) was commercially obtained and the other alloys were obtained by arc melting under an argon atmosphere. These alloys were reduced to powder of less than 400 meshes and some powders were used to make an alloy electrode.

For making the alloy electrode, alloy powder (less than 400 meshes), Ni powder and PTFE (polytetrafluoroethylene) were mixed in the ratio of 72:24:4 (%) and the mixture was rolled into a sheet by rolling a roller on a steel board. An alloy electrode was made by sandwiching a nickel gauze between the two aforementioned sheets containing the alloy mixture and pressing them together. The electrode size was about 1.5×2.5×0.08 cm.

The interaction between the alloy powder and hydrazine was measured by stirring 2.0 g of alloy powder in 6 M KOH solution (750 ml) containing 5 to 20 vol.% hydrazine monohydrate at 20°C. The hydrogen quantity absorbed in the alloy powder and the decomposition quantity of hydrazine were calculated from the volume of the generated gas collected by a gas burette and the proportion of hydrogen gas measured by gas chromatography of the

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Table 1

Rate of hydrogen extraction from hydrazine and maximum hydrogen quantity of alloys in the 6 M KOH and hydrazine solution

No.	Composition of the alloy	Rate of hydrogen extraction		N <sub>2</sub> H <sub>4</sub> mAh/g	KOH mAh/g
		(1) <sup>1</sup>	(2) <sup>1</sup>		
1	Zr <sub>0.97</sub> Nb <sub>0.03</sub> (V <sub>0.10</sub> Ni <sub>0.55</sub> Mn <sub>0.30</sub> Co <sub>0.05</sub> ) <sub>2.09</sub>	0.81 × 10 <sup>-5</sup>	1.40 × 10 <sup>-5</sup>	429	427
2	Zr <sub>0.61</sub> Ti <sub>0.39</sub> (V <sub>0.10</sub> Ni <sub>0.57</sub> Mn <sub>0.28</sub> Co <sub>0.05</sub> ) <sub>1.80</sub>	1.15 × 10 <sup>-5</sup>	1.66 × 10 <sup>-5</sup>	410	413
3	LaNi <sub>3.4</sub> Co <sub>1.2</sub> Mn <sub>0.1</sub> Al <sub>0.3</sub>	4.80 × 10 <sup>-5</sup>	5.61 × 10 <sup>-5</sup>	345	343
4	Mg <sub>1.85</sub> Ni	3.86 × 10 <sup>-4</sup>	2.13 × 10 <sup>-4</sup>	267	252

(1) Initial rate (=initial rate of hydrogen absorption). (2) Latter rate; N<sub>2</sub>H<sub>4</sub>:maximum hydrogen quantity absorbed in 6 M KOH containing 5 vol.% N<sub>2</sub>H<sub>4</sub>; KOH:maximum hydrogen quantity absorbed electrochemically in 6 M KOH without hydrazine. 1: molH<sub>2</sub>/(min·g-alloy).

mixed gas of hydrogen and nitrogen. The total amount of hydrazine decomposed during the measurement of the extraction reaction was below  $3 \times 10^{-2}$  mol (about 2.6% of the total amount of hydrazine).

The dischargeability of the alloy electrode was measured in a 6 M KOH solution containing 10 vol.% hydrazine monohydrate as follows. At first, the alloy electrode was immersed in 6 M KOH until the electrode potential became stable and then the electrode was transferred into the solution containing hydrazine and the relation between the electrode potential and current density was measured in the range of 100 to 800 mA/g. The hydrazine concentration was kept constant by adding hydrazine monohydrate during these measurements. Furthermore, the same measurement was also carried out for the activated electrode by cycling charge/discharge in 6 M KOH solution without hydrazine.

