Available online at www.sciencedirect.com
ScienceDirect
Journal of Power Sources 159 (2006) 132–134
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Short communication

Hydrogen uptake characteristics of mischmetal based alloy

Ankur Jain, R.K. Jain, I.P. Jain *

Material Science Laboratory, Centre for Non-Conventional Energy Resources, 14 – Vigyan Bhawan, University of Rajasthan, Jaipur 302004, India

Available online 23 May 2006

Abstract

Hydrogen storage properties of $Mm_{39.2}Ni_{42.1}Mn_{4.9}Al_{1.25}Co_{10.2}Fe_{2.35}$ alloy have been systematically studied in the present work. An attempt is made to relate the content of hydrogen with change in resistance. It is found that the resistance of material increases with the increase in value of *H*/*M* due to hydrogen absorption. Pressure composition (P-C-T) isotherm using water displacement method has been investigated in the temperature and pressure ranges of $308 \leq T \leq 338$ K and $0.5 \leq P \leq 10$ bar, respectively. The P-C isotherms show the presence of two single α and β regions one mixed α + β phase. The maximum *H* (wt%) was found to be around 1.53 at 308 K and around 6 bar. Since enthalpy is an index of thermochemical stability of metal hydride the thermo dynamical parameters viz., the relative partial molar enthalpy (ΔH) and relative partial molar entropy (ΔS) of dissolved hydrogen have been calculated by plotting the Van't Hoff plot. The variation of ΔH and ΔS with the hydrogen concentration confirm the phase boundaries.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Hydrogen Storage; P-C-T isotherm; Hydrogen absorption; Thermodynamics

1. Introduction

Storing hydrogen in the form of reversible metal hydride is a viable alternative to low storage density forms such as high-pressure gas or cryogenic liquids. Hydrides offer low volume without disadvantages of the cryogenics required for liquids, or the hazards and the inefficiency associated with gas storage. Ideally, metal hydride for commercial applications should be able to release H_2 at relatively low temperature, having high volumetric density, low mass density, rapid hydriding/dehydriding rate, high resistance to pulverization and low cost in both fabrication and acquisition of raw material. The rare earth based hydrogen storage alloys have been widely used due to their high energy density, high rate of charge discharge ability, long charge discharge cyclic lifetime and environment capability [1–3].

The typical rare earth based hydrogen storage alloy is $MmNi_5$, in which Mm denotes mischmetal (a commercial mixture consist of mainly rare earth elements La, Ce, Pr, and Nd). Now a days, two kinds of mischmetal, namely La rich and Ce rich mischmetal owing to different mineral resources and extractive metallurgical methods, have been utilized widely in commercial hydrogen storage alloys. Several authors [4–7] have reported that the contents of La and Ce in mischmetal had a promising influence on the hydrogen absorption desorption properties, thermodynamical parameters, plateau pressure, and cycle lifetime.

The storage capacity of the $MmNi_5$ system is found to lie between 1.2 and 1.4 wt% [8]. One has to bear in mind the fact that one of the criteria for increasing the hydrogen storage capacity through replacement of Ni will be to find a more electron attractive element taking the place of Ni [9]. Srivastav and co-workers [10] have studied Fe in low concentration in Ni ($Ni_{0.9}Fe_{0.1}$) and found that the hydrogen storage capacity has been found to increase to a value of 1.66 wt%. However, when the Fe concentration is increased further the hydrogen storage capacity starts decreasing. Tang et al. [11] studied the microstructure and the electrochemical properties of $Mm_{0.7}Ni_{2.8}Co_{0.6}$ hydrogen storage alloy and found the highest concentration to be 1.58 wt%. In the present work the hydrogen absorption isotherms and reaction kinetics of $Mm_{39.2}Ni_{42.1}Mn_{4.9}Al_{1.25}Co_{10.2}Fe_{2.35}$ alloy have been measured. The thermodynamical parameters, i.e. the enthalpy and entropy of hydride formation have also been calculated.

2. Experimental

The alloy was supplied by Dr. Balachandra of Defence Metallurgical Research Laboratory (DMRL), Hyderabad, India and it was well characterized by him for its composition homogeneity.

* Corresponding author. Tel.: +91 141 2701602; fax: +91 141 2710880.
E-mail addresses: ankurjainankur@sify.com (A. Jain), ipjain46@sify.com (I.P. Jain).

