



HYDROGEN ABSORPTION PROPERTIES OF Mg-BASED COMPOSITE MATERIALS

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ABSTRACT

Mg + x wt % $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ (x = 5, 15 and 25) composite materials have been prepared by reaction ball milling method and were characterized by powder X-ray diffraction analysis and scanning electron microscopy. The pressure-composition isotherms of these composite materials have been obtained in the pressure range 0.1 – 50 bar at 300°C using a pressure reduction method to investigate the effect of amount of catalyst on the hydrogen storage properties. Maximum storage capacity of 4.9 wt % at 300°C is obtained in Mg + 5 wt % $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$. Hydrogen absorption kinetics of these materials have been performed at 300°C and the data have been analyzed using rate equations to understand the mechanism of hydrating reaction process.

Key words: Composite materials, Hydrogen absorption, X-ray diffraction, SEM, Kinetics of hydrogen absorption

1. INTRODUCTION

Hydrogen is the ideal means of storage, transport and conversion of energy for a comprehensive clean-energy concept. Metal hydrides are of considerable interest for safe and practical hydrogen storage. In addition metal hydrides have the highest volumetric capacity. Numerous research works have been carried out on Zr-based AB_2 alloys, aluminates, carbon nanotubes, Mg-based alloys and composites and others [1]. Although suffering from slow reaction kinetics, high work temperature and high thermodynamic stability, magnesium hydride is still considered as a potential hydrogen storage material because of its high storage capacity and low cost [2]. Intensive research works have been carried out to reduce the Mg-H binding energy by using some catalyst, so as to reduce the work temperature and to increase the sorption kinetics. Improvement in hydrogen absorption kinetics have been achieved by different approaches, mainly by [3]; forming multi component alloys, with partial substitution of transition metals at Mg site; forming a composite material by adding a second phase with Mg, which possess good hydrogen absorption properties at favorable conditions. Zaluska et al [4] showed that the reduction in the particle size of magnesium due to ball milling would lead to the increase in the sorption kinetics of Mg. There are several reports to improve the sorption kinetics of Mg by forming composite material with metals, alloys and oxides as a catalyst [5, 6]. Our earlier hydrogen absorption studies on non-stoichiometric Ti/Zr based alloys [7] revealed that $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ has fast hydrogen absorption kinetics at room temperature. The present work discusses the results obtained from the systematic investigation of the effect of amount of catalyst in Mg + x wt % $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ (x = 5, 15 and 25) on the hydrogen storage properties. Here we present the pressure-composition (P-C) isotherms and kinetics of absorption of Mg + x wt % $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ (x = 5, 15 and 25) composite materials at 300°C and discuss the results.

