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Diffusion of hydrogen interstitials in Zr based AB₂ and mischmetal based AB₅ alloys

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Abstract

The Zr based AB₂ alloys ZrMnFe_{0.5}Ni_{0.5}, ZrMnFe_{0.5}Co_{0.5} and mischmetal (Mm) based AB₅ alloy MmNi_{3.5}Al_{0.5}Fe_{0.5}Co_{0.5} have been prepared and characterized by means of powder x-ray diffractograms. The hydrogen absorption kinetics of these alloys have been studied in the temperature and pressure ranges 450–650 °C and 10–100 mbar respectively with a maximum H to host alloy formula unit ratio of 0.01, using a pressure reduction technique. The diffusion coefficient of the hydrogen interstitials has been determined from hydrogen absorption kinetics experiments. The dependence of the diffusion coefficient on the alloy content has been discussed. For Mm based MmNi_{3.5}Al_{0.5}Fe_{0.5}Co_{0.5} alloy, the diffusion coefficient is about an order of magnitude higher than that of the Zr based alloys.

1. Introduction

During hydrogen absorption and desorption, diffusion of hydrogen atoms in the alloy occurs together with charge-transfer reactions on the alloy surfaces. There are reports available on evaluating the diffusion coefficient of hydrogen in metals, e.g. for Pd and Ni and alloys such as TiFe, Mg₂Ni and LaNi₅, using quasi-elastic neutron scattering and nuclear magnetic resonance methods [1]. In addition, the diffusion coefficient of hydrogen in LaNi₅ was determined from electrochemical techniques [2–5]. The timescales of electrochemical absorption and desorption of hydrogen in relation to the dimensions and geometries of the host metal hydride electrodes have also been reported [6]. Alternatively, the same information about the diffusion of hydrogen can be obtained from the hydrogen absorption–desorption kinetics [7, 8]. One of the common difficulties of this method is that, in many cases, the surface acts as a barrier to

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the flow of hydrogen. Therefore, the experimental technique requires that the surface barrier effects are negligible in order to investigate the actual bulk diffusion behaviour. The surface barrier effects are more pronounced at lower temperatures. Besides this, it is well known that alloys disintegrate into fine particles owing to the presence of hydrogen atoms due to the formation of β phase, which results in a large volume expansion. Thus disintegration should be avoided in order to truly find the bulk diffusion behaviour of hydrogen. The bulk diffusion behaviours of hydrogen in Ti_3Ir and NiTi alloys have been studied using the hydrogen absorption kinetics at low pressure and high temperatures [9, 10].

In this paper, we report the diffusion behaviour of hydrogen in the Zr based AB_2 alloys $\text{ZrMnFe}_{0.5}\text{Ni}_{0.5}$, $\text{ZrMnFe}_{0.5}\text{Co}_{0.5}$ and Mm based AB_5 alloy $\text{MmNi}_{3.5}\text{Al}_{0.5}\text{Fe}_{0.5}\text{Co}_{0.5}$ obtained from hydrogen absorption kinetics. Using the hydrogen absorption isotherms of $\text{ZrMnFe}_{0.5}\text{Ni}_{0.5}$, $\text{ZrMnFe}_{0.5}\text{Co}_{0.5}$ and $\text{MmNi}_{3.5}\text{Al}_{0.5}\text{Fe}_{0.5}\text{Co}_{0.5}$ for the temperature range 30–100 °C published already [11–13], the experiments were performed at high temperature (450–650 °C) and at low hydrogen pressure (10–100 mbar) with small hydrogen concentrations ranging up to $r = 0.01$, where r is the number of hydrogen interstitials per host alloy formula unit, such that the effects due to the surface barrier and the segregation are safely excluded and the hydrogen equilibrium pressures follow Sievert's law.