0378-7753/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2006.04.002

To study P-C-T isotherms the data were collected using an experimental set-up based on water displacement method developed in our laboratory [12]. To study in situ resistance measurements with changes in hydrogen pressure a modified reactor vessel has been used for containing the material having an electrode with ceramic insulation. Five grams of alloy was kept in reactor vessel, which has a provision of heating, measuring temperature by thermocouple and hydrogen pressure by pressure gauge. Prior to an absorption run the whole system was evacuated to 1×10^{-3} Torr and the sample was heated at 473 K for 1 h in order to remove any gases present in sample and then slowly cooling down to room temperature. The sample was again heated to 473 K and exposed to hydrogen at 1 atm pressure. This process was repeated for five cycles. In this way a virigin surface is produced for hydrogen storage. After each cycle the sample was degassed at 473 K under a vacuum of 1×10^{-3} Torr.

3. Results and discussion

Variation of resistance with *H*/*M* is shown in Fig. 1. It is clear from figure that the resistance increases with hydrogen concentration. The increase in resistance with hydrogen concentration can be explained as hydrogen takes an electron from the conduction band of alloy and become hydrogen anion; therefore the number of electrons in conduction band decreases, so that the resistivity of alloy increases.

The hydrogen absorption kinetics of the alloy was studied at room temperature. Fig. 2 shows the rate of the kinetics of hydrogen absorption of the alloy for an initial pressure 10 bar. The kinetics of absorption is quite fast at 308 K and taken between 20 and 25 min to reach the equilibrium value.

Hydrogen absorption isotherms of the alloy in the pressure range $0.5 \leq P \leq 10$ bar and temperature range $308 \leq T \leq 323$ K are shown in Fig. 3. The maximum hydrogen concentration is found to be 1.53 at 6 bar and 308 K. These P-C isotherms indicate two single α, β and one mixed α + β phase regions in temperature and pressure range. The initial slope correspond to hydrogen going in solid solution, this phase reaches the saturation limit of solution and metal hydride begins to form in the second α + β phase. Here the pressure remains constant with the increase in hydrogen concentration. With further addition of hydrogen, the β phase appears and hydrogen pressure rises steeply again in this phase, which means that this material is safe for hydrogen storage. The effect of temperature on general features of P-C isotherm is shown in Fig. 3. The increase of isotherm temperature from 308 to 313 K causes the plateau pressure to increase from 1 to 3 bar and reduces the width of plateau, which represents the miscibility regime of α and β phases.

The enthalpy, ΔH and entropy, ΔS of hydride formation have been derived by utilizing Van't Hoff plot of $\ln P_{eq}$ versus $1/T$ shown in Fig. 4, according to the well known equation:

$$\ln P_{eq} = \frac{2(\Delta H - T\Delta S)}{RT}$$

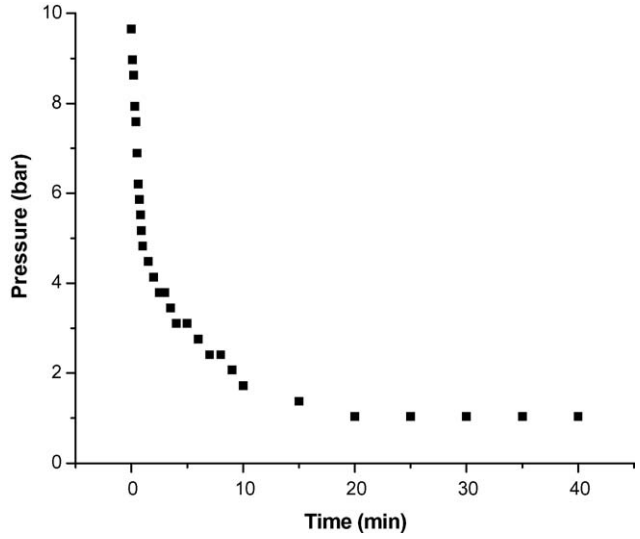

Fig. 2. Hydrogen absorption kinetics of $Mm_{39.2}Ni_{42.1}Mn_{4.9}Al_{1.25}Co_{10.2}Fe_{2.35}$.

