INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 34 (2009) 7125–7130

Available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/he

Prediction of the thermal conductivity of metal hydrides – The inverse problem

Mohd Fahmi Abdul Ghafir[a], *Mohd Faizal Mohideen Batcha*[a], *Vijay R. Raghavan*[b,*]

[a]*Faculty of Mechanical Engineering, University Tun Hussein Onn Malaysia, 86400 Parit Raja, Johor, Malaysia*
[b]*Department of Mechanical Engineering, University Technology Petronas, Bandar Seri Iskander, 31750 Tronoh, Perak, Malaysia*

ARTICLE INFO

Article history:
Received 15 November 2007
Received in revised form
27 April 2008
Accepted 14 June 2008
Available online 5 October 2008

Keywords:
Hydrogen storage
Metal hydrides
Particle thermal conductivity
Inverse method

ABSTRACT

With sustainability as an important and driving theme, not merely of research, but that of our existence itself, the effort in developing sustainable systems takes many directions. One of these directions is in the transport sector, particularly personal transport using hydrogen as fuel, which logically leads on to the problem of hydrogen storage. This paper deals with the prediction of the effective conductivity of beds of metal hydride for hydrogen storage. To enable modeling of the effective thermal conductivity of these systems, it is necessary to arrive at the functional dependence of the thermal conductivity of the solid hydride on its hydrogen concentration or content. This is the inverse problem in thermal conductivity of multiphase materials. Inverse methods in general are those where we start from known consequences in order to find unknown causes. Using published and known data of the effective thermal conductivity of the hydride–hydrogen assemblage, we arrive at the unknown hydride conductivity by analysis. Among the models available in the literature for determination of the effective conductivity of the bed from the properties of the constituent phases, the model of Raghavan and Martin is chosen for the analysis as it combines simplicity and physical rigor. The result is expected to be useful for predicting the thermal conductivity of hydride particles and determining the optimum heat transfer rates governing the absorption and desorption rates of hydrogen in the storage system.

© 2008 International Association for Hydrogen Energy. Published by Elsevier Ltd. All rights reserved.

1. Introduction

It is widely accepted that powering automobiles by hydrogen is vastly superior to the use of fossil fuels from the point of view of sustainability. It produces only water vapour and does not add to the CO_2 load in the environment. It produces none of the air pollutants that create smog and cause health problems. Instead of hydrogen combustion to produce the motive force to run the engine, the fuel cell that converts chemical energy of hydrogen directly to electrical energy to drive the car, is the preferred choice. Another advantage is that the conversion efficiency of a fuel cell is higher as energy generation in a fuel cell is not limited by the Carnot efficiency.

Fuel cells can be powered by hydrogen–oxygen, hydrogen–air, methane–oxygen or methane–air combinations. The highest efficiency is obtained from hydrogen fuel. Hence, solutions need to be found for carrying hydrogen in the automobile. One way is to liquefy hydrogen and fill up high-pressure cylinders with it, allowing the cylinder pressure to increase tremendously as it reaches ambient temperature. A second, more

* *Corresponding author*. Tel.: +60 17 716 8255.
E-mail addresses: vrr@iitm.ac.in, vrraghavan@hotmail.com (V.R. Raghavan).
0360-3199/$ – see front matter © 2008 International Association for Hydrogen Energy. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijhydene.2008.06.033

practical method is to carry the hydrogen in the form of metal hydride at normal pressures and temperatures. The design of such a system and prediction of storage and discharge times in it requires a knowledge of the thermophysical properties of metal hydride and their variation with hydrogen content in the discrete particles.

2. Background literature

Metal hydrides are powders whose particles are typically a few microns in size. When these metal powders absorb hydrogen to form hydrides, heat is released. Conversely, when heat is absorbed, hydrogen is released from the hydride. In the absorption process, hydrogen gas molecules break down into hydrogen atoms and penetrate into the interior of the metal crystal to form a metal hydride. In the desorption process, hydrogen atoms migrate to the surface of the metal hydride, combine into hydrogen molecules and flow away as hydrogen gas, allowing the material to form the original metal structure [1].

