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Hydrogen storage properties of Mg-based mixtures elaborated by reactive mechanical grinding

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The hydrogen sorption properties of Mg + 10 wt% WO_3 and Mg + 5 wt% Cr_2O_3 mixtures made by reactive (under hydrogen) mechanical grinding were studied and compared with those of elemental Mg subjected to a similar preparation procedure. It was observed that both oxides have an important catalytic effect on hydrogen absorption and desorption. Moreover, in the case of Cr_2O_3 addition, both milling speed (i.e, milling energy and milling mode) and ball to powder weight ratio influence drastically the hydrogen sorption kinetics.

1. Introduction

The most serious environmental problem today is the green house global warning caused mainly by CO_2 accumulation in the atmosphere, which can not be arrested as long as carbon is present in any form in the fuel used. This leaves us with hydrogen as the only choice as it is the only known carbon free combustible material. However, the problem of production and storage of hydrogen has to be solved. Production of hydrogen is generally achieved by natural gas reforming but new process are actually under study such as production (i) from biomass and (ii) by bio-organisms. For the storage, liquid and compressed H_2 are commonly used but the safety is not sufficient to extend the use to particulars. Then, the metal hydrides appear as the only way to store H_2 safely and without any energetic coast. Among all the materials, Mg is one of the most promising metals mainly due to its low weight and high H-storage capacity, its abundance on the earth's crust and its low cost. However, it needs high temperature and the sorption kinetics are very low. To improve it, the surface of Mg can be modified by (i) using mechanical alloying or reactive mechanical grinding (RMG) and (ii) adding metals, non-metal and intermetallics [1–4]. More recently, it has been reported that addition of metal oxides also produces a catalytic effect on hydrogen absorption and desorption properties of Mg [5–8]. Generally, it was observed that multivalence metals induce a more pronounced catalytic effect in hydrogen sorption.

This work is devoted to the effect on hydrogen sorption properties of (i) the addition of WO_3 to Mg by RMG and (ii) the milling conditions in the case of Mg+Cr_2O_3 mixtures. Cr_2O_3 addition is well known as a hydrogen sorption catalyst, and WO_3 combine both the effect of multivalence metal and the fact that it forms a bronze ($H_{0,23}WO_3$) in special conditions [9].

2. Experimental

The various mixtures (composed of powder of at least 99.8% purity) were prepared in a glove box and then, mixed in a planetary ball mill (Fritsch P5) under 1.1 MPa of hydrogen. The milling was stopped every 15 min for 5 min of rest and every 30 min, the milling vial was refilled with H_2 to ensure a constant pressure.

At regular intervals a small amount of powder was removed from the container to follow the evolution of the mixture by XRD (Philips PW 1050 diffractometer using Bragg-Brentano geometry and Cu-Kα radiation), EPMA (CAMECA SX-100 Instrument) and granulometric measurements in liquid media (Malvern Mastersizer Hydro 2000S). For selected samples, we also studied the kinetics of absorption and desorption of H_2 by performing several hydriding and dehydriding cycles at temperatures ranging from 100 to 330°C in a Hera volumetric apparatus. The absorption and desorption rates are calculated as the ratio between the amount absorbed (desorbed) and the time taken to go from 20 to 80% of full capacity.

3. Results and discussion

During RMG, MgH_2 is formed and the relative quantity of MgH_2 reaches approximately 80% after 10 h of milling whatever the added oxides. It is also worth pointing out that the higher the milling speed is, the quicker is the formation of MgH_2. The obtained value can be compared with the amount of hydride obtained by Huot *et al*. [10] by milling Mg + 5 at.% V + graphite

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at 573 K which changes from 64 wt% after 30 min of milling to almost the completion after 1 h. However, it is important to note here that the relative quantity determined by XRD (Huot *et al.*) is always underestimated because it does not allow to take into account the amorphous matrix of magnesium. The crystallite size estimated by XRD data decreases with increasing milling time (mt) and reaches a minimum size of 10 nm after 10 h of mt. The increase of mt does not allow to reduce more the crystallinity of the mixtures. Finally, the reduction of oxides is not observed during milling.