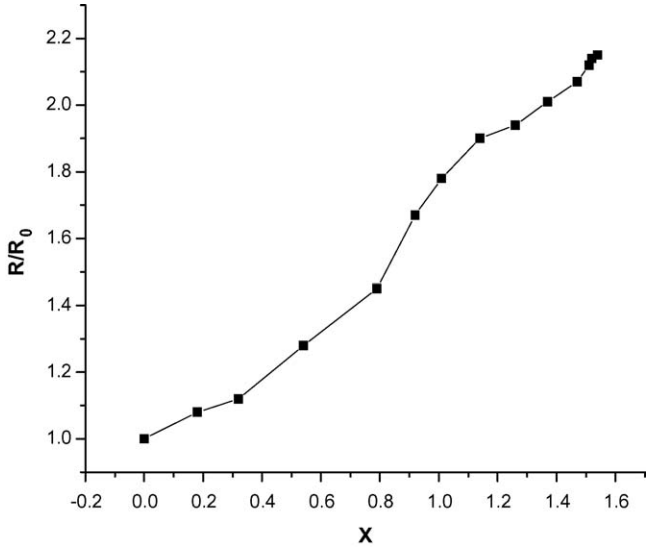

Fig. 1. Variation of resistance with hydrogen concentration.

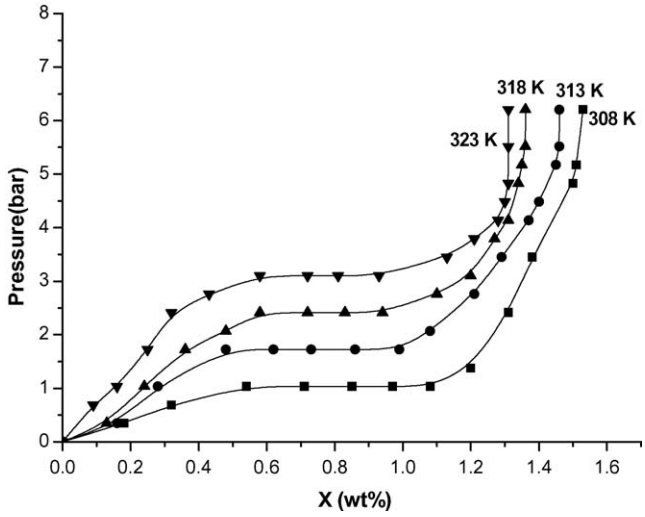

Fig. 3. Hydrogen desorption isotherms of alloy.

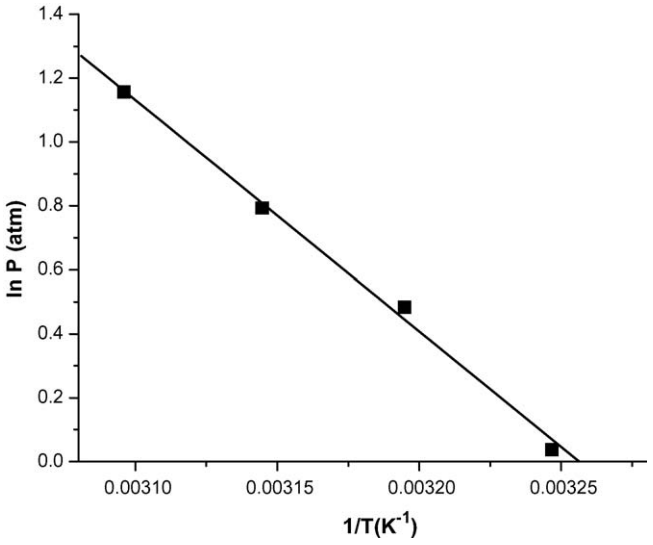

Fig. 4. Typical Van't Hoff plot for plateau region of desorption isotherm.

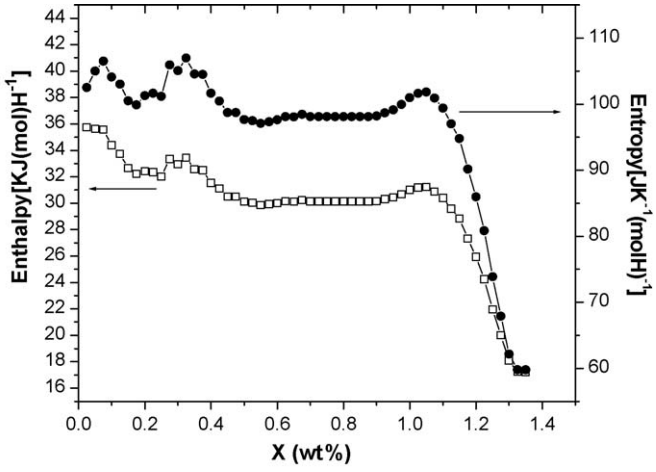

Fig. 5. The variation of of ΔH and ΔS with hydrogen concentration in $Mm_{39.2}Ni_{42.1}Mn_{4.9}Al_{1.25}Co_{10.2}Fe_{2.35}$.