In order to maintain a low weight and volume of hydride, it is critical to maintain short cycle times for charging and discharging hydrogen. Heat transfer is the rate limiting process that controls hydrogen uptake or removal and is determined by the effective conductivity of the hydride bed. The dynamic response of a hydrogen storage system is important in the design of metal hydride based energy conversion. Hence it is necessary to predict transient heat and mass transfer in the metal hydride bed [2].

However, it is known that absorption and desorption of hydrogen are limited by the thermal conductivity of the metal hydride bed [3]. The effective thermal conductivity is a function of the conductivity of the hydrided metal and interstitial hydrogen gas. The conductivity of hydrogen and its interstitial volume concentration are essentially constant. But the conductivity of hydrided metal varies as a function of the concentration of the chemisorbed hydrogen. This means that the effective conductivity changes during the process. Thus, the heat transfer rate is not constant during absorption and desorption. The change in the heat transfer rate causes the rates of storage/discharge of hydrogen to vary. The effective property of the powder bed can be measured, but modeling of the absorption/desorption times is complicated by the fact that the thermal conductivity of the hydrided metal cannot be determined independently by experiment. The problem then is to devise suitable methods to calculate the variation in the hydride particle thermal conductivity as a function of the hydrogen concentration from the experimentally obtained effective conductivity of the powder.

3. Modeling of two-phase conduction

3.1. *Parallel and series resistances*

Experimental investigations on the effective thermal conductivity of hydride beds have been performed by various testing procedures. In some cases results were presented in simple polynomial equations. Pressure affects thermal conductivity

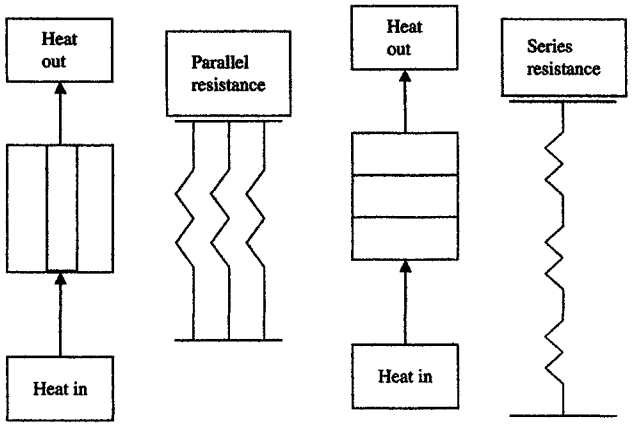

Fig. 1 – Parallel resistances and series resistances.

of powdery metal hydrides only little provided the mean free path of the filling gas molecules is small compared to the dimension of the pores; i.e. for higher pressures.

For a disperse phase in a continuous medium, its overall resistance can be presented as resistances in parallel or resistances in series (Fig. 1). The one-dimensional unit cube model is based on this premise. These are only limiting values and neither is the actual resistance.

3.2. *Field solutions*

A closed form solution was obtained by Maxwell [4] for three-dimensional heat flow for small concentrations of the particulate phase as:

$$K = \frac{1+2\beta c}{1-\beta c}, \tag{1}$$

where K is the non-dimensional conductivity, $k_{effective}/k_{gas}$, β is the ratio $(\alpha-1)/(\alpha+2)$, α is the ratio of conductivities $k_{particle}/k_{gas}$ and c is the volume concentration of the dispersed phase, $0<c<1$.