2. EXPERIMENTAL DETAILS

$\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ has been prepared by arc melting the constituent elements in a stoichiometric ratio under argon atmosphere. The alloy button was remelted six times by turning it upside down after each solidification, to ensure homogeneity. Single phase nature of the alloy was confirmed using Fe-K α powder X-ray diffractogram. Mg + x wt% $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ ($x = 5, 15$ and 25) composite materials have been prepared by reaction ball milling Mg and alloy powder in tungsten carbide bowl under hydrogen atmosphere in P5 ball mill for 10 h. The ball to powder ratio (BPR) was kept to 10:1. Hydrogen gas was introduced into the bowl every one hour again to keep the hydrogen atmosphere at ~ 1 bar. The composite materials were then characterized by powder X-ray diffractograms (XRD) and scanning electron microscopy (SEM). The P-C absorption isotherms of these composite materials at 300°C in the pressure range $0.1 - 50$ bar were obtained using a conventional gasometric technique. The system was calibrated at various initial pressures and the sample cell volume has been measured with van der Waals correction for the volume of the gas molecules and molecular interactions. Several blank tests were carried out at different initial pressures and the drop in pressure during the same time interval as that of the experiment was taken in to account while calculating the sample cell volume and hence for the precise measurement of the hydrogen adsorption capacity, extreme care was taken to eliminate the leakage of the system [8]. About 0.5 g of sample in the form of a pellet was introduced in the high pressure reactor and evacuated to 10^{-6} torr. For activation purposes, composite powders were exposed to hydrogen atmosphere at a pressure of 20 bar and a temperature of 300°C . From the reduction of hydrogen pressure, the amount of hydrogen absorbed by the composite material has been calculated. As in a high-pressure experiment, the pressure changes arising from temperature variations can be mistakenly interpreted as substantial absorption, the room temperature in our laboratory was maintained at $25 \pm 1^\circ\text{C}$. All these effects including the inherent leakage of the system were taken into account in the analysis of the hydrogen absorption results as suggested in [8]. The P-C relationships were obtained by calculating the hydrogen storage capacity in wt % from the pressure drop during the hydrogen absorption at constant temperature. Dehydriding was performed by evacuating and heating the hydride powder at 400°C for 3h. After three such absorption/desorption cycles, the amount of hydrogen absorbed by the composite remains same. After activation process, absorption/desorption isotherm data were collected, following each experiment the sample was degassed at 400°C under a vacuum of 10^{-6} torr. The kinetics data were collected by recording the change in pressure as a function of time at constant temperature. The accuracy in the temperature measurement is $\pm 1^\circ\text{C}$.

3. RESULTS AND DISCUSSION

Fig. 1 shows the powder X-ray diffraction patterns of 10h ball milled Mg + x wt % $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ ($x = 5, 15$ and 25) composite materials. The XRD patterns show the existence of Braggs reflections corresponding to Mg and alloy particles. In addition, Braggs reflection corresponding to MgH_2 is also observed. The formation of $\beta\text{-MgH}_2$ at very low pressure and at room temperature can be attributed to the decrease in the values of a and c are with an accuracy of $0.001(\text{\AA})$ and $0.001(\text{\AA})$ respectively. The values of the unit cell volume is with an accuracy of $0.1(\text{\AA}^3)$. Grain size of Mg due to the increase in milling time, the dispersion of $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ alloy particles on the surface of Mg matrix, the exposure of fresh surface of Mg and alloy particles continuously to the hydrogen atmosphere and the dissociation of hydrogen molecules into atoms due to

catalytic $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ alloy particles. The lattice parameters and unit cell volumes of Mg and alloy phases have been separately evaluated using a least square refinement technique and are listed in Table 1. Micro structural characterization of the ball-milled materials has been obtained from the SEM observations. Fig. 2 shows the SEM images of Mg + 25 wt % $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ composite particle surfaces. EDAX patterns of the composite material show that the bright phase (b) corresponds to alloy particle and dark background phase (a) corresponds to Mg.

Pressure-composition isotherms of Mg + x wt % $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ ($x = 5, 15$ and 25) composite materials have been obtained at 300°C in the pressure range $0.1 - 50$ bar and is shown in Fig. 3. Two single phase regions (α and β) and a single plateau region ($\alpha+\beta$) is observed in the pressure range studied. The plateau pressure is measured at the mid point of the plateau region. For technical applications plateau slope can be represented as plateau slope factor, which is given by $\ln(P_2/P_1)$, where P_1 represents the $\alpha \rightarrow \alpha+\beta$ phase transition pressure and P_2 represents the $\alpha+\beta \rightarrow \beta$ phase transition pressure [9]. Table 2 gives the plateau pressure and the plateau slope of [Mg + x wt % $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$]-H ($x = 5, 15$ and 25). Maximum hydrogen intake capacity of 4.9 wt % has been achieved at 300°C in Mg + 5 wt % $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ composite material.

