Journal of Alloys and Compounds 293–295 (1999) 385–390

Journal of
ALLOYS
AND COMPOUNDS

Evaluation of kinetics by utilizing the normalized pressure dependence method for the alloy $Ti_{0.95}Zr_{0.05}Mn_{1.48}V_{0.43}Fe_{0.08}Al_{0.01}$

V.M. Skripnyuk*, M. Ron

Faculty of Materials Engineering, Technion, Haifa 32000, Israel

Abstract

A recently suggested normalized pressure dependence method, NPDM, was utilized in this study. For the decomposition process the NPDM includes a pressure dependence function $F(P)=(P_{eq}-P)/P_{eq}$ which changes in the limits of $0<F(P)\leq 1$. $F(P)$ is inserted into an integrated rate equation as follows, $R_i(\alpha)=ktF(P)$, where i refers to a particular mechanism or process order. A best fit line of experimental values of $R_i(\alpha)/F(P)$ *vs*. t yields a temperature only dependent kinetic constant, k. Isothermal measurements were carried out in a closed volumetric system for different system volumes, V_s, and different initial pressures, P_0, and interpreted according to the NPDM. Hydride decomposition/formation kinetics of the alloy $Ti_{0.95}Zr_{0.05}Mn_{1.48}V_{0.43}Fe_{0.08}Al_{0.01}$, labeled C5, were studied in the temperature range of −20 to 20°C. The kinetics were found to correspond to a first order process for which the preexponential factor and the activation energy were $k_0=6.0\times 10^6$ s^{-1} and $E_a=40$ kJ/mol, respectively. For the decomposition of the $LaNi_5$ hydride in the temperature range of −6 to 60°C, the results were found to correspond to a first order process with the kinetic parameters $k_0=3.1\times 10^7$ s^{-1} and $E_a=52.8$ kJ/mol. The hydride decomposition/formation thermodynamic equilibrium parameters ΔH and ΔS for both considered alloys were derived. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Metal hydride; Kinetics; Absorption; Desorption; Pressure dependence

1. Introduction

The knowledge of kinetic properties of rechargeable metal hydrides (MHs) is essential for the design of applications in the area of environmentally benign and renewable energy, such as safe storage of hydrogen as a non-polluting fuel; M–MH rechargeable batteries; hydrogen heat pumps (HHP) and the like. A number of investigators have pointed at the existence of large discrepancies between published kinetic results obtained by various research groups [1–3]. In some cases results, which were derived under apparently similar experimental conditions, diverge [1]. The large discrepancies have recently been related to the difference in the pressure dependence used by various investigators [4,5].

A new approach dubbed the normalized pressure dependence method (NPDM), has been suggested [4,5]. The method consists in general terms of:

- The pressure dependence function is taken to be for the decomposition process

$$F(P)=(P_{eq}-P)/P_{eq} \tag{1}$$

- The pressure in the system may vary only within the inherent confines $0\leq P<P_{eq}$ and thus $0<F(P)\leq 1$.
- Enclosing $F(P)$ into an integrated rate equation yields

$$R_i(\alpha)=F(P)kt \tag{2}$$

here i refers to a particular mechanism or process order and α is the reacted fraction.

Under isothermal conditions a linear regression of experimental values of $R_i(\alpha)/F(P)$ vs. t renders the intrinsic kinetic rate constant, k, which depends on temperature only. Once k has been derived, the reacted fraction for desorption into vacuum can be calculated from each experimental run, with $P\neq 0$.

The hydride decomposition/formation kinetics of the alloy of composition $Ti_{0.95}Zr_{0.05}Mn_{1.48}V_{0.43}Fe_{0.08}Al_{0.01}$, labeled C5, were studied in the temperature range of −20

---

*Corresponding author.

