

Solubility and diffusion of hydrogen in AB₂-type Laves phase alloys

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Abstract

Solubility of H₂ gas and diffusion of H interstitials were studied in Ti_{0.1}Zr_{0.9}Mn_{0.9}V_{0.1}Fe_{0.5}Ni_{0.5}, (Ti_{0.1}Zr_{0.9})_{1.1}Mn_{0.9}V_{0.1}Fe_{0.5}Ni_{0.5} and Ti_{0.1}Zr_{0.9}Mn_{0.9}V_{0.1}Fe_{0.5}Co_{0.5} alloys with C14 hexagonal structure. Data were taken between 400 and 600 °C, for H₂ gas pressures up to 100 mbar and H concentrations up to 0.012 H atoms per host-metal formula unit (solid solution phase). H₂ absorption is exothermic, and the partial enthalpy of solution per H atom is $-(210 \pm 10)$ and $-(248 \pm 10)$ meV for the two alloys Ti_{0.1}Zr_{0.9}Mn_{0.9}V_{0.1}Fe_{0.5}Ni_{0.5} and (Ti_{0.1}Zr_{0.9})_{1.1}Mn_{0.9}V_{0.1}Fe_{0.5}Ni_{0.5}, respectively. The diffusion coefficient of the H interstitials was determined for all three samples from the kinetics of H₂ gas absorption. At 500 °C, the diffusion coefficients are $\sim 5 \times 10^{-5}$ cm²s⁻¹, with activation energies between 292 and 423 meV. © 2005 Elsevier B.V. All rights reserved.

Keywords: Hydrogen absorption; Hydrogen solubility; Hydrogen diffusion; Laves phase alloys

1. Introduction

Zr-based AB₂ Laves phase H-storage alloys are promising candidates for the negative electrode in Ni–metal hydride batteries [1–3]. The battery performance depends on H solubility and absorption kinetics, where the latter involves also H diffusion within the alloys.

This paper reports experiments in which we studied H₂ gas solubility of and H diffusion in the three Zr-based Laves phase alloys Ti_{0.1}Zr_{0.9}Mn_{0.9}V_{0.1}Fe_{0.5}Ni_{0.5}, Ti_{0.1}Zr_{0.9}Mn_{0.9}V_{0.1}Fe_{0.5}Co_{0.5} and (Ti_{0.1}Zr_{0.9})_{1.1}Mn_{0.9}V_{0.1}Fe_{0.5}Ni_{0.5}. The experiments were performed between 400 and 600 °C and for small H concentrations ranging up to $r = 0.012$, where r is the number of H interstitials per host-metal formula unit. For all investigated alloys, the small H concentrations guaranteed that H was in solid solution (α -phase). Our experiments differ in this respect from previous H absorption studies on the same alloys, carried out with high H concentrations (up to $r = 3.4$) [4].

2. Experimental details

The Ti_{0.1}Zr_{0.9}Mn_{0.9}V_{0.1}Fe_{0.5}Ni_{0.5}, Ti_{0.1}Zr_{0.9}Mn_{0.9}V_{0.1}Fe_{0.5}Co_{0.5} and (Ti_{0.1}Zr_{0.9})_{1.1}Mn_{0.9}V_{0.1}Fe_{0.5}Ni_{0.5} alloys were prepared from the constituent elements in an arc furnace under an argon atmosphere of about 0.8 bar. The samples were remelted six times by turning them upside down to ensure homogeneity. X-ray powder diffraction (Fe K α radiation) confirmed for all investigated alloys C14 hexagonal structure with space group *P6₃/mmc*. Other phases were not observed. The lattice parameters a and c are listed in Table 1.

H₂ gas solubility was determined in a vacuum system equipped with a temperature-controlled sample cell (accuracy ± 0.3 °C) and a sensitive membrane pressure gauge. The investigated alloy in the cell was exposed to H₂ gas (pressures between 0.1 and 100 mbar) and the absorbed H concentrations were determined from the pressure decrease following absorption.