The kinetics of hydrogen absorption has been obtained by measuring the hydrogen pressure change during the hydrogen absorption process in a closed system of constant volume. In alloy hydrides, the absorption rate is controlled by different mechanisms when the reactions proceed through different phase regions. The possible rate determining steps involved in the hydrogen absorption kinetics are the surface process, the interface process and diffusion. The surface process, chemisorption and nucleation of the hydrides occur at the initial stage of absorption. As the absorption process proceeds further, the hydride phase nuclei start growing. After some time, the growing hydride phase nuclei contact with each other with a corresponding decrease in interfacial area and in this process the reaction rate is controlled by the phase transformation at the $\alpha \rightarrow \beta$ interface. When the β phase hydride is formed completely, the diffusion of hydrogen should constitute the rate-determining step [10, 11]. However in magnesium hydride, MgH_x , the two phase region at 510°C is from $x \sim 0.06$ to $x \sim 1.98$ and hence the hydrogen absorption by Mg is difficult to explain using a diffusion controlled process. Therefore in the present investigation of hydrogen absorption of Mg + x wt % $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ ($x = 5, 15$ and 25) we restrict our discussion only to the hydrogen reaction mechanism. Fig. 4 shows the kinetics of hydrogen absorption of Mg + x wt % $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ ($x = 5, 15$ and 25) composites at 300°C . It can be seen from the kinetics data that the rate of absorption is fast for the composite material with more catalyst which is due to the dispersion of $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ alloy particles on the surface of Mg matrix and dissociation of hydrogen molecules into atoms more easily due to catalytic alloy particles. The kinetics data were analyzed using Avrami-Erofeev rate equation:

$$F = 1 - e^{-Btm} \quad (1)$$

where F is the fraction of material reacted with hydrogen, t is the time, B and m are constants. The rate equation which best fits the experimental data can be found for the appropriate value of m . It is found that, in the present investigation, for $x = 25$ the experimental rate follows a first order rate equation

$$-\ln(1 - F) = kt \quad (2)$$

where F is the fraction of material reacted with hydrogen and k is the rate constant

For $x = 5$ and 15 , first order fitting shows a poor description of the experimental data. Hence, the kinetics of absorption in these composite materials ($x = 5$ and 15) were analyzed using second order rate equation

$$[-\ln(1-F)]^{1/2} = kt \quad (3)$$

and the results are plotted in Fig. 5. It was found from the P-C isotherms, that the concentration at which the slope changes correspond to the $\alpha+\beta$ phase to β phase transition region [12]. The first linear segment corresponds to the $\alpha+\beta$ phase and the second one to the β phase and the rate constants have been obtained from the slope of the fitting. The values of rate constant in the $\alpha+\beta$ phase and β phase for $[\text{Mg} + x \text{ wt \% Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}]\text{-H}$ ($x = 5, 15$ and 25) are listed in Table 2. Since the alloy particles can dissociate hydrogen molecules more easily and will provide path for the hydrogen diffusion through the Mg matrix, it is expected that the kinetics of hydrogen absorption increase with increase of amount of alloy particles.

4. CONCLUSION

Mg + x wt % $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ ($x = 5, 15$ and 25) composite materials were synthesized by reaction ball milling. Hydrogen storage capacity increases with decrease in the amount of catalyst and the maximum storage capacity is found to be 4.9 wt % in Mg + 5 wt % $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$. Since the dispersed alloy particles provide path for hydrogen diffusion through Mg matrix, the kinetics of hydrogen absorption is faster in Mg + 25 wt % $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$. The rate constants in the $\alpha+\beta$ and β phases of $[\text{Mg} + x \text{ wt \% Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}]\text{-H}$ are in the ranges 3.19×10^{-3} - $1.17 \times 10^{-2} \text{ s}^{-1}$ and 1.95×10^{-4} - $1.76 \times 10^{-3} \text{ s}^{-1}$ respectively.