2. Experimental details

The mischmetal (Mm) (Bharat Rare Earth Metals, India) used has the following composition: Ce 50%, La 35%, Nd 5%, Pr 8 %, Fe 0.5% and other rare earth elements 1.5%. The alloys were prepared from the constituent elements (purity 99.999%) as described in [11–13]. The alloy was annealed for three days at 900 °C in vacuum. The materials were characterized by means of powder XRD [11–13].

The hydrogen absorption kinetics is determined in a vacuum system equipped with a temperature-controlled sample cell (the volume of the sample cell is about 20 cm³) which can be connected to a calibrated standard volume of 200 cm³ and a sensitive membrane pressure gauge. The sample is kept in one closed end of a quartz tube which is inserted into the centre of the furnace. The temperature of the sample is measured by keeping a thermocouple very close to the quartz tube. The sample temperature can be measured with an accuracy of ± 1 °C. Hydrogen gas purified by a Pd permeation cell is first admitted to a partial volume of the system, and the measurement of the hydrogen gas pressure admitted and the standard volume yields the amount of the added hydrogen. First of all, the volumes of the sample cell at different temperatures are obtained by the pressure reduction method by doing the experiment without the sample. This allows us to take into account the diffusion of hydrogen through the quartz tube at high temperatures (if any), along with the volume of the sample cell. The sample is then loaded and, after evacuation, the alloy investigated is exposed to hydrogen gas by opening a valve to the sample cell. The time dependence of the hydrogen pressure in the system is thus related to the hydrogen diffusion in the bulk of the sample.

The diffusion coefficient of the hydrogen in the essentially spherical alloys (the geometry of the samples has been made as close as possible to a sphere of radius 3 ± 0.1 mm and mass of approximately 0.8 g) is determined from the time dependence of the pressure decrease in the sample chamber during the absorption process. In the present situation, we measure the true diffusion coefficient of the hydrogen interstitials by performing the measurements only at and above 450 °C, a temperature where surface reactions tend not to impede H_2 absorption significantly. Our later results for the diffusion coefficient will also clearly indicate that bulk diffusion dominated the absorption process.

