Hydrogen Sorption Behaviors of a Core–Shell Structured Mg@Fe Composite Powder

Jianxin Zou1,2,*, Sheng Long1, Lifu Zhang1, Chong Lu1, Xi Chen1, Xiaojin Zeng1,2 and Wenjiang Ding1,2

1Shanghai Engineering Research Center of Mg Materials and Applications & National Engineering Research Center of Light Alloy Net Forming, Shanghai Jiao Tong University, Shanghai 200240, P. R. China
2State Key Laboratory of Metal Matrix Composite & School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

In the present work, a Fe covered pure Mg ultrafine powder–Mg@Fe- was prepared through electroless plating of Fe on the arc plasma evaporated Mg powder in a FeCl3 n-butyl alcohol solution. The phase components, microstructure and hydrogen sorption behaviors of the Mg@Fe composite powder were investigated using XRD, TEM and PCT techniques. TEM observations revealed that those ultrafine Mg particles were covered by nano α-Fe grains reduced by Mg during electroless plating. The hydrogenation enthalpy of the Mg@Fe composite is determined to be −78kJ/mol H2 based on PCT measurements. Meanwhile, the hydrogen absorption activation energy of Mg@Fe composite is reduced to 54.6kJ/mol H2 and the onset desorption temperature of hydrogenated Mg@Fe is lower down to 620 K when compared to those for pure Mg powder. The improved hydrogen sorption kinetic properties of Mg@Fe composite over pure Mg powder can be mainly attributed to the catalytic effects from nano α-Fe covered on the Mg ultrafine particles. [doi:10.2320 matertrans.MG201418]

(Received February 12, 2014; Accepted May 7, 2014; Published July 11, 2014)

Keywords: hydrogen storage, magnesium, arc plasma method, electroless plating, core–shell structure

1. Introduction

Hydrogen is widely considered as an optimum clean energy source for future human society. However, the lack of efficient and safe hydrogen storage carriers is now becoming the bottle neck toward “hydrogen economy”.1,2) Generally, hydrogen can be stored in its gaseous or liquid states in high pressure tanks or in physically/chemically combined states in solid hydrogen storage materials. The advantages of solid state hydrogen storage lie in the high storage capacity, high safety and low costs. In the past decades, different types of hydrogen storage materials have been developed, such as metal hydrides, complex hydrides, carbon nanotubes, metal–organic frameworks (MOFs), etc.3,4) Among these solid hydrogen storage materials, Magnesium hydride (MgH2) is an attractive candidate for on-board or stationary applications due to its high hydrogen capacity up to 7.6mass% and low costs.1,3) However, the sluggish kinetics of de/re-hydrogenation of Mg at moderate temperatures has limited its practical applications. Indeed, pure MgH2 must be heated to about 400°C to achieve an adequate rate of de/re-hydrogenation. Therefore, the search for effective approaches to improve both thermodynamic and kinetic properties of Mg-based hydrogen storage materials is becoming essential. Recently, the size effect on the hydrogen storage properties of Mg has attracted much attention.5,6) It has been established experimentally and theoretically that hydrogen sorption thermodynamic and kinetic properties of Mg can be significantly improved when its particle size is reduced to several nm due to the so called “nano-size effect”.6–8) On the other hand, catalysts addition and alloying of Mg/MgH2 with transition metals (TM) are also proved to be efficient approaches to improve the hydrogen sorption thermodynamic and kinetic properties. For instance, mixing Mg with 3d transition metal elements or their oxides (including rare earth metal oxides) can efficiently accelerate the hydriding and dehydriding rates of Mg.9–12) Recently, Mg–RE (RE = La, Nd, Gd, Er) composites with a special metal-oxide core–shell structure were prepared through an arc plasma method followed by passivation in air.13,14) Experimental investigations revealed that the nano RE oxides covered on the Mg ultrafine particles can effectively improve the hydrogen sorption kinetics and protect Mg particles from severe oxidation.14) Considering Mg is chemically more active than most 3d TM, it is thus possible to cover a TM catalytic layer on Mg ultrafine powders through chemical methods, such as electroless plating.15) In this work, an Fe covered pure Mg ultrafine powder–Mg@Fe- was prepared through electroless plating of Fe on the arc plasma evaporated Mg powder in a FeCl3 solution. The effect of Fe layer on the hydrogen sorption thermodynamic and kinetic properties of Mg ultrafine particles will be investigated in details.