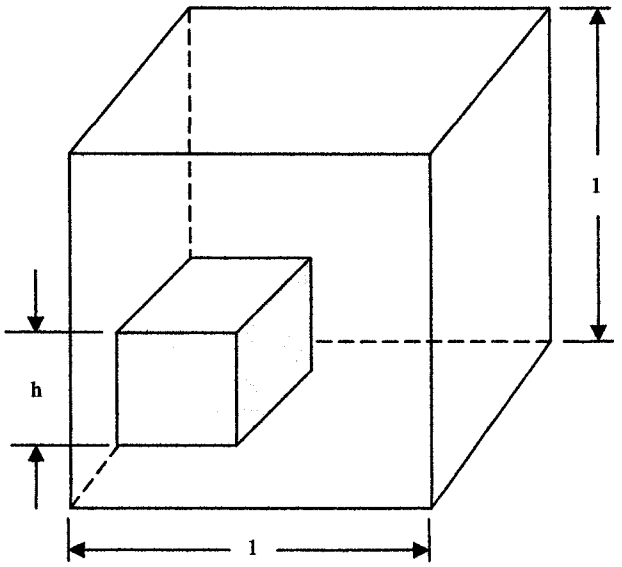

Fig. 2 – Schematic of the unit cube showing the height 'h'.

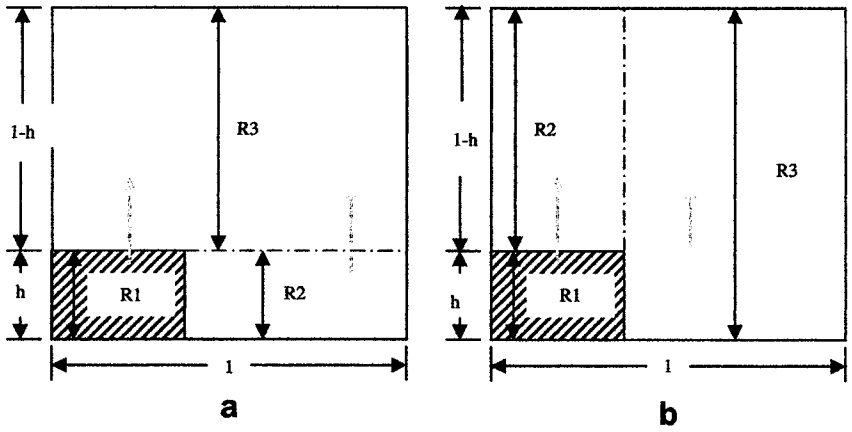

Fig. 3 – Unit cube with (a) parallel isotherms (b) parallel heat flow lines.

3.3. *The Raghavan–Martin model*

Raghavan and Martin [5] considered one-dimensional heat flow in a unit cube as shown in Fig. 2 and showed that the Ohm's law approach can be reconciled with the multidimensional field solution of Maxwell, by modeling the field distortions by means of distortions of the geometry. The ease of application of the unit cell and the exactness of approach of the field calculation are combined in this manner.

The effective resistance of the unit cube can be calculated by using either the parallel isotherms or parallel heat flow lines as shown in Fig. 3a and b. The height '*h*' of the inclusions shown in these figures is a quantity that can be varied or 'distorted' in accordance with all the factors that would cause a change in the effective conductivity of the medium.

The result for equivalence of Ohm's law approach and Maxwell's approach is expressed by the remarkably simple relation:

$$h = (2 + c)/3 \tag{2}$$

This value of '*h*' will be termed h_{Maxwell}. In the real material of finite concentration, the following formula applies as shown by Raghavan and Martin [5]:

$$K = 1 + \frac{c}{\frac{\alpha}{\alpha - 1} - h_{\text{maxwell}} \times F} \tag{3}$$

where F is a modifying function that accounts for the geometric distortions equivalent to the distortions in isotherms and heat flow lines. It will have a value equal to unity when concentration tends to zero as in Maxwell's model.

The 'h' versus 'c' plot (Fig. 4) is a useful new tool for the analysis not only of thermal conductivity models but models of transport properties in general. With only the assumption of macroscopic homogeneity and isotropy, the new approach described here leads to a simple and physically illustrative formula for calculating the conductivity of two-phase dispersions.