PII: S0925-8388(99)00375-8

to 20°C. Isothermal measurements were carried out in a closed volumetric system. For comparison, the hydride decomposition kinetics of $LaNi_5$ in the temperature range of −6 to 60°C are presented. The kinetic experiments were interpreted according to the NPDM for which it is essential to know the equilibrium values of pressure, P_{eq}, vs. H/M for each measuring temperature. Particulars of the NPDM were elucidated

The comparison of the reacted fraction, $\alpha(t)$, for the two above mentioned MHs is shown for the case of desorption into vacuum which, however, was derived from experiments with $P \neq 0$. Equilibrium thermodynamic parameters, for the MH decomposition/formation processes for the two alloys, were derived according to the Van't Hoff relationship.

2. Experimental

The starting materials $Ti_{0.95}Zr_{0.05}Mn_{1.48}V_{0.43}Fe_{0.08}Al_{0.01}$ — labeled C5 — and $LaNi_5$ were supplied by GFE Metalle und Materialien, Germany, and Ergenics Cooperation, NJ, USA, respectively. Desorption experiments in the $\alpha+\beta$ region were carried out under isothermal conditions with temperature deviations not exceeding ±1°C. The 'thermal ballast' method was applied [1]. The mechanically crushed metal hydride forming materials were admixed, in proportions between 1:20 to 1:33, with fine Ni powder or fine brass chips.

The samples were activated applying a chemical process aimed at the reduction of oxidized surface layers [6,7]. The activation process was always accomplished by carrying out a number of hydrogenation cycles [8,9]. The particle mean diameter was found to be scattered around 10–20 μm. An external bath of fixed temperature and an especially designed brass, double wall reactor were used [10].

The measuring apparatus was a closed volumetric system with computerized data acquisition arrangements. Before starting the experimental desorption run the pressure in the reactor was kept above the equilibrium pressure, P_{eq}. After opening a valve for releasing hydrogen from the reactor into the system (which was kept at vacuum) an instantaneous initial pressure, P_0, sets. The magnitude of P_0 is determined by the pressure in the reactor (before the valve was opened) and by the free volume of the system chosen for a specific experiment. The systems free volume, V_s, consists of a volumetric reservoir (or combination of several reservoirs), the volume of the connecting ducts and the volume of the reactor except of the volume occupied by the specimen. The pressure in the system, P, vs. t was recorded from which instantaneous values of α and $F(P)$ were calculated and recorded.

A *PCT* curve was taken for each measuring temperature, as required for the application of the NPDM. The equilibrium values of pressure, P_{eq}, vs. H/M (the *PCT* curves) were established, for the same specimen and using the same set-up.

3. Results

In the present work the decomposition/formation kinetics of the alloy labeled C5, in the $\alpha+\beta$ region, in the temperature range of −20 to 20°C were investigated. The kinetic experiments were performed in a closed volumetric system and interpreted according to the NPDM. In order to elucidate the particulars of the NPDM measurements of desorption kinetics at 20°C are displayed in detail.

PCT relationships for the MH forming alloys C5 and $LaNi_5$ experimentally derived at 20°C are seen in Fig. 1. As required by the NPDM equilibrium values of pressure, P_{eq}, vs. H/M must be known for each measuring temperature. From these data the MH decomposition/formation processes equilibrium thermodynamic parameters, for the alloys C5 and $LaNi_5$, were derived according to the Van't Hoff relationship, see Table 1. For an isothermal desorption experiment, at a constant system volume, at 20°C, the pressure in the system, P, starting from an initial pressure P_0 was measured as a function of t. From these measurements it is possible to determine the reacted fraction, α, vs. t. The change of the system pressure, P, vs. t, for three different system volumes, V_s, and corresponding initial pressures, P_0, is shown in Fig. 2.