### 3. Results and discussion

#### 3.1. Extraction of hydrogen from hydrazine with alloy powder

Fig. 1 shows the time-course of the quantity of hydrogen extracted from hydrazine and the quantity of hydrogen

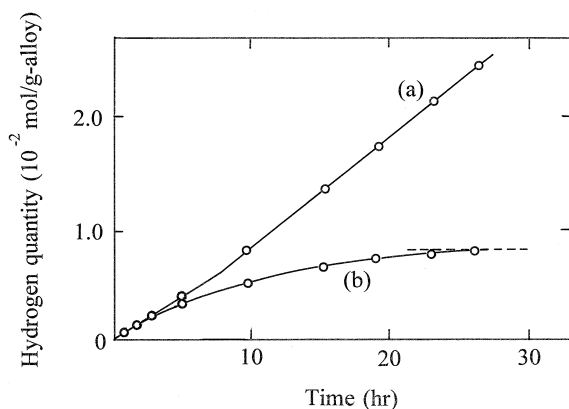


Fig. 1. Time-course of the quantity of hydrogen extracted from hydrazine and the quantity of hydrogen absorbed into No. 2 alloy. (a) Quantity of hydrogen extracted from hydrazine. (b) Quantity of hydrogen absorbed into No. 2. (broken line): Maximum quantity of hydrogen absorbed electrochemically in 6 M KOH. Hydrazine concentration: 5 vol.%; reaction temperature: 20°C.

absorbed in the No. 2 (C14 type) alloy powder in 6 M KOH solution containing 5 vol.% hydrazine monohydrate. The rate of hydrogen generated by the decomposition of hydrazine seemed to be changed after several hours. When these were approximated by two straight lines, the initial rate was  $1.15 \times 10^{-5}$  mol H<sub>2</sub>/(min·g-alloy) and that of the latter was  $1.66 \times 10^{-5}$  mol H<sub>2</sub>/(min·g-alloy) (Table 1). On the other hand, the rates of the No. 1 (C15 type) alloy powder were  $0.81 \times 10^{-5}$  molH<sub>2</sub>/(min·g-alloy) and  $1.40 \times 10^{-5}$  molH<sub>2</sub>/(min·g-alloy), respectively (Table 1). In the case of the Nos. 3 (AB<sub>5</sub>) and 4 (Mg–Ni) alloy powders, the rates were  $4.80 \times 10^{-5}$ – $5.61 \times 10^{-5}$  molH<sub>2</sub>/(min·g-alloy) and  $2.13 \times 10^{-4}$ – $3.86 \times 10^{-4}$  molH<sub>2</sub>/(min·g-alloy). Consequently, the activity of the hydrazine decomposition of the Nos. 1 and 2 alloys was lower than that of the Nos. 3 or 4 alloys.

In the beginning, the useless decomposition of hydrazine was not observed and all the generated hydrogen was absorbed into the alloy. The rate of hydrogen absorption into the alloy, although it was equal to that of hydrogen extraction at the beginning of the reaction, decreased with the increase of the quantity of hydrogen absorbed (Fig. 1, Table 1). The initial rate of hydrogen absorption of the Laves phase alloy (Nos. 1 and 2) was in the range of 26.2 to 30.0 mA/g. The quantity of hydrogen absorbed into the Laves phase alloys increased with increase in the time of immersion and the ratio of the hydriding value to saturated value reached about 75% after 15 h. At this point, about 50% of the hydrogen generated by the decomposition of hydrazine was absorbed into the alloy and the residual hydrogen was evolved as gas. The hydrogen quantity in the alloys reached saturation point after about 30 h. The saturated values (No. 1: 429 mAh/g, No. 2: 410 mAh/g) agreed with the quantity of hydrogen (427 mAh/g, 413 mAh/g) absorbed electrochemically in 6 M KOH solution without hydrazine (Table 1). On the other hand, the initial rate of hydrogen absorption of Nos. 3 and 4 alloy powders was faster than that of the Laves phase alloy and Nos. 3 and 4 reached saturation point within several hours (Fig. 2). When the ratio of the hydriding value to the saturated value reached 75%, the useless decomposition of hydrazine of the No. 3 alloy was 11% and that of the No. 4 alloy was 36%. These values were smaller than that of the Laves phase alloy.