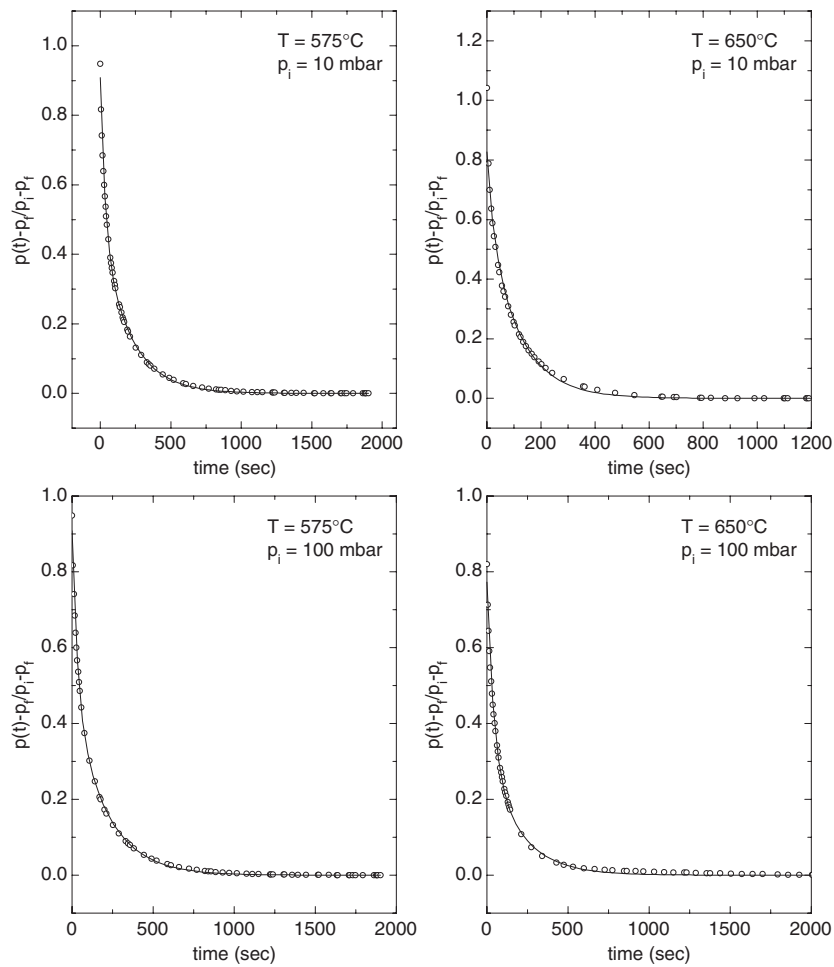


Figure 1. Normalized presentation of the time dependent decrease in pressure during the absorption processes at 575 and 650 °C for ZrMnFe_{0.5}Ni_{0.5} at initial pressures of 10 and 100 mbar.

3. Results and discussion

The time dependent pressure decrease in the sample cell due to hydrogen absorption, for ZrMnFe_{0.5}Ni_{0.5}, ZrMnFe_{0.5}Co_{0.5} and MmNi_{3.5}Al_{0.5}Fe_{0.5}Co_{0.5} systems, has been taken at different temperatures. The absorption rate increases with increasing temperature, as expected for a thermally activated diffusion reaction. For an absorption process controlled by bulk diffusion in a spherical sample with radius R , the diffusion coefficients can be obtained using equation (1) [14]:

$$\frac{p(t) - p_f}{p_i - p_f} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-n^2\pi^2 D}{R^2} t\right) \quad (1)$$

where p_i , p_f and $p(t)$ are the hydrogen initial pressure, final pressure and pressure at any instant of time. The normalized presentation of the pressure decrease in equation (1) is given in figures 1–3. The theoretical line from equation (1) exactly fits the experimental data for the hydrogen absorption kinetics in the ZrMnFe_{0.5}Ni_{0.5}, ZrMnFe_{0.5}Co_{0.5} and

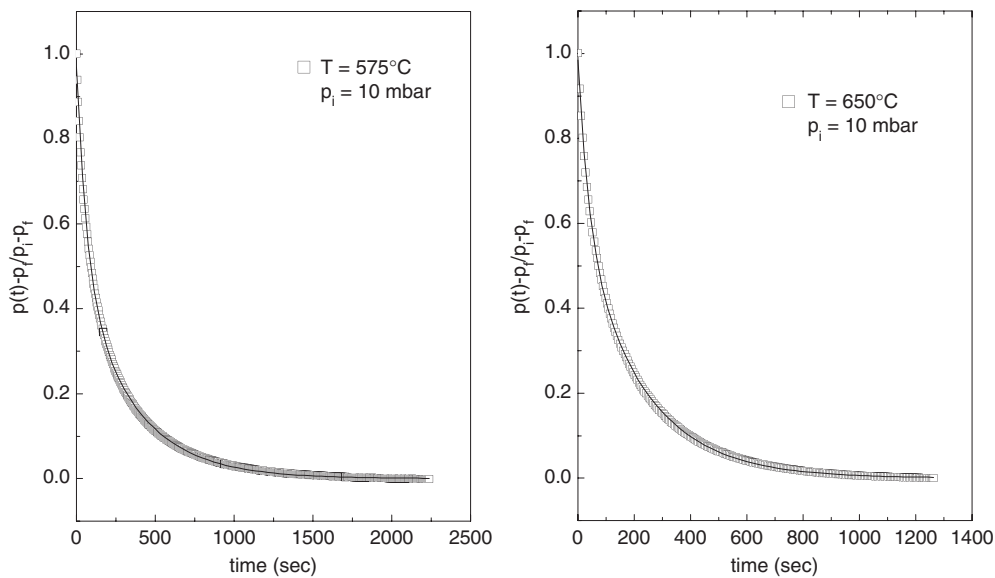


Figure 2. Normalized presentation of the time dependent decrease in pressure during the absorption processes at 575 and 650 °C at an initial pressure of 10 mbar for $\text{ZrMnFe}_{0.5}\text{Co}_{0.5}$.