For a specific experiment, with V_s = 320 ml and P_0 = 2.7 bar, the corresponding concentration in the solid, H/M, was calculated from the measurements of P. In Fig. 3 the change of the pressure in the system, P, is presented vs. H/M along with the pertinent *PCT* desorption branch at 20°C. It is seen that the pressure differential, $P_{eq} - P$, as

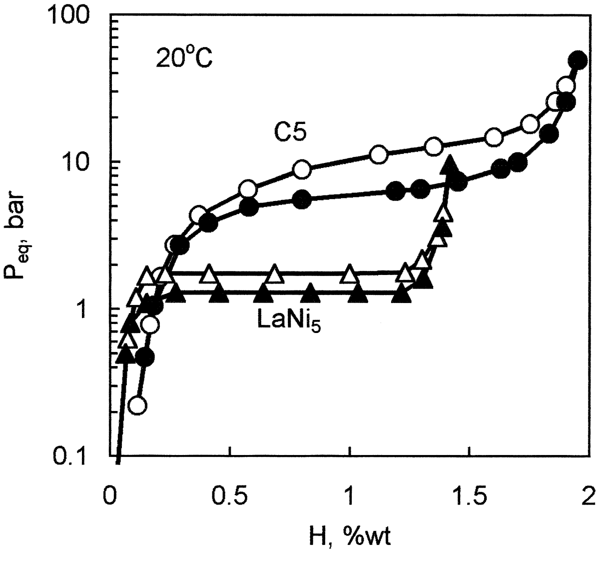


Fig. 1. *PCT* −20°C isotherms for C5 and $LaNi_5$.

Table 1
Kinetic and thermodynamic characteristics of decomposition/formation processes for C5 and $LaNi_5$ base metal hydrides

Alloy	k_0 (s^{-1})	E_a (kJ/mol)	ΔH_{abs} (kJ/mol)	ΔH_{des} (kJ/mol)	ΔS (kJ/mol)	Temperature range (°C)
C5	$6\cdot10^6$	40	25.6	29.4	106.5	−20 to 20
$LaNi_5$	$3.1\cdot10^7$	52.8	31.6	32.3	112.5	−6 to 60

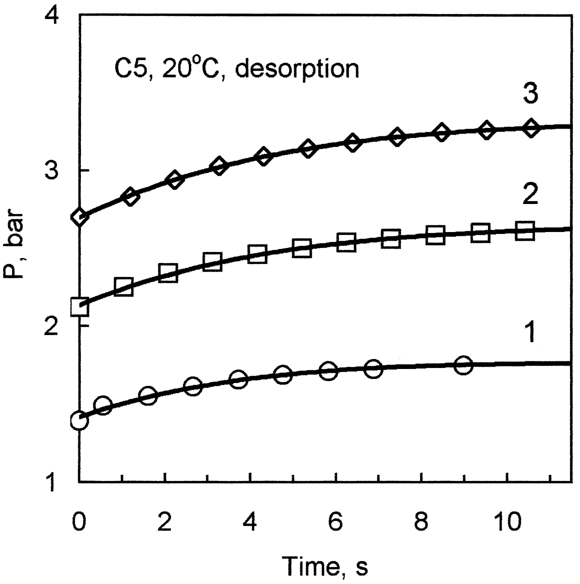


Fig. 2. C5. Change of pressure P, vs. t for isothermal desorption kinetics experiments at 20°C for three system volumes, V_s, and initial pressures, P_0: (1) $V_s = 620$ ml, $P_0 = 1.4$ bar, (2) $V_s = 420$ ml, $P_0 = 2.1$ bar, (3) $V_s = 320$ ml, $P_0 = 2.7$ bar.