2. Experimental

2.1 Sample preparation

The Mg@Fe composite powder was prepared as follows. First, pure Mg powder was prepared from bulk Mg (99.9% in purity) by using the arc plasma method.16,17) The preparation procedures can be found in our previous investigations.14) What is different in the present work is that the pure Mg powders are collected without any further passivation treatments. This is to keep the fresh surface and avoid the formation of MgO on the Mg ultrafine particles. Second, the pure Mg powder was put into a FeCl3 n-butyl alcohol solution with a Mg : FeCl3 mass ratio of about 8 : 1. This gives a maximum Fe content of 3.8 mass% in the Mg@Fe composite assuming FeCl3 can be totally reduced by Mg and covered on the Mg particles. The electroless plating was carried out at 70°C for 3 h with magnetic stirring. After
electroless plating, the coated Mg powder was filtered out from the solution and was dried at 250°C for 1h to remove the remaining n-butyl alcohol or water in the powder.

2.2 Characterization

The phase identifications of the Mg@Fe composite samples at different states were carried out by using a X-ray diffraction (XRD) apparatus (D/max 2550VL/PCX) equipped with a Cu-Kα radiation source. The microstructures of the Mg@Fe powders were observed by using a JEM-2100F transmission electron microscopy (TEM). A conventional Sievert type pressure–composition–temperature (PCT) volumetric apparatus was used to obtain the hydrogen pressure–composition isotherms and dynamic absorption curves of the Mg@Fe composite at various temperatures. The dehydriding behaviors of the hydrogenated Mg@Fe composite powder was investigated by using Synchronous Thermal Analysis [Thermogravimetry/differential scanning calorimetry (TG/DSC), Netzsch STA449F3 Jupiter] under 0.1 MPa of argon at a heating rate of 10 K/min.

3. Results and Discussions

3.1 Phase components and microstructures of the Mg@Fe composite powder

Figures 1(a) and 1(b) shows XRD patterns of the as prepared Mg@Fe composite powder and the powder after hydrogenation, respectively. XRD pattern in Fig. 1(a) shows that the majority phase in the Mg@Fe composite powder is Mg. Besides, MgO and α-Fe are also detected as minority phases. Therefore, the following reaction has occurred during electroless plating:

$$2\text{FeCl}_3 + 3\text{Mg} = 3\text{MgCl}_2 + 2\text{Fe},$$

through which Mg ultrafine particles are covered by α-Fe. The XRD pattern of the hydrogenated Mg@Fe powder (Fig. 1(b)) reveals that most of the Mg has transformed into MgH2 after 1h of hydrogen absorption at 673 K under 4 MPa pressure while α-Fe kept unchanged after hydrogenation. No trace of Mg2FeH6 phase is present in the XRD pattern. Besides, a small amount of MgO and residual Mg, are also present in the hydrogenated sample.

TEM observations have been done on the Mg@Fe composite powder before and after hydrogenation. Figures 2(a) and 2(b) shows a typical bright field TEM micrograph and the corresponding selected area electron diffraction (SAED) pattern for the as prepared Mg@Fe composite powder, respectively. As seen from Fig. 2(a), the Mg particles in the Mg@Fe powder have other hexagonal or spherical shape. Their particle size is in the range from 100 to 600 nm. Such kind of morphology and size distribution were typical features of pure Mg or Mg based composite powders prepared using arc plasma method.13,14,18 The corresponding SAED pattern of these particles (Fig. 2(b)) confirmed the presence of Mg, MgO and Fe. A dark field TEM image given in Fig. 2(c) is drawn from a portion of diffraction rings of α-Fe(110) and MgO(200). It can be seen from the image that those MgO or α-Fe particles, shown in bright contrast and in the range of several nms to 10 nm, are distributed at the edge of the particles. This means that a Fe+MgO shell covers on Mg core particles. Similar TEM observations were also done on the hydrogenated Mg@Fe powder. Figure 2(d) shows a typical TEM bright field image taken for the Mg@Fe composite powder after hydrogenation. After hydrogenation,
most of the Mg particles keep their hexagonal except that some particles break into pieces due to the large volume expansion arising from hydrogenation. The corresponding SAED pattern given in Fig. 2(e) can be indexed by MgH₂, α-Fe, and MgO phases, which is in accordance with the XRD analyses shown in Fig. 1. The dark field TEM image (Fig. 2(f)) taken also from α-Fe(110) and MgO(200) show that those nano sized α-Fe and MgO phases are still present and covered on the MgH₂ particles.