The diffusion coefficient of the H interstitials in the essentially spherical alloys (radii R between 3.0 and 3.1 mm) was determined from the time dependence of the pressure decrease in the sample cell during the absorption process. In this situation, a prerequisite for measuring a true diffusion co-

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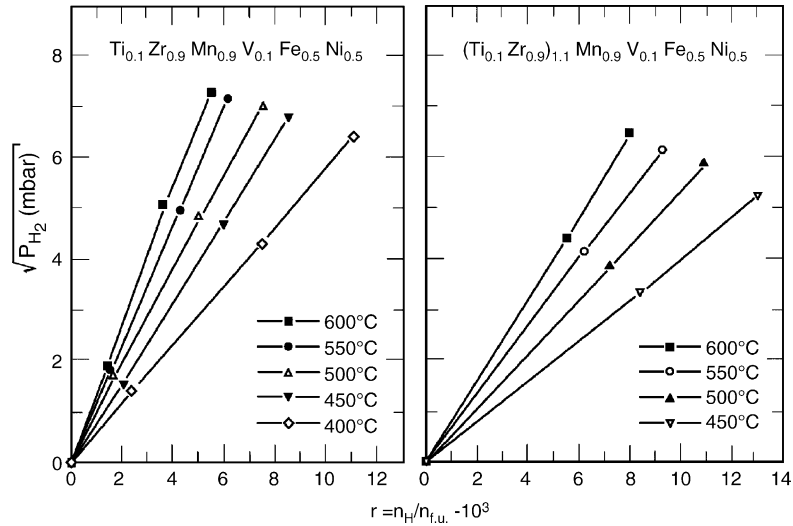


Fig. 1. Hydrogen absorption isotherms $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ (left) and $(\text{Ti}_{0.1}\text{Zr}_{0.9})_{1.1}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ (right). For the indicated temperatures, the square root of the H_2 gas pressure is plotted vs. H concentration r .

efficient is that H_2 absorption kinetics is dominated by bulk diffusion, and not by surface barrier effects. Therefore, we performed measurements only at and above 400°C where surface barriers become less important. The consistency of our results for the diffusion coefficients will also show that bulk diffusion dominated the absorption kinetics.

3. Results and discussions

3.1. Hydrogen solubility

Fig. 1 presents the H absorption isotherms obtained from the $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ and $(\text{Ti}_{0.1}\text{Zr}_{0.9})_{1.1}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ alloys, respectively. For each temperature, H concentration r is proportional to the square root of H_2 gas pressure p . Therefore, the isotherms obey Sieverts' law [5–9] which demonstrates that H–H interaction effects are negligible and, in particular, that the H was in solid solution in the investigated H concentration and temperature range.

H absorption is quantitatively described by the partial enthalpy of solution Δh and the non-configurational partial entropy of solution $\Delta s^{(0,nc)}$ [5–9]. For the present pressures where an ideal H_2 gas can be assumed these two quantities are defined by $\Delta h = h_{\text{H}} - \frac{1}{2}h_{\text{H}_2}$ and $\Delta s^{(0,nc)} = s_{\text{H}}^{nc} - \frac{1}{2}s_{\text{H}_2}^0$, where h_{H_2} is the enthalpy per H_2 gas molecule and $s_{\text{H}_2}^0$ is, for a standard reference pressure $p_0 = 1 \text{ atm} = 1.01325 \text{ bar}$,

the entropy per gas molecule. Further, h_{H} is the partial enthalpy and s_{H}^{nc} is the non-configurational part of the partial entropy of a H interstitial in the respective alloy. The total partial entropy of the H interstitials is the sum of s_{H}^{nc} and the configurational partial entropy $-k_{\text{B}} \ln(r/r_0)$, where r_0 is the number of interstitial sites per host-metal formula unit. The value of r_0 is not precisely known, or at least under discussion [10], so that we arbitrarily assume $r_0 = 1$. It is obvious that a different r_0 value, for instance $r_0 = n$, will add the term $-k_{\text{B}} \ln(n)$ to s_{H}^{nc} and $\Delta s^{(0,nc)}$ [5–9].