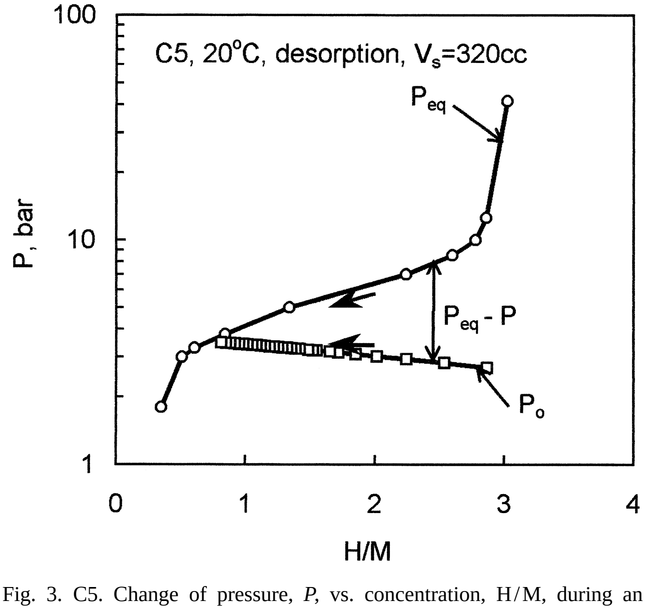


Fig. 3. C5. Change of pressure, P, vs. concentration, H/M, during an isothermal desorption kinetics experiment at 20°C, for $V_s = 320$ ml and $P_0 = 2.7$ bar. The pertinent *PCT* desorption branch is also shown.

well as the pressure dependence function, F(P), change continuously with H/M during the experiment.

For the same specific experiment, with $V_s = 320$ ml and $P_0 = 2.7$ bar, at 20°C, the change of P and F(P), presented vs. t, along with values of P_{eq} taken for the corresponding concentrations, H/M, are shown in Fig. 4a. It is seen that in course of an experiment the pressure differential, $P_{eq} - P$, as well as F(P), change continuously with time. In the same manner, for two specific experiments, at 20°C, with $V_s = 420$ ml and $P_0 = 2.1$ bar and $V_s = 620$ ml and $P_0 = 1.4$ bar, the change of P and F(P), presented vs. t, along with values of P_{eq} taken for the corresponding concentrations, H/M, are shown, in Fig. 4b and c, respectively.

The variation with time of F(P), defined by Eq. (1) is shown in Fig. 5 for all three experiments considered. The function F(P) is seen to level of at times short in comparison to times required for the system pressure to achieve equilibrium values. The values of the pressure dependence function, F(P), are larger the larger the free volume of the system, V_s.

