Hydrogenation Mechanisms of Mg during Reaction Ball Milling

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Magnesium hydrides are considered as the potential hydrogen storage materials. However, high work temperature, slow reaction kinetics and hard activation process limit the practical application of Mg-based hydrides system. Recently, the reaction ball milling (RBM) technique has been successfully introduced to prepare hydrogen storage materials [1, 2]. It combines the courses of sample preparation, activation and hydrogenation into one step. Pure Mg milled under the hydrogen atmosphere was studied by Gennari [3]. In his study, the metastable $\gamma$-MgH$_2$ was generated by the RBM process. A reduction of particle and crystallite size and an increase of specific surface were observed. Unfortunately, only half of Mg was transformed into hydrides and the crystallite size was still very big. Moreover, it took many hours to finish the hydriding process. Some researchers tried to improve the reaction efficiency between Mg and H$_2$ by addition of some second phases, such as FeTi$_{1.2}$ [4], TiO$_2$ [5], and amorphous TiMn$_{1.5}$ [6]. Due to the excellent kinetic properties, the reaction efficiency was greatly improved. However, few investigations have been directed to the mechanisms of hydriding process in the RBM process, especially with the existence of catalyst. Further investigation is much needed.

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In this work, Ti$_{37.5}$V$_{25}$Cr$_{37.5}$ (bcc structure) alloy was used as catalyst due to good hydriding properties and high hydrogen storage capacity [7]. Ti$_{37.5}$V$_{25}$Cr$_{37.5}$ alloy was prepared using arc melting with electromagnetic stirring (EMS) in an argon atmosphere. The starting materials were of a purity of 99.9% and the alloy was turned and melted for four times to improve the homogeneity. Then the as-cast alloy was crushed into powder, which passed through a 0.5mm screen. Finally, the powder of the as-cast alloy (30wt. %) was mixed with Mg (purity>99%, 100 mesh) and then mechanically milled in a SPEX8000 machine. A cylindrical stainless steel vial was used with the stainless steel balls and the ball to powder ratio is 20:1. The vial was sealed by an O-ring and connected to a gas reservoir under an initial pressure of 1 MPa, as shown in Fig. 1 [8, 9]. The total volume of the system was 260 cm$^3$ and about 2.7 g material could be produced. The milling was carried out for the duration of 5 h. During the milling, small changes in the hydrogen pressure representing absorption of hydrogen by the sample were monitored continuously. The method proposed by Bab et al [9] was adopted to measure the absorption kinetics. Subsequently, the mixture of magnesium powder and the as-cast alloy powder was also milled under the same condition as mentioned above. At selected time, small amount of powder was successively taken out of the vial to characterize the phase structure. For the sake of comparison, the as-cast Ti$_{37.5}$V$_{25}$Cr$_{37.5}$ alloy powder was separately milled under the same condition as mentioned above. The powder was characterized at different duration during the milling. Phase structure of the powder was examined using an X-ray diffraction (XRD) machine equipped with a monochromator with Cu K$_\alpha$
radiation.

The XRD spectra as a function of milling time for the Mg+ Ti$_{37.5}$V$_{25}$Cr$_{37.5}$ in hydrogen atmosphere are shown in Fig. 2. Tetragonal $\beta$-MgH$_2$ is generated after 1 h milling. The relative intensity of Mg-XRD patterns decreases and the peaks broaden drastically after 2 h milling. The reduction of relative intensity for Mg rests on two reasons. One is hydriding of Mg; another is reduction of grain size of Mg. After 5 h milling, XRD patterns of Mg almost disappear and nanometer-scaled $\beta$-MgH$_2$ becomes a principal part of the alloy. Interestingly, orthorhombic $\gamma$-MgH$_2$ also appears after 3 h milling. This is similar to the work of Schulz et al [10]. With increasing the milling time, the width of the diffraction peaks of $\beta$-MgH$_2$ and $\gamma$-MgH$_2$ is significantly broadened due to reduction of grain size. Another possible reason is the concentrated micro-strain caused by the high-energy ball milling. The patterns of Fe can be observed after 5 h milling, which indicates that iron is introduced into the alloy during the ball milling. The crystal size of $\beta$-MgH$_2$ milled for 5 h can be estimated using the Scherrer equation and is about 10 nm. The XRD patterns of Ti$_{37.5}$V$_{25}$Cr$_{37.5}$ alloy milled in a hydrogen atmosphere were also detected, as shown in Fig. 3. The patterns of hydrides of vanadium exist in the initial stage of milling, indicating the Ti$_{37.5}$V$_{25}$Cr$_{37.5}$ alloy powder to be easily hydrided by mechanical energy. The relative intensity for the Ti$_{37.5}$V$_{25}$Cr$_{37.5}$ alloy and its hydrides still remains stable after 5 h milling.