The thermal conductivity of hydrogen is lower than the thermal conductivity of metal hydride, i.e. the value of α is >1. For this ratio of α, the effective conductivity of metal hydride goes up as the concentration of hydrogen increases (Fig. 5).

Many studies have been made on the method of estimation of the effective conductivity of packed beds, but only a little information is available either on experimental data or on the estimating method for metal hydrides.

4. Experimental data on effective conductivity

Experimental studies have been carried out by Suda et al. [6] to measure the effective thermal conductivity of $TiMn_{1.5}$ hydride using a steady state method, and the data were used to correlate the effective thermal conductivity with hydrogen pressure, temperature and hydride composition. Effective thermal conductivity was found to take different values in absorption and desorption processes where a hysteresis exists in the *p*–*C* relationship and to vary according to the bed temperature. The effect of hydride composition on the effective thermal conductivity was also studied and correlated as a linear relationship in hydride beds.

Experimental results on the $TiMn_{1.5}$ hydride are presented and are correlated through the kinetic theory of gases and equilibrium behavior. The effective conductivity k_e is defined as the sum of two independent terms, that is, the pressure-related $(k_e)_p$ and the composition related $(k_e)_{H/M}$ terms, and an empirical equation based on the experimental data is

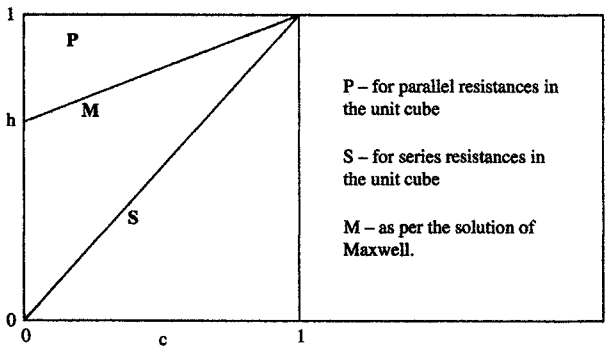

Fig. 4 – Dimensionless height 'h' as a function of volume concentration c.

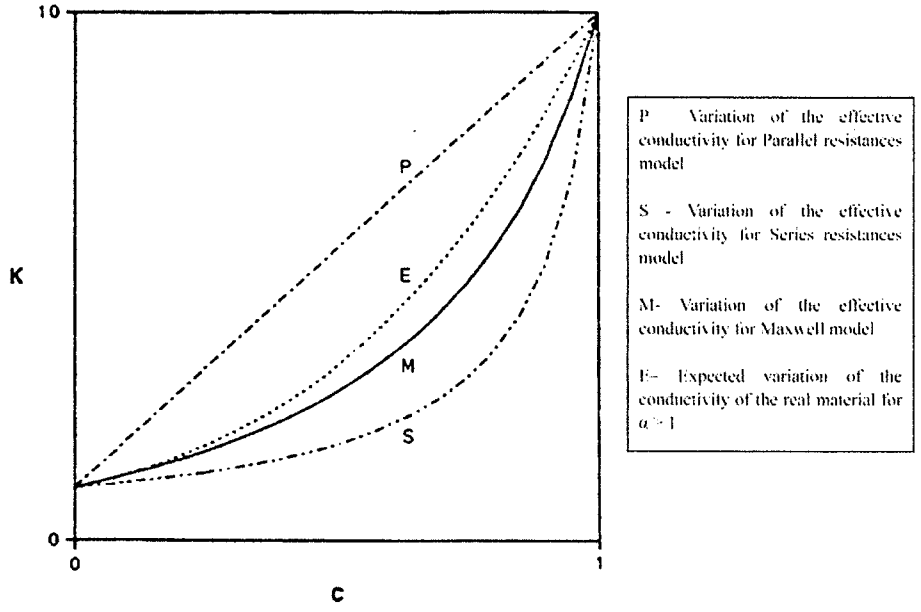

Fig. 5 – Conductivity K as a function of c for $\alpha = 10$.

derived for $TiMn_{1.5}$ hydride [6].

$$k_e = 0.56 + 0.19(\ln p) - 0.006(\ln p)^2 - 0.052(\ln p)^3 + 0.46(H/M) \quad (4)$$

where H/M is the hydrogen-to-metal atomic ratio.