Assuming a first order reaction Eq. (2) yields

$$\ln(1-\alpha) = -\mathrm{F}(P)kt \qquad (3)$$

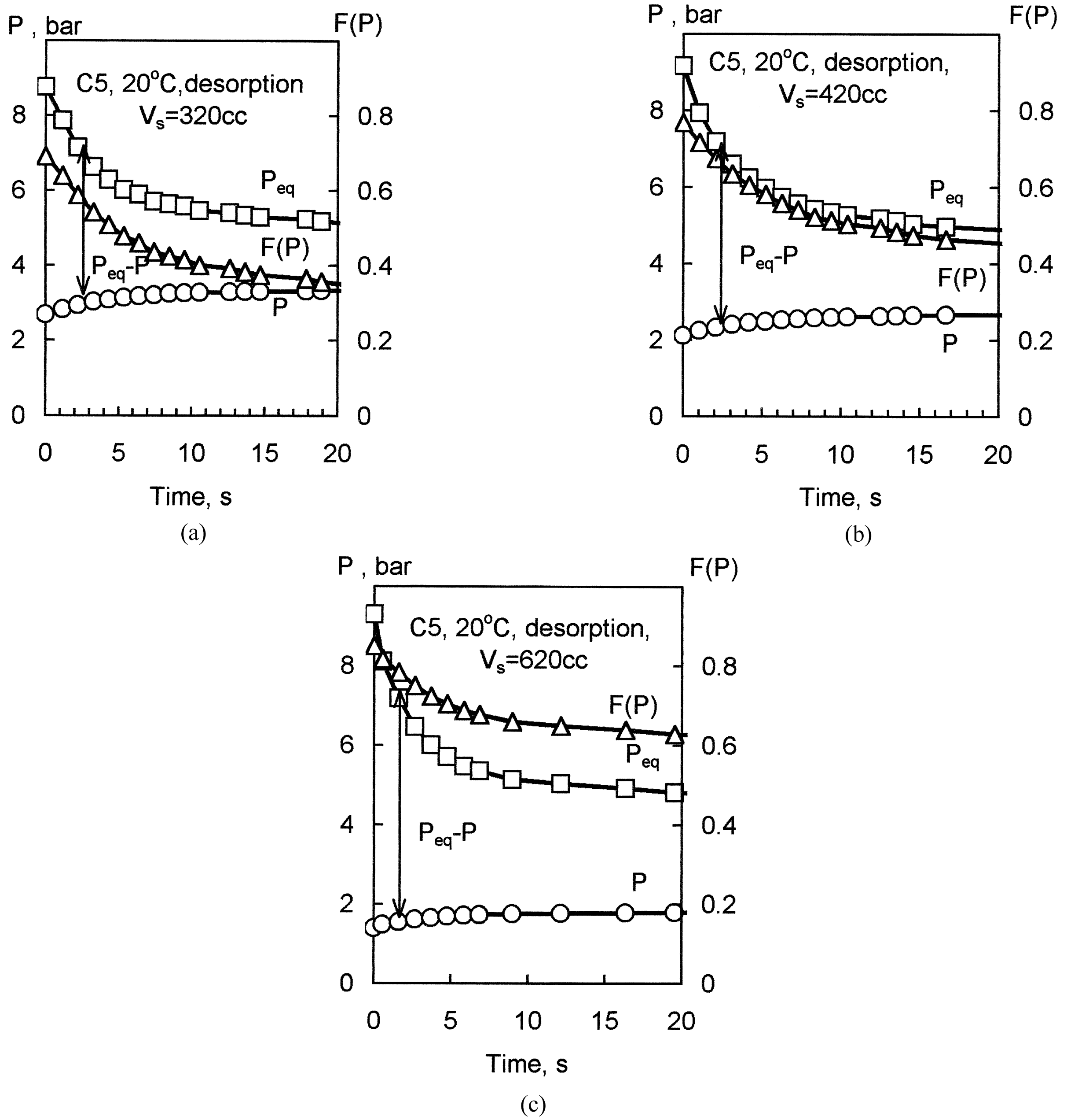
Linear regressions of $R^*_1 = \ln(1-\alpha)/\mathrm{F}(P)$ for all three specific experiments plotted vs. t are seen, in Fig. 6, to fall on a single line. The slope of this line renders a kinetic constant, $k = 4.3 \times 10^{-1}\ s^{-1}$, at 20°C. The fit is seen to be good. The derived here kinetic constant, k, is an intrinsic parameter that depends only on temperature.

The reacted fractions, α, vs. t, were derived for each of the three specific experiments and are shown in Fig. 7. Once the kinetic constant, k, was derived it is possible to determine α_v vs. t for a process of decomposition into vacuum. For a such process $\mathrm{F}(P) = 1$ and relationship (3) becomes

$$\ln(1-\alpha) = -kt \qquad (3a)$$

The reacted fraction α_v vs. t for a process of desorption into vacuum, shown by a dashed curve in Fig. 7, was derived by means of Eq. (3a).

By the same procedure, applying the NPDM, the kinetic rates were evaluated for eight more temperatures in the range of −20 to 20°C. The kinetic rate constant for the C5 hydride decomposition, in the $\alpha+\beta$ region, is presented by an Arrhenius plot in Fig. 8. The corresponding kinetic parameters are listed in Table 1. The $LaNi_5$ hydride decomposition kinetic rate constant, within the $\alpha+\beta$



(a)

(b)

(c)

Fig. 4. Desorption kinetics experiment at 20°C, P and F(P) are plotted vs. t for: (a) $V_s = 320$ ml, $P_0 = 2.7$ bar (b) $V_s = 420$ ml, $P_0 = 2.1$ bar (c) $V_s = 620$ ml, $P_0 = 1.4$ bar. Values of P_{eq} correspond to concentrations, H/M, measured in course of an experiment.

region, in the temperature range of −6 to 60°C is presented in Fig. 8, for comparison. The corresponding kinetic parameters are also given in Table 1.

