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Hydriding/dehydriding properties of magnesium–$ZrCr_2$ composites

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Abstract

Composites of Mg and the intermetallic compound (IMC) $ZrCr_2$ have been prepared by mechanical alloying. The crystallographic structure, composition and morphology of the composites were analysed by means of X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX). XRD patterns show that no alloy formation takes place during milling. EDX data show that milling time is a key parameter to control the morphology of the composites. Short milling times of 10 min give composites with the IMC attached to the Mg particle surface, while it is irregularly distributed in the Mg bulk for longer milling times of 70 min. Hydriding/dehydriding properties of the composites were studied by the solid–gas reaction method. Composites with a distribution of the IMC in the Mg bulk are easily activated and show faster hydriding/dehydriding kinetics than untreated Mg, which indicates that $ZrCr_2$ acts as a catalytic compound for the Mg–hydrogen reaction.

Keywords: Hydrogen storage materials; Metals; Gas–solid reactions; Mechanical alloying

1. Introduction

Metal hydride systems are becoming very popular at the moment, not only because of the well known Ni–metal hydride batteries but also for their future use in fuel cells. A very attractive material for such applications is magnesium hydride (MgH_2) due to its low weight, abundance and low price. Mg can store up to 7.6 wt% of hydrogen, a value which compares very favourably to other hydrogen storage metal compounds (for example $LaNi_5H_{6.7}$, 1.5 wt%). However, the use of MgH_2 in practical applications requires two major problems to be overcome: the high stability of the hydride (the equilibrium pressure at 560 K is 0.1 MPa) and its poor kinetics for hydrogen absorption/desorption [1]. As a consequence, a lot of work is being done to improve the thermodynamic and kinetic properties of Mg. Alloying of Mg with other elements [2], modifications of its morphology [3], formation of composites [4] or preparation of thin films [5], have been tried to improve the hydrogenation characteristics of Mg.

In this work, experimental results concerned with an attempt to improve the kinetics properties of Mg are presented. Mg–$ZrCr_2$ composites with different morphologies have been prepared by the mechanical alloying technique. Their behaviour against hydrogen absorption/desorption has been investigated.

2. Experimental

The studied materials were composites formed by magnesium (99.8% purity and particle size in the millimetre range) as base material plus an intermetallic compound of the type AB_2 as additive, specifically, $ZrCr_2$ (particle size ~20 μm). The additive was synthesised by melting the pure elements several times in an arc furnace. An additional annealing treatment ($t=5$ h, $T=1400$ K) was applied to homogenise the compound.

About 10 g of the base material and the additive (10:1 weight ratio) were treated in a planetary type ball mill (Fritsch 'Pulverisette 6') with stainless steal mill balls (total mass of 34 g). Milling was carried out in an argon atmosphere at an acceleration of 140 m s^{-2}. A sequence of 1-min work–4-min rest was followed during the milling time. Two total milling times of 10 and 70 min were used.

The morphological, structural and compositional characterisation of the composites was carried out before and after their hydrogenation by means of X-ray diffraction,

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scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). The diffraction patterns were obtained with Cu Kα radiation in a $\theta-2\theta$ Siemens D-500 powder diffractometer. Quantitative analysis of the X-ray diffraction pattern was carried out with the Fullprof software [6]. The SEM images were obtained by using a Phillips XL30 equipped with an EDX analyser.

A mass of ~0.25 g of the composites was placed in a Sieverts type apparatus to study their hydrogenation/dehydrogenation properties. For comparison purposes, untreated Mg powder, with an initial particle size in the range of 45 μm, was also studied. Hydriding/dehydriding of the samples was measured from the pressure drop/increase in a calibrated volume. Sample temperature was accurately measured with a thermocouple in direct contact with it.

3. Results and discussion

3.1. Morphology, composition and structure of the composites

A visual inspection of the composites after their preparation shows, qualitatively, some general aspects of the effect of the mechanical treatment. In the first place, the particles experience plastic deformation resulting in a flake-like shape, with one dimension much smaller than the other two. In addition, because of continuous fracture and cold welding of the particles, their size distribution becomes broader. This effect is specially important for the longer investigated milling time of 70 min, where a good fraction of the initial Mg particles are stuck to the container walls.