3.2 Hydrogen sorption behaviors of the Mg@Fe composite powder

The hydrogen sorption thermodynamic and kinetic properties of the Mg@Fe composite powder were measured by using the PCT technique. Figure 3(a) shows the PC isotherms of the Mg@Fe composite powder measured at different temperatures. The data obtained from PCT measurements are given in Table 1. It is seen from these PC isotherms that the maximum hydrogen absorption capacity varies slightly with temperature, reaching 5.34 mass% at 673 K. This capacity is lower than that of the pure Mg ultrafine powder (~6.24 mass%) measured at the same temperature. This is due to existence of Fe in the Mg@Fe composite.

The hydrogen sorption enthalpies of the Mg@Fe composite are calculated by using van’t Hoff equation based on the PCT data. Using the absorption/desorption plateau pressures given in Table 1 and according to the linear fitting of ln P vs. 1000/T shown in Fig. 4(b), the hydrogen absorption and desorption enthalpies of the Mg@Fe powder are determined to be ~78 kJ/mol H₂ and 80.7 kJ/mol H₂, respectively. The absorption enthalpy of the Mg@Fe composite powder is fairly close to the hydrogenation enthalpy of pure Mg ultrafine powder (~78.7 kJ/mol H₂), indicating that the thermodynamics of Mg particle is not influenced by the α-Fe shell.

Figure 4(a) shows the hydrogen absorption profiles of Mg@Fe powder measured at different temperatures and TG/DSC curves of the hydrogenated Mg@Fe composite powder obtained at 673 K under 4 MPa H₂ for 4 h.
5.1 mass% after 2 h of hydrogenation at 523 K. The hydrogen absorption rate of the Mg@Fe composite powder is much faster than that of the pure Mg powder, especially at lower temperatures. For instance, the Mg@Fe powder can absorb 1.73 mass% of hydrogen at 473 K within 15 min, while only 0.27 mass% of hydrogen can be absorbed by the pure Mg powder.\(^{14}\) It has been established that hydrogen absorption in metals involves several steps: the adsorption of hydrogen molecular on the surface, the dissociation of hydrogen molecular, penetration of hydrogen atoms into metal, formation of the metal hydride and the diffusion of hydrogen in the bulk metal or its hydride.\(^{19}\) The energy barrier involved in the above steps, namely, the apparent activation energy \(E_a\), can be used to characterize the absorption kinetics. According to the Johnson-Mehl-Avrami-Komogolov (JMAK)\(^{16}\) model and based on the isothermal absorption and desorption, and thereby improve significantly the hydrogen sorption kinetics of Mg.

4. Conclusions

In the present work, a core–shell structured Mg@Fe hydrogen storage composite powder was prepared through an arc plasma evaporation of Mg followed by electroless plating of Fe in a FeCl\(_3\) n-butyl alcohol solution. The phase components, microstructure and hydrogen sorption behaviors of the composite powder were carefully investigated. XRD analyses and TEM observations showed that the as prepared Mg@Fe composite powder was mainly composed of ultrafine Mg particles covered by nano-sized \(\alpha\)-Fe and MgO. The nano \(\alpha\)-Fe layer formed during the electroless plating through reduction of Fe ions by Mg. Based on the PCT measurements, the hydrogenation and dehydrogenation enthalpies of Mg in the Mg@Fe composite powder were determined to be \(-78\) kJ/mol H\(_2\) and 80.7 kJ/mol H\(_2\), respectively. The Mg@Fe composite powder showed improved hydrogen absorption kinetics in comparison to pure Mg prepared also using arc plasma method with an apparent activation energy of 54.6 kJ/mol H\(_2\). The nano \(\alpha\)-Fe covered on Mg/MgH\(_2\) particles can act as channels for hydrogen sorption and thereby improve the hydrogen sorption kinetics of Mg/ MgH\(_2\).

Acknowledgment

Prof. Zou would like to thank the support from the Science and Technology Committee of Shanghai under No. 10JC1407700, No. 11ZR1417600, and ‘Pujiang’ project (No. 11PJ1406000). This work is partly supported by the Research Funds for the Doctoral Program of Higher Education of China (No. 20100073120007) and from the Shanghai education commission (No. 12ZZ017). Lifu Zhang would like to thank the support from Hui-Chun Chin and Tsung-Dao Lee Chinese Undergraduate Research Endowment (CURE).

REFERENCES