Table 1. Activation energy and diffusion coefficient for $\text{ZrMnFe}_{0.5}\text{Ni}_{0.5}\text{-H}$, $\text{ZrMnFe}_{0.5}\text{Co}_{0.5}\text{-H}$ and $\text{MmNi}_{3.5}\text{Al}_{0.5}\text{Fe}_{0.5}\text{Co}_{0.5}\text{-H}$ systems.

Alloy hydrides	Activation energy (meV)	D ($\text{cm}^2 \text{s}^{-1}$)	
		(550 °C)	D_0 ($\text{cm}^2 \text{s}^{-1}$)
$\text{ZrMnFe}_{0.5}\text{Ni}_{0.5}\text{-H}$	295 ± 20	$(7.9 \pm 0.5) \times 10^{-5}$	$(6.5 \pm 0.5) \times 10^{-3}$
$\text{ZrMnFe}_{0.5}\text{Co}_{0.5}\text{-H}$	295 ± 20	$(3.1 \pm 0.2) \times 10^{-5}$	$(2.0 \pm 0.5) \times 10^{-3}$
$\text{MmNi}_{3.5}\text{Al}_{0.5}\text{Fe}_{0.5}\text{Co}_{0.5}\text{-H}$	285 ± 20	$(3.2 \pm 0.2) \times 10^{-4}$	$(2.1 \pm 0.5) \times 10^{-2}$

$\text{MmNi}_{3.5}\text{Al}_{0.5}\text{Fe}_{0.5}\text{Co}_{0.5}$ systems. Figures 1–3 show a good fitting of the experimental data for the three samples, which supports the suggestion that the absorption process is controlled by a diffusion process without a surface barrier effect. In the present work, the deviation of the geometry of the sample from a perfect sphere is assumed to be small. The diffusion coefficients D were determined from the fitting parameters and the values obtained for the three alloys investigated are presented in a semilogarithmic plot of D versus the reciprocal temperature T , and they are shown in figure 4. The dependence of the diffusion coefficients on temperature presented in figure 4 is well described by an Arrhenius relation $D = D_0 \exp(-\frac{E_a}{k_B T})$ where E_a is the activation energy, D_0 is the pre-exponential factor and k_B is Boltzmann's constant. The values for the activation energy E_a and pre-exponential constant D_0 , determined from the fitted solid lines in figure 4 for $\text{ZrMnFe}_{0.5}\text{Ni}_{0.5}\text{-H}$, $\text{ZrMnFe}_{0.5}\text{Co}_{0.5}\text{-H}$ and $\text{MmNi}_{3.5}\text{Al}_{0.5}\text{Fe}_{0.5}\text{Co}_{0.5}\text{-H}$, along with their diffusion coefficients D at 550 °C, are presented in table 1.

It was already pointed out that the absorption measurements yield correct diffusion coefficients only as long as the surface barrier effects are negligible. In the present study, the surface barrier effects did not noticeably influence the data. This can be realized from the fact that the absorption induced pressure decrease in figures 1–3 is well described by equation (1), which presupposes an absorption that is dominated by bulk diffusion. Besides this, the variation of the diffusion coefficients with temperature (figures 1–3) clearly exhibits