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TABLES

Table 1. Lattice parameters and unit cell volumes of Mg and AB₂ phases in Mg + x wt % Ti_{0.1}Zr_{0.9}Mn_{0.9}V_{0.1}Fe_{0.5}Ni_{0.5} (x = 5, 15 and 25) composite materials

Material					Mg phase			AB ₂ phase		
					a (Å)	c (Å)	v (Å ³)	a (Å)	c (Å)	v (Å ³)
Mg	+	5	wt	%	3.208	5.211	46.4			
Ti _{0.1} Zr _{0.9} Mn _{0.9} V _{0.1} Fe _{0.5} Ni _{0.5}										
Mg	+	15	wt	%	3.210	5.215	46.5	5.002	8.199	177.6
Ti _{0.1} Zr _{0.9} Mn _{0.9} V _{0.1} Fe _{0.5} Ni _{0.5}										
Mg	+	25	wt	%	3.211	5.216	46.6	5.009	8.201	178.2
Ti _{0.1} Zr _{0.9} Mn _{0.9} V _{0.1} Fe _{0.5} Ni _{0.5}										

Table 2. Plateau pressure, hydrogen storage capacity, plateau slope and rate constants in [Mg + x wt % Ti_{0.1}Zr_{0.9}Mn_{0.9}V_{0.1}Fe_{0.5}Ni_{0.5}]-H (x = 5, 15 and 25)

Hydride	Plateau pressure** (bar)	Storage capacity (wt %)	Plateau slope	k (α+β) phase (s ⁻¹)	k β phase (s ⁻¹)
[Mg + 5 wt % Ti _{0.1} Zr _{0.9} Mn _{0.9} V _{0.1} Fe _{0.5} Ni _{0.5}]-H	3.6	4.9	1.54	3.19 x 10 ^{-3*}	1.95 x 10 ^{-4*}
[Mg + 15 wt % Ti _{0.1} Zr _{0.9} Mn _{0.9} V _{0.1} Fe _{0.5} Ni _{0.5}]-H	2.2	4.2	1.17	4.91 x 10 ^{-3*}	2.52 x 10 ^{-4*}
[Mg + 25 wt % Ti _{0.1} Zr _{0.9} Mn _{0.9} V _{0.1} Fe _{0.5} Ni _{0.5}]-H	1.4	3.4	1.19	1.17 x 10 ⁻²	1.76 x 10 ⁻³

* Values obtained from second order fitting

** The plateau pressure is measured at the mid point of the plateau region as in [9].

FIGURES

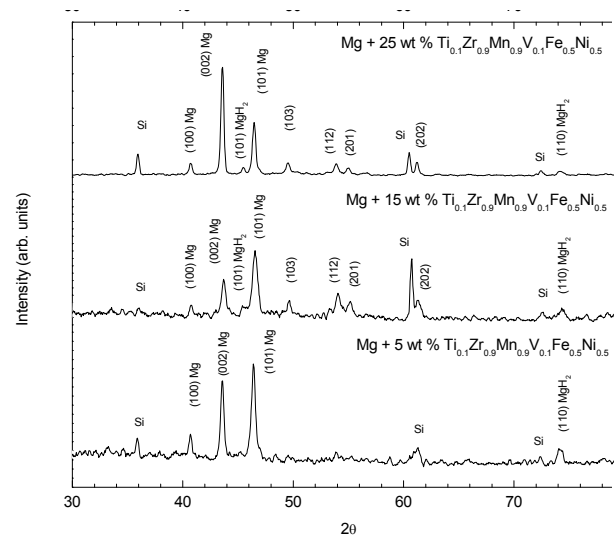


Fig. 1. XRD patterns of $\text{Mg} + x \text{ wt } \% \text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ ($x = 5, 15$ and 25) composite materials