The change of the reacted fractions, α_v, during the MH decomposition process into vacuum for C5 and $TiNi_5$ is shown in Fig. 9, for comparison. The reacted fractions α_v vs. t was determined from non-vacuum desorption experiments ($P \neq 0$) by means a closed volumetric measuring system, applying the NPDM.

A kinetic absorption experiment at −2°C was carried out for the C5 alloy. According to the NPDM a limitation on the initial pressure, $P_0 < 2P_{eq}$ [4,5] is required. This limitation was preserved. Due to the considerably slopped plateau of the C5 alloy it was possible to carry out the measurements on a part of the plateau extending from 0.6 to 1.7 H/M. The results yielded $k = 1.15 \times 10^{-1}$ s^{-1}. This value is identical with the kinetic rate constant obtained for desorption at the same temperature, −2°C, see Fig. 8.

A kinetic absorption experiment at −20°C was also carried out for the C5 alloy. In order to preserve the above mentioned limitation on the initial pressure, $P_0 < 2P_{eq}$, the measurements were carried out in the following sections of concentration: $0.4 < H/M < 1.1$, $1.1 < H/M < 1.6$, $1.6 < H/M < 2.1$ and $2.1 < H/M < 3.1$. The measured values for

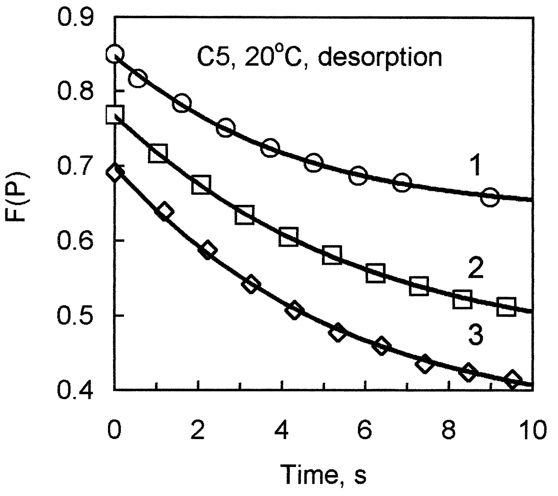


Fig. 5. C5. Change of F(P), for desorption kinetics experiments at 20°C for three system volumes, V_s, and initial pressures, P_0: (1) $V_s = 620$ ml, $P_0 = 1.4$ bar, (2) $V_s = 420$ ml, $P_0 = 2.1$ bar, (3) $V_s = 320$ ml, $P_0 = 2.7$ bar.

all sections fall on one linear regression line for $R^*_1 = R_i(\alpha)/\mathrm{F}(P)$ vs. t which rendered a value of $k = 3.7 \times 10^{-2}$, see also Fig. 8. This value is close to one obtained for desorption at −20°C, see Fig. 8.

4. Conclusions and discussion

The kinetic rates of hydride decomposition/formation in the $\alpha + \beta$ region for the alloy $Ti_{0.95}Zr_{0.05}Mn_{1.48}V_{0.43}Fe_{0.08}Al_{0.01}$ labeled C5, were established in the temperature range of −20 to 20°C.

For comparison, by the same method, the kinetic constant, k, for $LaNi_5$ was determined in the temperature range of −6 to 60°C.