The incorporation of the additive to the Mg particles has been investigated by means of SEM and EDX analysis. Fig. 1a–d shows the X-ray mapping (Fig. 1a and c) and corresponding back-scattered electron (BSE) images (Fig. 1b and d) of cross-sectional views of mechanically polished composites. Fig. 1a and b corresponds to a composite milled for 70 min while Fig. 1c and d corresponds to a composite milled for 10 min. The X-ray maps are constructed by overlapping the X-ray (Kα lines) signals from Mg (light gray spots) and Zr and Cr (dark gray spots). Therefore, brighter areas in Fig. 1a and c correspond to Mg rich areas while darker ones correspond to IMC rich areas. The distribution of the X-ray signals correlates well with the BSE images of Fig. 1b and d, but in this case, Mg rich areas appear dark (low *Z* number), while IMC rich areas appear bright. The important conclusion obtained is that two very different composite morphologies are obtained depending on the milling times. At short milling time of 10 min (Fig. 1c and d), the IMC is mainly attached to the near surface region of the Mg particles. On the other hand, for longer milling times of 70 min, the additive is irregularly distributed in the Mg bulk.

The crystallographic structure of the composites was

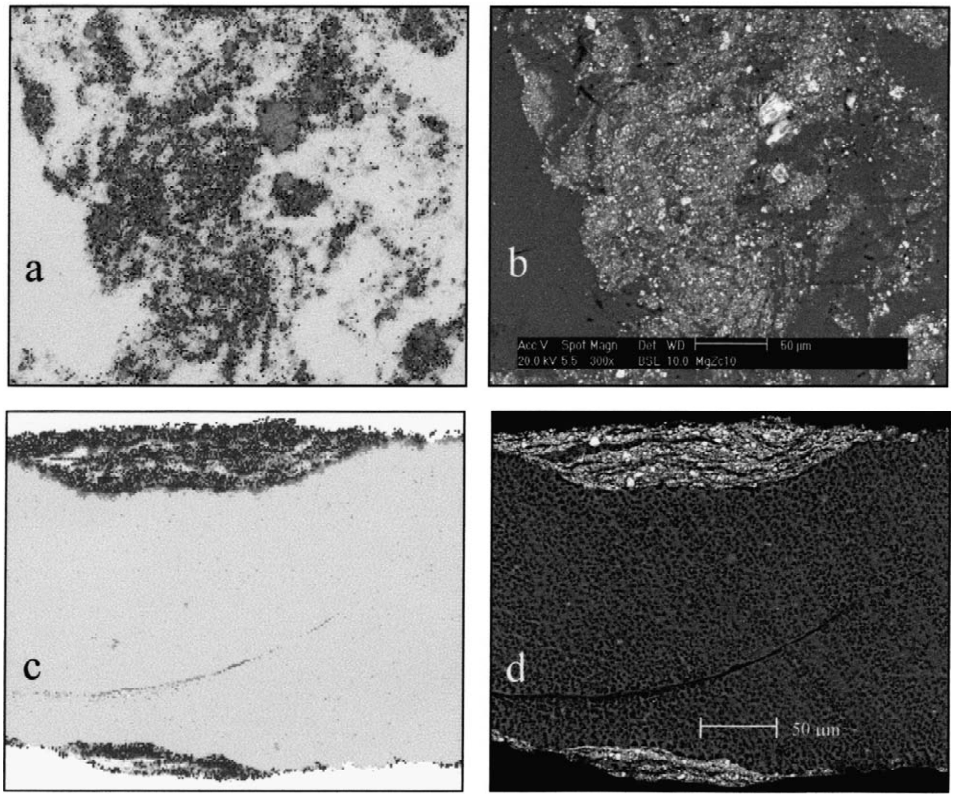

Fig. 1. X-ray map (a,c) and corresponding BSE images (b, d) for composites milled for 70 min (a, b) and 10 min (c, d).