As can be seen from Fig. 3, the initial rate of hydrogen

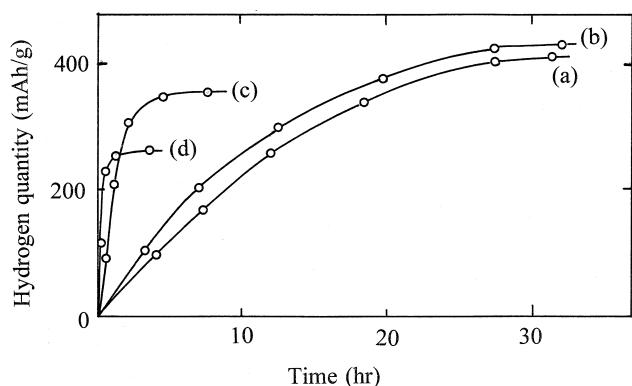


Fig. 2. Time-course of the quantity of hydrogen absorbed in the Nos. 1–4 alloys. (a) No. 1. (b) No. 2. (c) No. 3. (d) No. 4; hydrazine concentration: 5 vol.%; reaction temperature: 20°C.

generated by the hydrazine decomposition has a maximum value at about 10 vol.% hydrazine. The reason for this is considered to be as follows. At the beginning of reaction, hydrogen was absent on the surface of alloy, since all the generated hydrogen atoms were absorbed into the alloy. Therefore, it is considered that the number of adsorption sites for hydrazine molecules decreases because the desorption of a nitrogen molecule from the alloy surface or the rate of recombination of nitrogen atoms on the surface was slow. On the basis of the data of Fig. 3, the measurement of the following electrochemical discharge was carried out in 6 M KOH solution containing 10 vol.% hydrazine monohydrate.

### 3.2. Dischargeability for alloy electrodes

The electrode potential of the Nos. 1–4 alloy electrodes in 6 M KOH without hydrazine reached  $-0.97$  to  $-0.99$  V versus Ag/AgCl after immersed for 8 h and reached  $-1.17$  to  $-1.5$  V versus Ag/AgCl in 6 M KOH solution

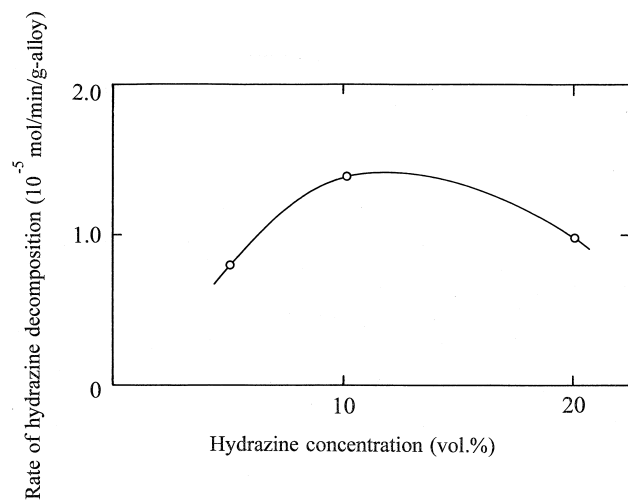


Fig. 3. Relation between the initial rate of hydrazine decomposition and the hydrazine concentration by the No. 1 alloy. Reaction temperature: 20°C.

containing 10 vol.% hydrazine monohydrate. The electrode potential at constant current density became stable after 1 to 1.5 h.