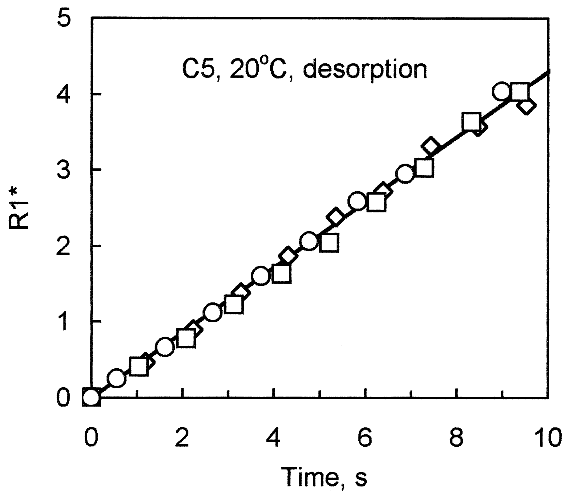


Fig. 6. C5. Linear regressions of ln $(1 - \alpha)/\mathrm{F}(P)$ vs. t using experimental results fall on a single line, for all three experiments: ○, $V_s = 620$ ml, $P_0 = 1.4$ bar, □, $V_s = 420$ ml, $P_0 = 2.1$ bar, ◇, $V_s = 320$ ml, $P_0 = 2.7$ bar.

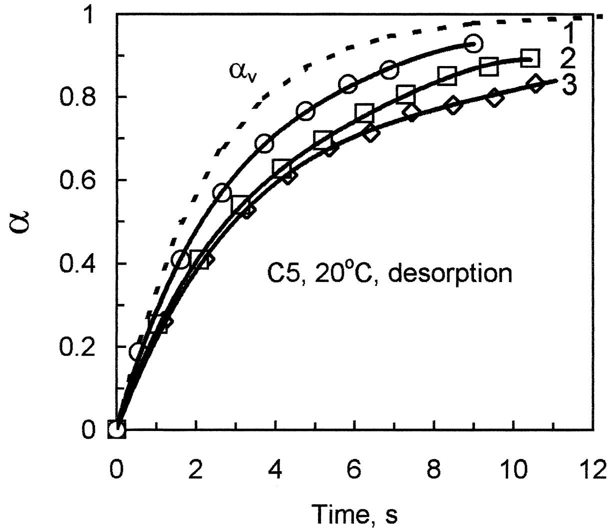


Fig. 7. C5. The reacted fraction, α, vs. t, for desorption experiments at 20°C: (1) $V_s = 620$ ml, $P_0 = 1.4$ bar, (2) $V_s = 420$ ml, $P_0 = 2.1$ bar, (3) $V_s = 320$ ml, $P_0 = 2.7$ bar, dashed curve, the reacted fraction, α_v, vs. t for desorption into vacuum.

Applying the NPDM renders a kinetic rate factor, k, depending on temperature only.

The particulars of the NPDM were elucidated by measurements of desorption kinetics at 20°C and displayed in detail.

The effectiveness of the NPDM is proved by the excellent fit of measured results to a straight line of $R_i(\alpha)/\mathrm{F}(P)$ vs. t for a very wide range of values of α.

It is a common practice to compare kinetic rates of two metal hydrides, at a certain temperature, by comparing the course of change of the reacted fractions, α vs. t. However, for this purpose the measurements must be carried out under identical pressure conditions. This requirement is technically very difficult if at all possible to fulfil, except

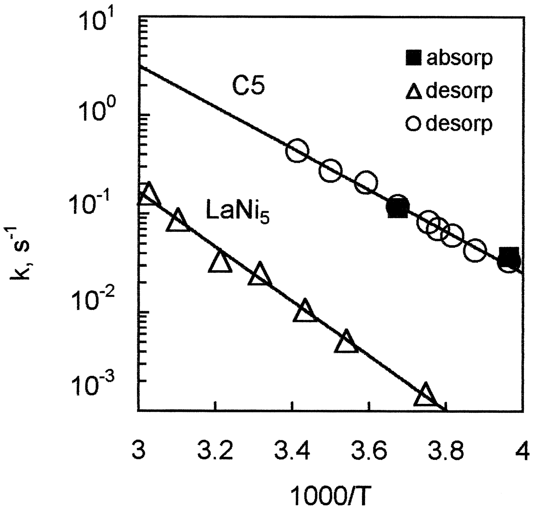


Fig. 8. Kinetic rate constant, k, vs. $1000/T$ for the C5 hydride decomposition/formation, in the temperature range of −20 to 20°C and for $LaNi_5$ hydride decomposition in the temperature range of −6 to 60°C.