With the two quantities Δh and $\Delta s^{(0,nc)}$ above, the relationship between H concentration r and H_2 gas pressure p can be written as [5–9]

$$\frac{r}{r_0} = \sqrt{\frac{p}{p_0}} \exp\left(\frac{-\Delta h}{k_{\text{B}}T}\right) \exp\left(\frac{\Delta s^{(0,nc)}}{k_{\text{B}}}\right) \quad (1)$$

where T is the temperature and k_{B} is the Boltzmann's constant.

Our numerical results for Δh and $\Delta s^{(0,nc)}$ were obtained by standard procedure from the absorption isotherms [5,6,8,9] and are collected in Table 1. The fact that Sieverts law holds means that Δh and $\Delta s^{(0,nc)}$ are concentration independent. The present absorption data show further that these two quantities do also not exhibit any temperature dependence within experimental accuracy.

Table 1

Comparison of results for lattice parameters a and c , partial enthalpy of solution, Δh , non-configurational partial entropy of solution $\Delta s^{(0,nc)}$, diffusion coefficient D at 500°C , activation energy E and pre-exponential factor D_0

Alloy	a (Å)	c (Å)	$-\Delta h$ (meV)	$-\Delta s^{(0,nc)}$ (meV/K)	D (500°C) (cm^2/s)	E (meV)	D_0 (cm^2/s)
1	4.993	8.152	210 ± 10	0.56 ± 0.10	$(5.9 \pm 0.5) \times 10^{-5}$	423 ± 25	3.5×10^{-2}
2	5.014	8.200	248 ± 10	0.56 ± 0.10	$(4.3 \pm 0.5) \times 10^{-5}$	292 ± 15	4.0×10^{-3}
3	4.990	8.161	–	–	$(4.6 \pm 0.5) \times 10^{-5}$	320 ± 44	6.0×10^{-3}

Alloy 1, 2 and 3 represents $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$, $(\text{Ti}_{0.1}\text{Zr}_{0.9})_{1.1}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ and $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Co}_{0.5}$, respectively.

3.2. Hydrogen diffusion

Fig. 2 presents, for the $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Co}_{0.5}$ alloy, examples for the time-dependent pressure decrease in the sample cell due to H_2 gas absorption after the gas was admitted at time $t = 0$. The data were taken at different temperatures and it is clearly seen that the absorption rate increases with increasing temperature, as expected for a thermally activated diffusion process.

The pressure decrease describes the amount of H_2 gas absorbed by the respective alloy. For an absorption process controlled by bulk diffusion in a spherical sample with radius R , the absorption-induced variation of pressure $p(t)$ with time t can be written as [11]

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

where D is the diffusion coefficient, p_i is the initial pressure at time $t = 0$ and p_f is the final pressure for $t = \infty$. The normalized presentation of the pressure decrease in Eq. (2) is identical to that of the data in Fig. 2. Eq. (2) considers a diffusion process with constant H concentration at the sample surface. This is not entirely correct since H_2 gas absorption implies a decreasing pressure $p(t)$ and, thus, a decreasing equilibrium H concentration at the sample surface. Therefore, the total pressure decrease $p_i - p_f$ was always kept sufficiently small against p_i in order to make this effect negligible.

Using Eq. (2), we determined diffusion coefficients D from our data with the help of a fit routine. The solid fitted curves in Fig. 2 demonstrate that Eq. (2) provides a good description of our data. This supports a diffusion dominated absorption since effective surface barriers would lead to an absorption behavior different from Eq. (2). The diffusion coefficients obtained for the three investigated alloys are collected in Fig. 3.

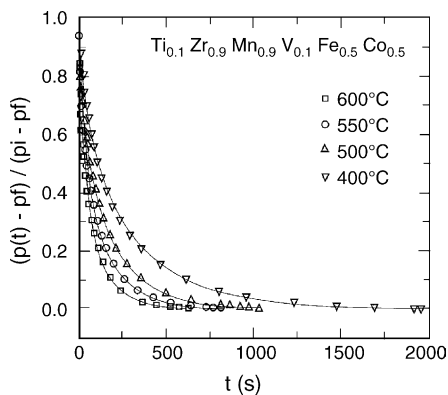


Fig. 2. H_2 gas pressure decrease following H absorption in $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Co}_{0.5}$ as a function of time t . The pressure decrease is given in the normalized form $(p(t) - p_f)/(p_i - p_f)$, where $p(t)$ is the pressure at time t , p_i the initial pressure and p_f is the final pressure.