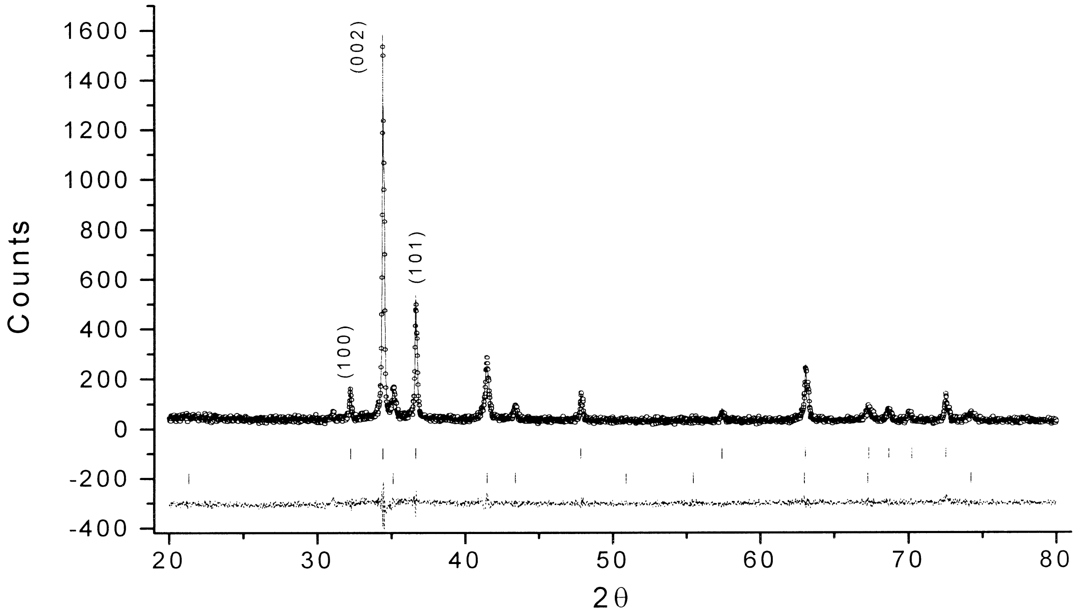

Fig. 2. X-ray diffraction pattern of the Mg–10wt%$ZrCr_2$ composite. Open circles stand for the experimental data. The solid line is the fitting curve obtained with Fullprof. Short vertical lines indicate the position of the Bragg's reflections for each phase (Mg: upper, $ZrCr_2$: lower). The difference curve between experimental and calculated patterns can be seen at the bottom of the figure.

investigated by X-ray diffraction. Fig. 2 shows a representative example of the XRD obtained patterns. It corresponds to a composite milled for 70 min. Fitting was accomplished with two crystallographic phases, hexagonal Mg ($P6_3/mmc$, $a=3.2100(4)$ Å, $c=5.2117(4)$ Å, 96.7 wt%) and cubic $ZrCr_2$ ($Fd\bar{3}m$, $a=7.2280(7)$ Å, 3.3 wt%). After including preferential orientation along the (001) direction for the Mg phase, very good agreement between the experimental data and the calculated pattern is obtained as can be seen from the difference curve (bottom of Fig. 2) and the agreement factors ($R_p=12.3$; $R_{wp}=15.7$; $R_e=13.7$; $\chi^2=1.31$). These factors correspond to points with Bragg reflection contribution and without background subtraction.

Some characteristics of the composites can be derived from the X-ray diffraction analysis. The lattice parameter of the Mg phase corresponds to that of untreated Mg although the sample exhibits a high degree of preferential orientation, with a plate-like habit, along the (001) direction, as can be qualitatively seen from the intensity relations between the first three diffraction peaks of the Mg phase. Randomly oriented Mg powder exhibits relative peak intensities of 25, 36 and 100 for (100), (002) and (101) reflections [7], respectively. This effect is also observed in the samples milled for 10 min. Preferential orientation along the (001) direction has been also noticed previously in the case of ball milled hexagonal titanium [8], which seems to suggest a general trend for the plastic deformation of hexagonal closed packed materials. The $ZrCr_2$ phase abundance obtained from the XRD measurements, 3.3 wt%, is smaller than the nominal value, 10 wt%, introduced into the mill container. Taking into account the irregular distribution of the additive in the Mg and the finite depth penetration of X-rays in the material, the former value should be considered as a lower limit for the amount of $ZrCr_2$ incorporated into Mg. Finally, another important conclusion from the XRD results is that no alloy formation takes place during milling.