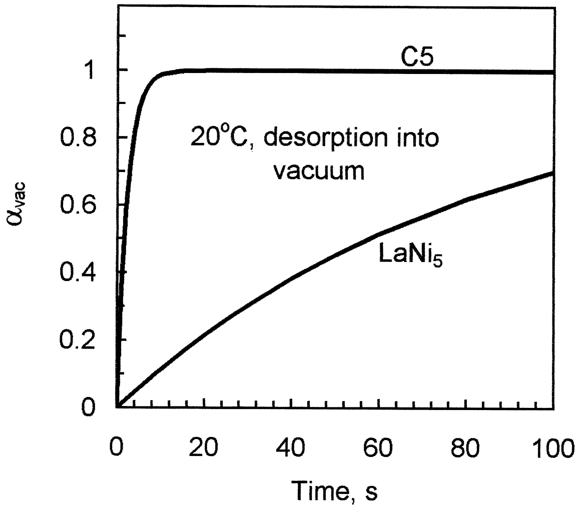


Fig. 9. Reacted fractions α_v vs. t, for processes of desorption into vacuum for C5 and $TiNi_5$ metal hydrides.

of one case, namely, of the desorption into vacuum. In the latter case the pressure conditions are identical as $P = 0$ for the whole duration of the experiment.

It is shown that applying the NPDM enables the comparison of the course of change of the reacted fractions, α_v, vs. t for a process of desorption into vacuum, for two different metal hydrides, using data obtained by non-vacuum experiments.

Comparing, from a practical point of view, the two metal hydrides it seen that the alloy C5 has, at RT, a considerably higher capacity and 40 times faster kinetics than $LaNi_5$.

Acknowledgements

The German Federal Ministry for Education, Science, Research and Technology (BMBF) Group BEO in cooperation with the Israeli Ministry of Science (MOS) are greatly appreciated for their research support under Project Number E 01062-GR 01471BEO. The support by the Center for Absorption in Science, Ministry of Emigrant Absorption, Israel, is greatly appreciated. This work was commenced during the stay of M. Ron in Germany as a recipient of the 1993 Alexander von Humboldt Research Award. The contribution of the Alexander von Humboldt Foundation is greatly appreciated.

References

[1] P.D. Goodel, P.S. Rudman, J. Less-Common Metals 89 (1983) 93.

[2] N. Gerard, S. Ono, in: L. Schlapbach (Ed.), Hydrogen in Intermetallic Compounds 2, Springer-Verlag, Berlin, 1992, Ch. 4.

[3] X.L. Wang, S. Suda, Int. J. Hydrogen Energy 15 (1990) 569.

[4] M. Ron, J. Alloys Comp. 283 (1999) 178.

[5] M. Ron, V.M. Skripnyuk, in: Proc. 12th World Hydrogen Energy Conference, Argentina, 1998.

[6] V.M. Skripnyuk, et al., Solution for removal of oxide films from titanium and titanium alloy surface. A.C. USSR No. 1696583, register August 8, 1991.

[7] T.N. Nesterenko, V.M. Skripnyuk, V.M. Anochin, in: Technology and Equipment For Production of Ferrous and Non-ferrous Metals and Alloys, Vol. 9, Higher school, Kiev, 1991, p. 43.

[8] L. Schlapbach, in: L. Schlapbach. (Ed.), Hydrogen in Intermetallic Compounds 2, Springer-Verlag, Berlin, 1992, Ch. 2.

[9] O. Bernauer, J. Topler, D. Noreus, R. Hempelmann, D. Richter, Int. J. Hydrogen Energy 14 (1989) 187.

[10] Y. Josephy, M. Ron, J. Less-Common Metals 147 (1989) 227.