Fig. 4 shows the stable electrode potential dependence on the current density. The results of the Laves phase alloy are shown by (b) (No. 1 alloy) and (c) (No. 2 alloy). These electrode potentials decreased linearly with the increase in discharge current density until about  $-0.9$  V versus Ag/AgCl. The discharge current densities were 664 mA/g (b) and 552 mA/g (c) at  $-0.9$  V versus Ag/AgCl. These current densities were larger values than compared with the current densities (working at about 100 mA/g) in 6 M KOH solution without hydrazine. On the other hand, the electrode potentials of the No. 3 (a) and No. 4 alloy (d) also decreased with increase in the discharge current density. The current density of these alloys at  $-0.9$  V versus Ag/AgCl was 819 mA/g (No. 3) and 413 mA/g (No. 4), respectively.

On the other hand, for the electrode activated by charge/discharge cycling in 6 M KOH solution without hydrazine, the current density was in the range of 661 mA/g (No. 2) to 844 mA/g (No. 1) and increased by 109 mA/g to 180 mA/g compared with the electrode before activation.

For the electrode before activation, the current density at  $-0.9$  V versus Ag/AgCl depended on the proportion (No. 1 alloy: 37.2 at.%; No. 2: 36.7 at.%; No. 3: 56.7 at.% and No. 4: 35.1 at.%) of nickel atoms in the alloy composition. It shows that the difference in current density was caused by the proportion of nickel atoms.

After all the measurements were completed, small crevices were observed on the electrode sheets in contact with the nickel gauze. But the sheets were not broken.

From the above results, it can be seen that hydrazine monohydrate can be used in the hydrogenation and pulverization of hydrogen-absorbing alloys. Also, the hydrogen-absorbing alloys may be applicable not only as the electrode of a fuel cell but also as the catalyst for the decomposition of hydrazine in industrial drainage containing hydrazine.

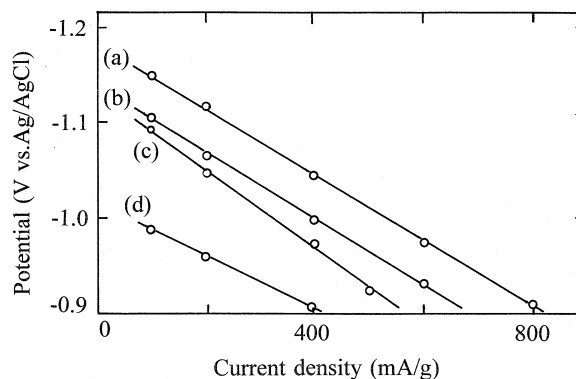


Fig. 4. Relation between electrode potential and current density for discharge in 6 M KOH solution containing 10 vol.% hydrazine monohydrate. (a) No. 3. (b) No. 1. (c) No. 2. (d) No. 4; reaction temperature: 20°C.

#### 4. Conclusions

For the Laves phase of C14 and C15 type, AB<sub>5</sub> and Mg<sub>1.85</sub>Ni alloys, the interaction with hydrazine was studied and the following results were obtained.

In the case of using alloy powders of the Laves phase with C14 and C15 structure, these powders extracted hydrogen from hydrazine and absorbed it. The initial extracting rates were in the range of  $0.81 \times 10^{-5}$  molH<sub>2</sub>/(min·g-alloy) to  $1.15 \times 10^{-5}$  molH<sub>2</sub>/(min·g-alloy) and these alloy powders reached saturation point at 410–429 mAh/g. The time for reaching saturation was slower than that of the No. 3 (AB<sub>5</sub>) and No. 4 (Mg<sub>1.85</sub>Ni) alloy powders.

Consequently, hydrazine solution can be used as the technique of hydrogenation and pulverization of hydrogen-absorbing alloys.

In the case of using the alloy electrodes of C14 and C15 type, these electrodes enabled large current density of 552 to 664 mA/g at  $-0.9$  V versus Ag/AgCl. The value of the current density was larger than that of the No. 4 and smaller than that of the No. 3 alloy electrodes. These current densities increased in the range of 20% to 33% when these electrodes were activated by charge/discharge cycling in 6 M KOH solution.

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