3.1. Addition of WO_3

The EPMA allows to highlight the evolution of the intermixing of the components as a function of mt (Fig. 1). The main changes occur during the first 8 h of milling. After 1 h mt, WO_3 locates mostly outside the Mg agglomerates and after 2 h mt, the average size of the Mg agglomerates decreases significantly with the consequent improvement in intermixing. This process goes on up to 8 h mt, when a good intermixing of Mg and WO_3 is attained. For longer mt, no significant change is observed. The granulometric measurements provide the same information as the median diameter of the mixtures changes from 120 μm after 1 h mt to 20 μm after 2 h, and to 4 μm after 4 h mt and finally to the minimum value of 0.5 μm for longer mt (i.e., 8, 12 or 16 h).

The absorption rate increases as milling proceeds and, in agreement with the evolution of the samples already discussed, the difference is more important between the samples milled 4 and 8 h than between the samples milled 8 and 16 h. Moreover, no activation of the samples was required and no significant degradation of the sorption characteristics were observed up to 15 cycles. The hydrogen sorption properties of the mixture and that of pure Mg milled for 8 h were studied and compared (Fig. 2). It clearly appears on Fig. 2 that the addition of WO_3 has an important effect on the hydrogen sorption properties of Mg, substantially accelerating the absorption and desorption processes. For absorption at 200°C the ratio between the rates is almost 8, and for desorption at 300°C the ratio is almost 9. Oelerich *et al.* [5] obtained a similar desorbing rate (i.e., 0.4×10^{-2} wt%/s at 300°C) for nanocrystalline Mg after 120 h of milling. The absorption of pure Mg at 250°C and that of Mg + 10%WO_3 at 200°C are almost the same and the absorption is even possible at 100°C for the mixture as it was impossible for pure Mg. For the desorption the same phenomenon was observed: the desorption at 300°C for pure Mg is even less rapid than that of the mixture. Then it can be concluded that the addition of WO_3 allows to reduce the temperature of use of magnesium by improving significantly the kinetics.

This was not a surprise as W is a multivalence transition metal but the formation of W bronze is not observed neither after milling nor after hydrogen sorption cycling. However, during the milling of pure WO_3 in our experimental conditions, a part of the hexagonal WO_3 is transformed into the monoclinic phase of WO_3 and reversibly. It is reported in the literature that the hexagonal phase of WO_3 transforms exothermally and irreversibly to the monoclinic phase of WO_3 upon heating [9], but to our knowledge there is no information concerning the phase evolution of WO_3 during mechanical milling. Up to now it is not clear why this transformation and retransformation occurs, but this is the subject of current research. The monoclinic phase is described as a vacancy oxides compounds ($WO_{3-\delta}$) and then this oxygen vacancy induces a electronic disorder acting as a catalyst for hydrogen sorption.