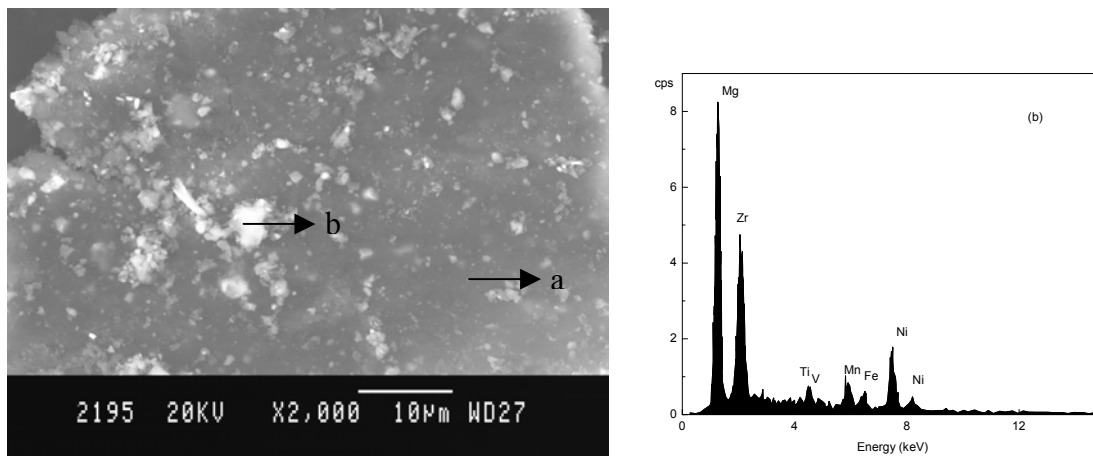


Fig. 2. SEM image and EDAX pattern of $\text{Mg} + 25 \text{ wt } \% \text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ composite materials

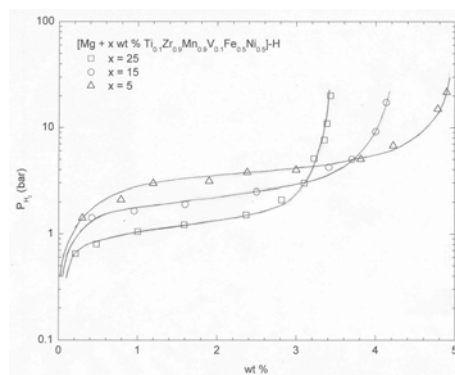


Fig. 3. Pressure-Composition isotherm of Mg + x wt % $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ ($x = 5, 15$ and 25) composite materials at 300°C

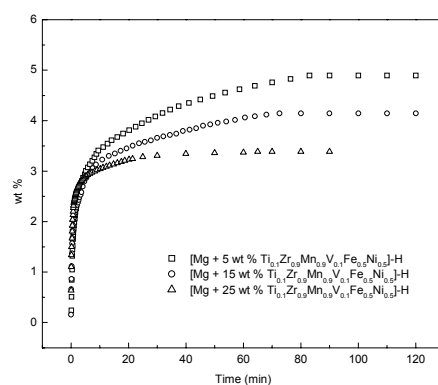


Fig. 4. Kinetics of hydrogen absorption of Mg + x wt % $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}$ ($x = 5, 15$ and 25) composite materials

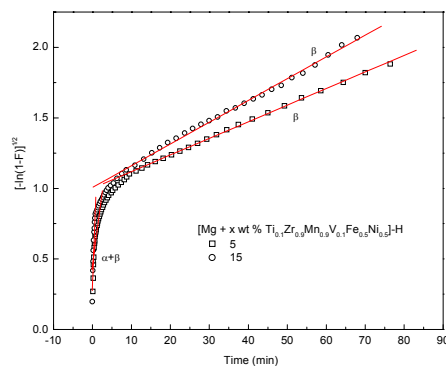


Fig. 5. $[-\ln(1-F)]^{1/2}$ vs t plots of $[\text{Mg} + x \text{ wt } \% \text{Ti}_{0.1}\text{Zr}_{0.9}\text{Mn}_{0.9}\text{V}_{0.1}\text{Fe}_{0.5}\text{Ni}_{0.5}]\text{-H}$ ($x = 5$ and 15)