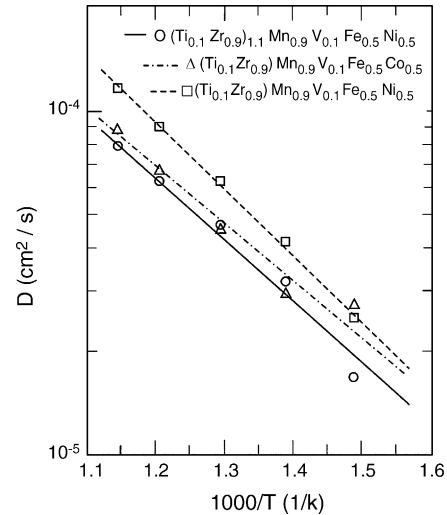


Fig. 3. Arrhenius plot of the diffusion coefficient of H in $(\text{Ti}_{0.1}\text{Zr}_{0.9})_{1.1}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$, $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Co}_{0.5}$ and $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$. The diffusion coefficient is logarithmically plotted vs. reciprocal temperature.

The solid, broken and dotted lines in Fig. 3 were fitted to our data for an Arrhenius relation $D = D_0 \exp\left(\frac{-E}{k_B T}\right)$, where D_0 and E are the pre-exponential constant and the activation energy, respectively. The lines describe our data well which again makes a noticeable influence of surface barriers unlikely since such barriers are particularly effective at lower temperatures and would, therefore, simulate an additional decrease of the measured diffusion coefficient at lower temperatures, thus causing deviations from an Arrhenius relation. The values for E and D_0 , as determined from the fitted lines in Fig. 3 are presented in Table 1, together with the value of D at 500°C .

The presently determined (chemical) diffusion coefficient D describes the H flux in a H-concentration gradient according to Fick's first law [5,12–15]. This diffusion coefficient is of potential relevance in technological applications since it describes absorption or desorption kinetics in a diffusion dominated situation. It has, to our knowledge, not yet been measured for Zr-based AB_2 Laves phase alloys. In previous studies, the self (or tracer) diffusion coefficient D_{self} was determined which characterizes diffusion of a single (tagged) H interstitial, even in the absence of H concentration gradients. Although D_{self} applies to a different situation and differs generally from the chemical diffusion coefficient D , it is interesting to compare our results for D , as given in Table 1, with literature data for D_{self} of H in the two representative Laves phase alloys $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMn}$ [16] and ZrCr_2 [17] (see further references in [16,17]). At 500°C , the D_{self} values in these alloys, obtained by a high-temperature extrapolation, are $1.1 \times 10^{-5} \text{ cm}^2/\text{s}$ [16] and $1.6 \times 10^{-5} \text{ cm}^2/\text{s}$ [17], thus being somewhat smaller than our results for D . Considering finally the activation energies, we find that the reported data, 220 meV [16] and 136 meV [17], vary much more than our values which are between 292 and 423 meV.

4. Conclusion

H₂ gas solubility of and H diffusion in Ti_{0.1}Zr_{0.9}Mn_{0.9}V_{0.1}Fe_{0.5}Ni_{0.5}, Ti_{0.1}Zr_{0.9}Mn_{0.9}V_{0.1}Fe_{0.5}Co_{0.5} and (Ti_{0.1}Zr_{0.9})_{1.1}Mn_{0.9}V_{0.1}Fe_{0.5}Ni_{0.5} were studied for low H concentrations (solid solution phase). The partial enthalpy of solution and the non-configurational partial entropy of solution for the (exothermic) absorption process were determined. The diffusion coefficients follow an Arrhenius relation with activation energies between 292 and 423 meV. At 500 °C, the diffusion coefficients have a value of $\sim 5 \times 10^{-5}$ cm²/s.

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