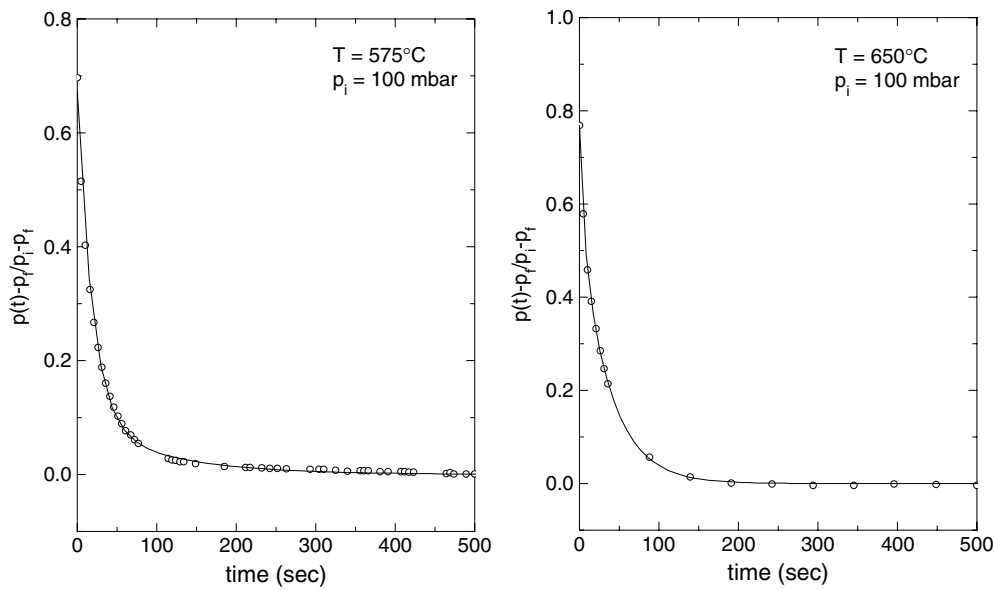


Figure 3. Normalized presentation of the time dependent decrease in pressure during the absorption processes at 575 and 650 °C for $\text{MmNi}_{3.5}\text{Al}_{0.5}\text{Fe}_{0.5}\text{Co}_{0.5}$ at an initial pressure of 10 mbar.

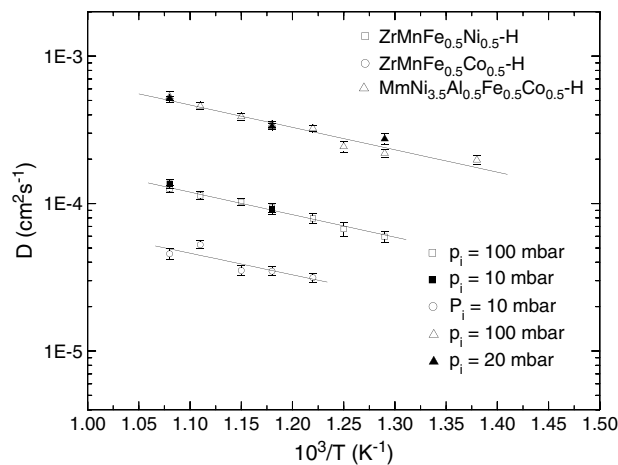


Figure 4. Diffusion coefficient of hydrogen in $\text{ZrMnFe}_{0.5}\text{Ni}_{0.5}$, $\text{ZrMnFe}_{0.5}\text{Co}_{0.5}$ and $\text{MmNi}_{3.5}\text{Al}_{0.5}\text{Fe}_{0.5}\text{Co}_{0.5}$ in a semilogarithmic plot versus the reciprocal temperature ($1/T$).

an Arrhenius behaviour. Surface barrier effects are expected to be more influential at lower temperature by decreasing the diffusion coefficient, resulting in deviations from the Arrhenius behaviour.