Experimental studies on metal hydride based heat-pump systems have clearly demonstrated the need for improving the heat transfer through a metal hydride bed. Considerable improvement of the thermal conductivity of metal hydride powder has been obtained when metal matrices such as aluminum foams and copper nets are inserted. The effective thermal conductivity k_e of a copper wire matrix augmented metal hydride bed of $MmNi_{4.46}Al_{0.54}$ powder has been measured by Nagel et al. [7] using a steady state method. The effect of the copper wire matrix, the metal hydride itself, the system pressure p and the hydrogen-to-metal atomic ratio H/M on k_e are analyzed and expressed through an empirical equation:

$$k_e = k_{gas}\left(f_{H/M} + f_p\right) + k_{Cu} + k_{MH}\left(1 + g_{H/M}\right) \quad (5)$$

An empirical expression for k_e was found by them as a function of p and the H/M ratio

$$k_e = 0.44 + (0.55H/M - 0.025p) + \ln(1.734 + 0.375p) \quad (6)$$

The effective thermal conductivity of a powdery material, comprising heat conduction in the solid particles and in gas and thermal radiation across the pores, was determined by Hahne and Kallweit [8] by the transient hot wire method. Two materials, $LaNi_{4.7}Al_{0.3}H_x$ and HWT 5800 ($Ti_{0.98}Zr_{0.02}V_{0.43}Fe_{0.09}Cr_{0.05}Mn_{1.5}H_x$) were investigated. The temperature range was −80 °C to +140 °C and the pressure range was 10 mbar to 60 bar. Concentration/Pressure isotherms (CPI) and the effective thermal conductivity k_e were measured. Various filling gases (H, He, N, Ar) were used. There is a clear effect of the gas in the state of delivery of the powder. It was concluded that the effective thermal conductivity depends primarily on the hydrogen pressure, while the temperature has only an indirect influence. The experimental data of Hahne and Kallweit have been chosen for the present work of demonstrating the

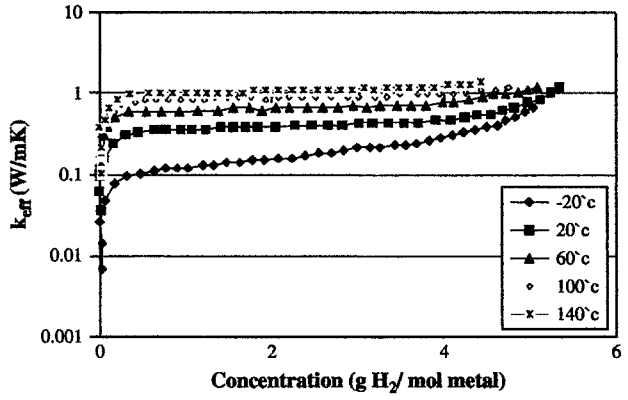

Fig. 6 – k_{eff} for $LaNi_{4.7}Al_{0.3}H_x$ vs. H_2 concentration with only absorption.

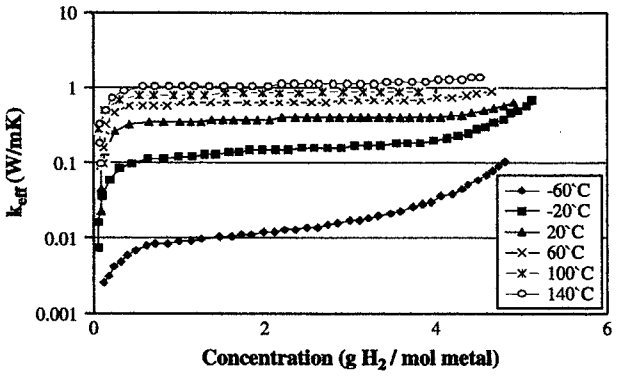

Fig. 7 – k_{eff} for $LaNi_{4.7}Al_{0.3}H_x$ vs. H_2 concentration with only desorption.