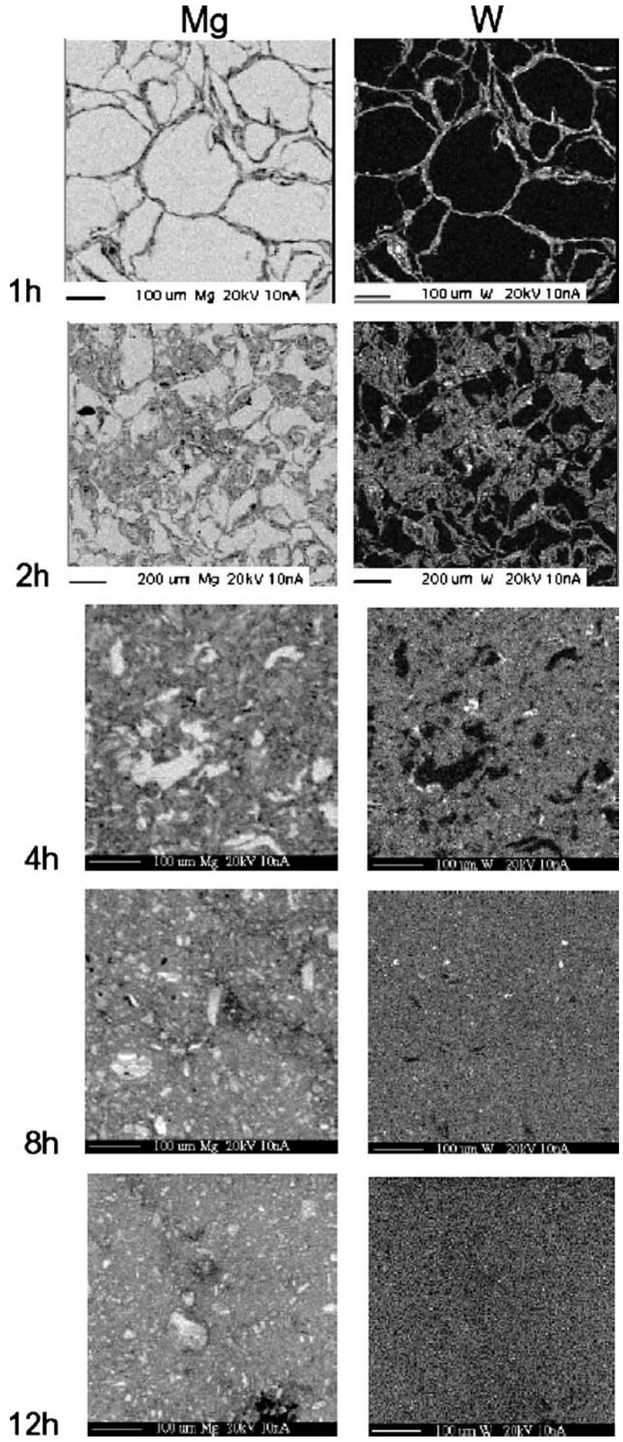

Figure 1 EPMA images showing the evolution of Mg and WO_3 intermixing with milling time (Mg characteristic radiation at the left, W at the right).

Finally, Oelerich *et al.* [5] obtained desorption rates ranging from 1.5×10^{-2} wt%/s to 3×10^{-2} wt%/s after

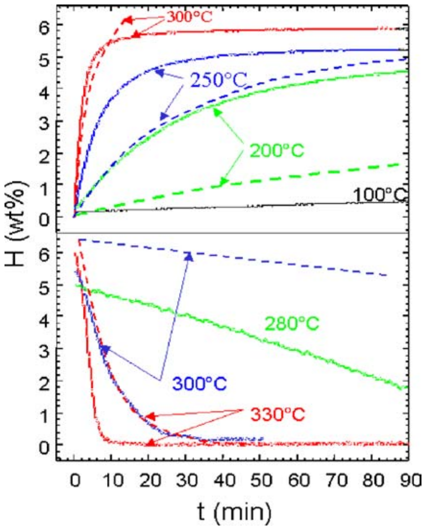

Figure 2 Absorption and desorption curves for both Mg + 10%WO_3 mixture (continuous lines) and pure Mg (discontinuous lines) as a function of temperature for different milling times.

120 h of milling with various oxides. The goal of the next part is to improve the sorption kinetics without increasing to much the mt. Cr_2O_3 was chosen because no structural or chemical changes during both milling and sorption cycle were observed.

3.2. Addition of Cr_2O_3

It is well known that the milling energy and mode is dependent of (i) the milling tools and (ii) the rotation speed. For example, the injected power for a vibratory miller is estimated at 0.24 W/g/ball as it is in the range 0.01 to 0.8 for a planetary miller [11]. Moreover, the frequency of shocks is 200 Hz for a vibratory miller as it is only 100 Hz for the planetary one. Assuming that the catalyst effect of oxides is mainly due to the creation of defects, the ball milling condition could drastically affect the sorption properties. The sorption properties of mixtures Mg + 5 wt%Cr_2O_3 elaborated with (i) the planetary ball miller at 3 different rotation speed (i.e., 200, 250 and 300 rpm) and (ii) the vibratory miller are presented in Fig. 3 as an example. For both absorption and desorption, the results obtained with the vibratory miller are close to that obtained with the planetary miller at higher rotation speed. It is in good agreement with previous results showing that at higher rotation speed the shock mode is predominant towards the friction mode [12]. Moreover, it confirms that the catalyst effect of oxides is strongly correlated to the formation of defects. The ratio between the rates calculated for the mixture milled at 300 and 200 rpm is approximately 4 at 200°C for absorption and 5 for the desorption at 280°C. Increasing the rotation speed or using vibratory miller allow to reduce more easily the crystallite and grain size and then, lead to the improvement of the sorption properties. For example a median diameter of 0.3 μm is attained after only 3 h of milling at 300 rpm as it takes more than 10 h at 200 rpm. However, the desorption rate is only 0.89×10^{-2} wt%/s which is still less than the value obtained by Oelerich *et al.* [5].