The time dependence of the hydrogen absorption during the milling is shown in Fig. 4. In the initial 10 min, an amount of hydrogen, about 1.05 wt % is absorbed quickly;
then, the hydrogen absorption is slowed down in the following 1 h. The hydrogen content increases rapidly during the period of 1 h to 3 h, and a saturated value of up to 6.39 wt. % is finally achieved.

The capacity of hydrogen absorption of Ti$_{37.5}$V$_{25}$Cr$_{37.5}$ alloy during the milling was also investigated separately. About 3.52 wt. % hydrogen was absorbed after 10 min milling, but no appreciated hydrogen was absorbed after 10 min. Therefore, it was considered that in the initial 10 min the hydrogen was mainly absorbed by the Ti$_{37.5}$V$_{25}$Cr$_{37.5}$ alloy but the absorption of the rest of hydrogen was attributed to the Mg for the mixture of Mg and Ti$_{37.5}$V$_{25}$Cr$_{37.5}$. In Fig. 3, it can be also seen that the XRD patterns of VH$_x$ exist at the beginning of the milling and keep stable in the remaining time. Considering the theoretical capacity of hydrogen absorption of Mg, it is clear that Mg particles are transformed into hydrides completely under the catalysis effect of Ti$_{37.5}$V$_{25}$Cr$_{37.5}$ alloy and the mechanical energy.

According to Johnson-Mehl-Avrami equation [11], the Avrami exponent (n) can be evaluated on the assumption that all Mg is in the form of hydride. Fig. 5 shows the relation between reaction volume fraction and milling time where the hydrogen absorbed by Ti$_{37.5}$V$_{25}$Cr$_{37.5}$ alloy (about 1.05 wt. %) is ignored. Also, it is assumed that no hydrogen is absorbed by Mg in the initial 10 min. Fig. 6 shows the plot of $\ln\ln(1/(1-x))$ versus $\ln t$ where x is reaction fraction and t is the time. Different values of Avrami exponents indicate different types of nucleation and growth mechanism [12]. Corresponding to 0~0.9 of the reaction fraction (x), the value of Avrami exponent (n) is in the range of 1.5~2.3. This fact implies that the formation of hydrides phases is a
three-dimensional growth mechanism with a reduced nucleation rate with time, which is controlled by the diffusion of hydrogen atom. During the ball milling, the catalytic phases, i.e. Ti$_{37.5}$V$_{25}$Cr$_{37.5}$ alloy, can distribute uniformly on the surface of Mg particles due to cold welding and shearing. By providing the diffusion passageway for hydrogen atoms and degrading the dissociation energy of hydrogen molecules breaking into atoms, Ti$_{37.5}$V$_{25}$Cr$_{37.5}$ can accelerate the hydriding process of magnesium particles. In addition, ball milling is a nonequilibrium process that can create a specific state on the surface of the materials. A large surface-to-volume ratio and a significant amount of defects and imperfections can enhance the accessibility of a material for hydrogen penetration. As a result, the addition of Ti$_{37.5}$V$_{25}$Cr$_{37.5}$ alloy and the mechanical force upgrade the diffusion capacity of hydrogen atoms, which is regarded as the key step for the hydriding process of milled Mg.

Hydrogenation mechanism in this Mg-based composite is mainly a three-dimensional growth mechanism controlled by the diffusion of hydrogen atom during the reaction ball milling. Ti$_{37.5}$V$_{25}$Cr$_{37.5}$ alloy degrades the dissociation energy of hydrogen molecules breaking into atoms and provides diffusion passageway for hydrogen atoms, thereby accelerating the hydriding process of the magnesium particles.
Acknowledgements

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References


Captions of figures

Fig 1 Schematic drawing of the reaction-ball-milling reactor used in this study.

Fig 2 X-ray diffraction patterns of mechanically milled mixture of Mg and Ti$_{37.5}$V$_{25}$Cr$_{37.5}$ in a hydrogen atmosphere after (a) 1 h, (b) 2 h, (c) 3 h and (d) 5 h of milling.

Fig 3 X-ray diffraction patterns of (a) arc melted Ti$_{37.5}$V$_{25}$Cr$_{37.5}$, (b) mechanically milled Ti$_{37.5}$V$_{25}$Cr$_{37.5}$ in a hydrogen atmosphere for 10 min, and (c) mechanically milled Mg and Ti$_{37.5}$V$_{25}$Cr$_{37.5}$ in a hydrogen atmosphere for 5 h.

Fig. 4 Hydrogen content as a function of milling time for Mg+Ti$_{37.5}$V$_{25}$Cr$_{37.5}$ alloy in hydrogen atmosphere.

Fig. 5 Reaction fraction as a function of milling time.

Fig. 6 LnLn [1/(1-x)] as a function of Ln t for the reaction ball milling.
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Fig. 3 Hu, Zhang, Yan, Ye, Ding and Hu
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Fig. 5 Hu, Zhang, Yan, Ye, Ding and Hu
Fig. 6 Hu, Zhang, Yan, Ye, Ding and Hu