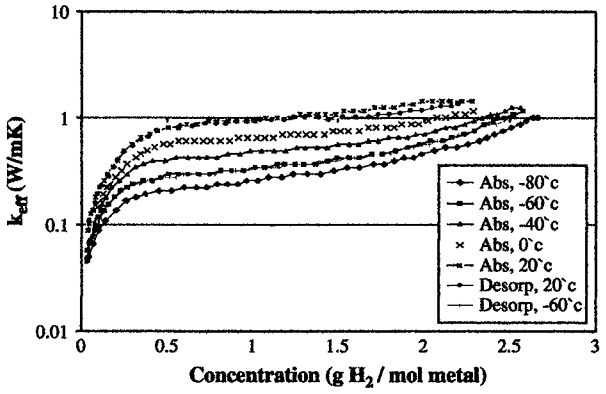

Fig. 8 – k_{eff} for HWT 5800 vs. H_2 concentration with absorption and desorption.

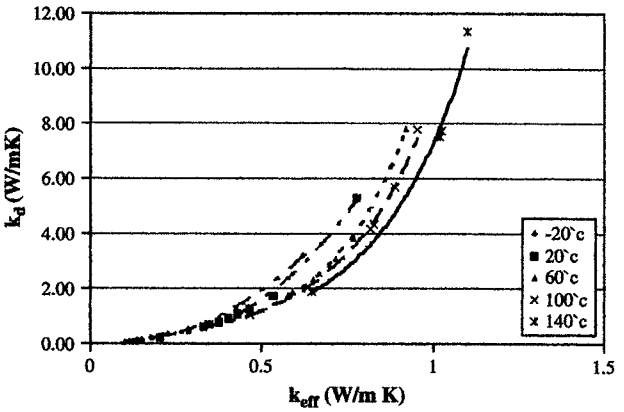

Fig. 10 – k_d as a function of k_{eff} for $LaNi_{4.7}Al_{0.3}H_x$.

inverse procedure of calculating the thermal conductivity of the particles.

The plotted graphs in the paper of Hahne and Kallweit [8] were converted into digitized values by use of Graph Digitizer software. Graph Digitizer provides us with three methods to digitize the data, i.e. auto digitization, semi-auto digitization and manual digitization. For the ease of use and the accuracy of data required in the work, this study used auto digitization.

Figs. 6–8 present the measured data of Hahne and Kallweit [8] for the effective thermal conductivity for the materials $LaNi_{4.7}Al_{0.3}H_x$ and HWT 5800, for the absorption cycle as well as for the desorption cycle at various temperatures. The effective conductivity of the metal hydride bed is a function of hydrogen concentration.

From the results of Hahne and Kallweit [8], it is seen that metal hydride exhibits the same behavior as the non-activated metal powder. Thus, the effective thermal conductivity strongly depends on pressure and accordingly on the temperature. This variation should then be taken cognizance of in calculations of heat and mass transport phenomena in the hydride bed. Besides, the thermal conductivity always increases with increasing hydrogen concentration in this experiment. This increase is very high for both materials when the hydrogen is first added to the non-hydrided powder and it becomes quite small in a range >1 g H_2/mol of metal.