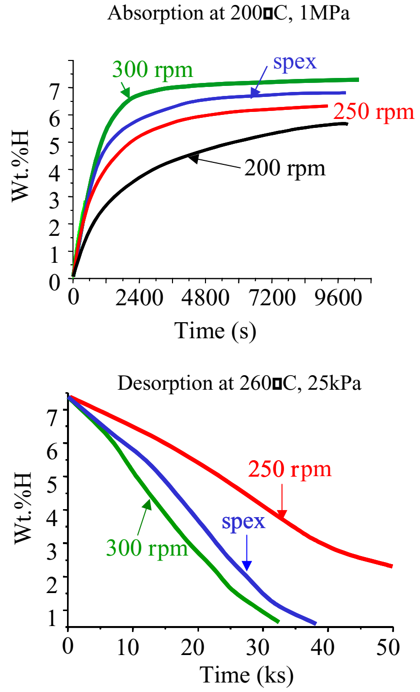

Figure 3 Influence of ball milling conditions (vibratory miller and planetary miller at various rotation speeds) on the sorption properties of Mg + 5%Cr_2O_3 mixtures.

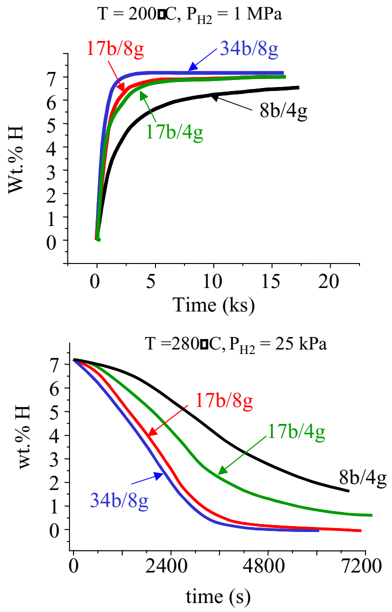

Figure 4 Influence of ball milling preparation (number of ball and powder weight) on the sorption properties of Mg + 5%Cr_2O_3 mixtures.

To increase the injected power of milling, it is also possible to increase the number of ball and then to modify the ball to powder weight ratio. For that purpose, we elaborated Mg + 5 wt% Cr_2O_3 mixtures in 4 different conditions: (i) 17 balls and 8 g of powder (the previous conditions), (ii) 17 balls and 4 g of powder, (iii) 8 balls and 3.8 g of powder and (iv) 34 balls and 8 g of powder. The sorption properties obtained for this mixtures are presented in Fig. 4. As previously mentioned the sorption properties can be directly correlated to both the grain and crystallite size. On Fig. 4, it appears that the use of 34 balls leads to the best sorption properties. It confirms that the increase of the injected power leads to an improvement of the sorption properties. Using

TABLE I Desorption rates of several samples

Sample	Pure Mg 200 rpm, 8 h*	Mg + 5%Cr_2O_3 200 rpm, 8 h*	Mg + 5%Cr_2O_3 300 rpm, 8 h*	Mg + 5%Cr_2O_3 300 rpm, 10 h, 34 balls	nano Mg 120 h [5]	Mg + 1%Cr_2O_3 120 h [5]
Desorption rate at 300°C (10^{-2} wt%/s)	0.05	0.59	0.89	1.32	0.4	1.52

*= this study and Ref [5].

17 balls and 8 g of powder or 17 balls and 4 g of powder lead to the almost the same sorption properties. In both case the injected power is the same and then the ratio injected power/powder weight is twice for the second experiment (i.e., 17 ball/4 g) and then, it could be expected that the sorption properties of this experiment would be improved. However, it should be consider that if the weight powder is too low, the probability of presence of powder during a ball/ball or ball/vial shock is low which decreases the efficiency of milling. From this first step analysis, the sample (8 g) milled 10 h with 34 balls at 300 rpm exhibits the better sorption properties.

4. Conclusion

By reactive mechanical alloying a mixture of Mg + 10 wt%WO_3 powders at room temperature, the hydrogen sorption properties of Mg were greatly enhanced. The samples were hydrided and dehydrided without activation, presented good capacity and showed no deterioration after 15 cycles. Also, an important improvement in absorption and desorption rates was observed. The formation of a tungsten bronze in the mixture was discarded as the origin of the effect of improving the sorption properties. However, the structural change of WO_3 during milling could act as a catalyst of hydrogenation

In the case of Mg + 5 wt%Cr_2O_3, it is reported that higher rotation speed of milling or vibratory milling allows to improve the sorption properties. It confirms that the formation of defects is of prime importance to explain the catalyst effects of oxides. The analysis of grain and crystallite size allows to predict the hydrogen sorption properties. Finally, modifying the milling conditions (changing the ball to powder weight ratio) also permits to change the sorption characteristics. The sorption rates obtained are then comparable to the other published as it can be seen in Table I.

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