where R is ideal gas constant and T is the thermodynamical temperature. The experimental errors of ΔH and ΔS are sensitive to the plateau slopes in isotherms—the higher the slope the bigger the uncertainty in determining the equilibrium pressure P_{eq}. ΔH and ΔS values for plateau region with their experimental errors are $30.12869 \pm 0.38\,kJ\,mol^{-1}\ H_2$ and $98.11099 \pm 0.9\,JK^{-1}\,mol^{-1}\ H_2$, respectively.

Since the heat of formation of the hydride alloy system is different for single and two phase regions, its variation with hydrogen concentration gives different slopes for different phase regions in the system. The variation of enthalpy and entropy is shown in Fig. 5 which clearly differentiate the boundaries of different phases. The enthalpy and entropy is found between 17.23617–35.75771 $kJmol^{-1}\ H_2$ and 59.7924–106.9888 $JK^{-1}\ mol^{-1}\ H_2$.

The practical significance of ΔH is that it is an index of thermochemical stability of metal hydride, low dissociation pressure and the requirement of moderately higher temperature to decompose it to liberate the hydrogen than hydride formation temperature [13].

4. Conclusion

Hydrogen absorption P-C isotherms of $Mm_{39.2}Ni_{42.1}Mn_{4.9}Al_{1.25}Co_{10.2}Fe_{2.35}$ have been investigated in the temperature and pressure ranges $0.5 \le P \le 10$ bar and $308 \le T \le 323$ K. This study revealed that the resistance of material increases with hydrogen concentration. P-C isotherm shows that the maximum hydrogen is absorbed at around 6 bar and 308 K. The plateau region width decreases with increase in temperature. The different phases are identified by the variation in ΔH and ΔS with hydrogen concentration. The kinetics of absorption in this alloy is quite fast even at room temperature during activation.

Acknowledgements

This work was supported by a grant of UGC. Authors are grateful to Dr. G. Balachandra of DMRL, Hyderabad, India for supplying alloy for this work. One of us Ankur Jain is grateful to the UGC for the financial support in the form of fellowship in the major research project.

References

[1] J.J.G. Willems, Philips J. Res. 39 (1984) 1.
[2] T.N. Veziroglu, Int. J. Hydrogen Energy 12 (1987) 99–129.
[3] T. Sakai, H. Miyamura, N. Kuriyama, A. Kato, K. Oguro, H. Ishikawa, J. Electrochem. Soc. 137 (1990) 795.
[4] M. Ohnishi, Y. Matsumura, K. Hasegawa et al., Abstr. 33rd National Japanese Semin. On Batteries, 1992, p. 163.
[5] K. Suzuki, N. Yanagihara, H. Kawano, A. Ohta, J. Alloys Compd. 192 (1993) 173–175.
[6] Y. Lei, J. Jiang, D. Sun, J. Wu, Q. Wang, J. Alloys Compd. 231 (1995) 553–557.
[7] V.Z. Mordkovich, Y.K. Baichtok, N.V. Dudakova, E.I. Mazus, V.P. Mordovin, J. Alloys Compd. 231 (1995) 498–502.
[8] D. Gary, E. Sandrock, H. Lee, Chem. Tech. (1981) 754.
[9] M. Bououdina, J.L. Soubeyroux, P. de Rango, D. Fruchart, Int. J. Hydrogen Energy 25 (2000) 1059–1068.
[10] R.K. Singh, B.K. Gupta, M.V. Lototsky, O.N. Srivastav, J. Alloys Compd. 373 (2004) 208–213.
[11] R. Tang, L. Liu, Y. Liu, G. Yu, Int. J. Hydrogen Energy 28 (2003) 815–819.
[12] I.P. Jain, Y.K. Vijay, M.I.S. AbuDaka, Int. J. Hydrogen Energy 27 (2002) 85.
[13] B. Viswanathan, M.V.C. Sastry, S.S. Murthy (Eds.), Metal Hydrides, Narosa Publishing Company, New Delhi, 1998.