5. Results and discussion

Fig. 9 depicts the variation of the disperse phase conductivity, found by inverse calculation by means of Eq. (3) of the Raghavan–Martin model, where $h_{Maxwell}$ is calculated from Eq. (2) for the reported concentration of 0.555. The average value of the unknown F was initially obtained from Eq. (3) by utilizing $k_{metal, kgas}$ and k_{eff} for beds with Helium, Neon and Argon as the interstitial gas. The F value here was reasonably constant as the metal did not absorb these gases. The effect of hysteresis is not strong here. However, the effect of the temperature of the process of absorption/desorption is quite pronounced. In general, the particle conductivity is higher for a higher temperature.

The results using the Raghavan–Martin model showed that k_d varies in a manner similar to the concentration pressure isotherms, having a steeper inclination at lower concentrations and then increasing steadily in the plateau region of

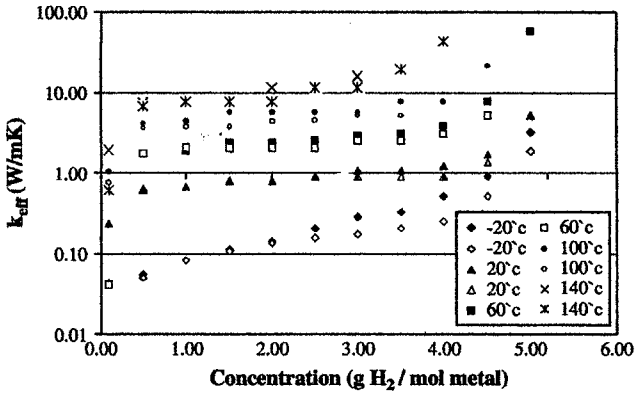

Fig. 9 – Dispersed phase conductivity k_d for $LaNi_{4.7}Al_{0.3}H_x$ as a function of H_2 concentration. (Absorption represented by filled symbols and × symbol, desorption by open symbols and *).

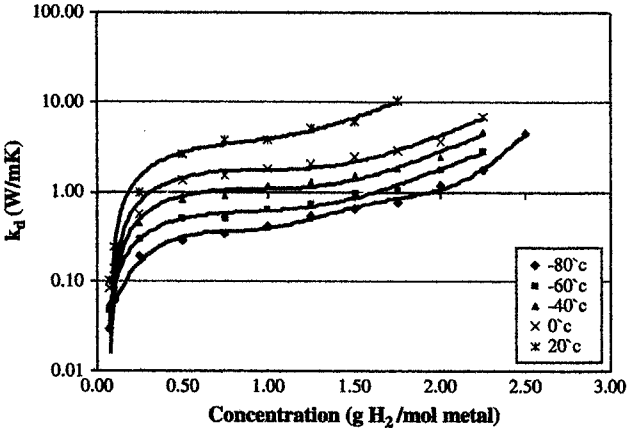

Fig. 11 – Dispersed phase conductivity for HWT 5800 vs. H_2 concentration for absorption.

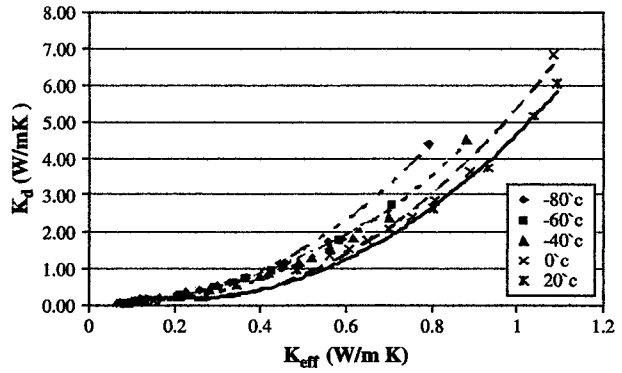

Fig. 12 – k_d as a function of k_{eff} for HWT 5800 with absorption.

CPI. The results reveal that k_d falls in the range of $k_g \leq k_{eff} \leq k_d$, with k_{eff} as the bulk conductivity, and increases with hydrogen concentration.