The activation energy for hydrogen diffusion in $\text{ZrMnFe}_{0.5}\text{Ni}_{0.5}$ and $\text{ZrMnFe}_{0.5}\text{Co}_{0.5}$ is 295 ± 20 meV, which is comparable to the reported value of $\text{ZrMn}_2\text{-H}_3$ (160 ± 20 meV) [15]. A number of reports on the activation energy of hydrogen in LaNi_5 and its substituted alloys are in the range 220 to 440 ± 20 meV [1]. The activation energy obtained in the present work for $\text{MmNi}_{3.5}\text{Al}_{0.5}\text{Fe}_{0.5}\text{Co}_{0.5}\text{-H}$ is 285 ± 20 meV. The hydrogen diffusion coefficient obtained

in the present investigation for $\text{MmNi}_{3.5}\text{Al}_{0.5}\text{Fe}_{0.5}\text{Co}_{0.5}$ ($\sim 10^{-4} \text{ cm}^2 \text{ s}^{-1}$) is about an order of magnitude higher than that for Zr based AB_2 alloys ($\sim 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) probably due to both the difference in crystal structure and the presence of rare earth metals in the Mm based alloy [16].

4. Conclusion

In the ranges of temperature and pressures (450–650 °C and 10–100 mbar) and concentration ($r < 0.1$) investigated, the diffusion coefficient $D = D_0 \exp(\frac{-E_a}{k_B T})$ of the hydrogen has the activation energy $E = 285 \pm 20$, 295 ± 20 and 295 ± 20 meV and the pre-exponential factor $D_0 = (2.1 \pm 0.5) \times 10^{-2}$, $(6.5 \pm 0.5) \times 10^{-3}$ and $(2.0 \pm 0.5) \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ respectively for $\text{MmNi}_{3.5}\text{Al}_{0.5}\text{Fe}_{0.5}\text{Co}_{0.5}\text{-H}$, $\text{ZrMnFe}_{0.5}\text{Ni}_{0.5}\text{-H}$ and $\text{ZrMnFe}_{0.5}\text{Co}_{0.5}\text{-H}$. The diffusion coefficient of hydrogen for the Mm based alloy is about one order of magnitude higher than that for the Zr based alloys probably due to the difference in crystal structure and the presence of rare earth metals in the Mm based alloy.

Acknowledgments

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References

- [1] Richter D, Hempelmann R and Bowman R C Jr 1992 *Hydrogen in Intermetallic Compounds—II* (Springer Topics in Applied Physics vol 67) ed L Schlapbach (Berlin: Springer)
- [2] Zuchner H, Rauf T and Hempelmann R 1991 *J. Less-Common Met.* **172–174** 611
- [3] Ciureanu M, Ryan D H, Strom-Olsen J O and Trudeau M L 1993 *J. Electrochem. Soc.* **140** 579
- [4] Zheng G, Popov B N and White R E 1995 *J. Electrochem. Soc.* **142** 2695
- [5] Zheng G, Popov B N and White R E 1996 *J. Electrochem. Soc.* **143** 834
- [6] Conway B E and Wojtowicz J 1992 *J. Electroanal. Chem.* **326** 277–97
- [7] Haraki T, Inomata N and Uchida H 1999 *J. Alloys Compounds* **293–295** 407–11
- [8] Oh J W, Kim C Y, Nahm K S and Sim K S 1998 *J. Alloys Compounds* **278** 270–6
- [9] Beisenherz A D, Guthardt D and Wipf H 1991 *J. Less-Common Met.* **172–174** 693
- [10] Schmidt B R, Schlereth M, Wipf H, Assumus W and Müllner M 1989 *J. Phys.: Condens. Matter* **1** 2473
- [11] Mani N, Kesavan T R and Ramaprabhu S 2002 *J. Phys. C: Solid State Phys.* **14** 3939–49
- [12] Mani N, Sivakumar R and Ramaprabhu S 2002 *J. Alloys Compounds* **337** 148–54
- [13] Mani N and Ramaprabhu S 2004 *J. Alloys Compounds* **363** 275–91
- [14] Hempelmann R, Richter D, Pugliesi R and Vinhas L A 1983 *J. Phys. F: Met. Phys.* **13** 59–68
- [15] Shinar J, Davidov D, Shaltiel D and Kaplan N 1979 *Z. Phys. Chem. NF* **117** 69
- [16] Chen J, Dou S X, Bradhurst D H and Liu H K 1998 *Int. J. Hydrogen Energy* **23** 177–82