Fig. 10 shows the variation of the calculated disperse phase conductivity as a function of the measured effective conductivity of the $LaNi_{4.7}Al_{0.3}H_x$ powder. This shows a distinctly non-linear relationship. The particle conductivities are higher than the effective conductivity of the powder. Calculations of absorption and desorption require the hydrided particle conductivity k_d on which the hydrogen uptake and release rates are dependent, rather than the experimental effective conductivity k_{eff} of the assemblage with interstitial hydrogen. Hydrogen diffuses into the discrete particles. It is quite incorrect to use effective conductivity of the bed here as has been done hitherto, as it would imply that hydrogen diffuses into interstitial hydrogen.

For the alloy HWT 5800, similar procedures as for the alloy $LaNi_{4.7}Al_{0.3}H_x$ were applied and similar results were obtained as shown in Figs. 11 and 12, demonstrating the consistency of the method. The particle conductivity of $LaNi_{4.7}Al_{0.3}H_x$ is higher, indicating that heat flow into and out of this alloy will be superior to that of HWT 5800 facilitating hydrogen uptake and discharge. This is one of the important considerations in the choice of material for hydrogen storage.

6. Conclusions

The effective thermal conductivity k_{eff} of metal hydride beds can be determined directly by experiments, but not that of the discrete hydrided particles, k_d. The conductivity of the particles, as a function of absorbed hydrogen concentration, is the important property for heat diffusion in the hydride and is in fact the property that needs to be used for calculation of rates and process times during cycles of charging and discharging.

This property k_d of the discrete metal hydride particles changes dynamically during sorption and desorption of hydrogen. It can be estimated by the selection of a suitable model and inverse calculation procedures. In this study, the Raghavan–Martin model has been chosen for its ease of use and physical rigor. However, the procedure is general and is applicable to any set of data of metal hydride thermal conductivity. The Raghavan–Martin model shows a good trend in finding k_d.

Figs. 9 and 11 yield the relationship between hydrogen concentration in g H_2 per mole of metal and the conductivity of the discrete particles found by inverse calculation procedures. In this particular case, it has been obtained for two materials, $LaNi_{4.7}Al_{0.3}H_x$ and HWT 5800. For any given material, one needs to start with the experimentally determined effective thermal conductivity of the powder as a function of hydrogen concentration in the particle, and then apply the calculation procedures as shown above. The obtained value then becomes the appropriate property to use in calculations of storage or discharge of hydrogen and determination of cycle times. Further, it serves as an input for performance comparisons and choice among various candidate materials.

Appendix A Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.ijhydene.2008.06.033.

REFERENCES

[1] Sakintuna B, Lamari-Darkrim F, Hirscher M. Metal hydride materials for solid hydrogen storage: a review. International Journal of Hydrogen Energy 2007;32:1121–40.
[2] Nakagawa T, Inomata A, Aoki M, Miura T. Numerical analysis of heat and mass transfer characteristics in the metal hydride bed. International Journal of Hydrogen Energy 2000; 25:339–50.
[3] Phate AK, Maiya MP, Murthy SS. Simulation of transient heat and mass transfer during hydrogen sorption in cylindrical metal hydride beds. International Journal of Hydrogen Energy 2007;32:1969–81.
[4] Maxwell JC. A treatise on electricity and magnetism. Oxford: Clarendon Press; 1873.
[5] Raghavan VR, Martin H. Modeling of two phase thermal conductivity. Chemical Engineering and Processing 1995;34: 439–46.
[6] Suda S, Kobayashi N, Yoshida K. Thermal conductivity in metal hydride beds. International Journal of Hydrogen Energy 1981;6(5):521–8.
[7] Nagel M, Komazaki Y, Suda S. Effective thermal conductivity of a metal hydride bed augmented with a copper wire matrix. Journal of Less Common Metals 1986;120:35–43.
[8] Hahne E, Kallweit J. Thermal conductivity of metal hydride materials for storage of hydrogen. International Journal of Hydrogen Energy 1997;23(2):107–14.