3.2. Hydriding/dehydriding characteristics of the composites

The hydriding/dehydriding characteristics of all prepared composites were studied and compared to that of untreated commercial Mg to establish the possible interest of the composites for hydrogen storage purposes. We concentrate here on the results obtained with the composite treated for a longer milling time. It shows the best hydrogen storage characteristics of all prepared composites.

In Fig. 3a and b, the reacted fraction for hydriding (Fig. 3a), and dehydriding (Fig. 3b), as a function of time is shown. In absorption experiments a reacted fraction value of 1 means that the whole sample transforms to MgH_2, while for dehydriding it means that the hydride transforms back to Mg metal. The temperature of the experiments was 606 K and the initial hydrogen pressure for hydriding/dehydriding was 0.92 MPa and 100 Pa, respectively. At this temperature, the hydride equilibrium pressure is ~0.4 MPa [9], so that hydriding and dehydriding reactions involve the transformation between the solid solution and the hydride phases.

A first interesting difference between the composite and the untreated Mg concerns their activation behaviour. For

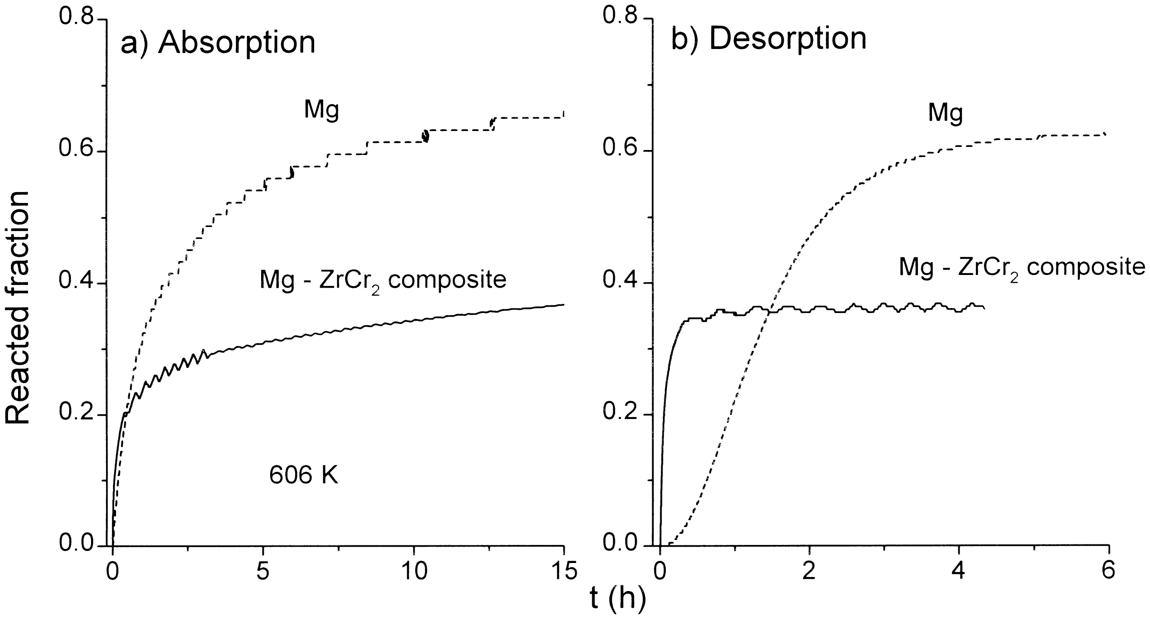

Fig. 3. Hydriding (a) and dehydriding (b) reactions at 606 K of Mg–ZrCr$_2$ composite, solid line, and Mg, dashed line.

the untreated Mg sample, the curves shown in Fig. 3a and b correspond to the fourth absorption/desorption cycle, the previous ones being much slower. On the other hand, the curves for the composite correspond to the first time the sample was exposed to hydrogen. The next absorption/desorption cycles reproduced the results of this first cycle. Therefore, activation for hydrogen absorption of the composite is easier than that of untreated Mg.

We note from Fig. 3a that the shape of the absorption curves for both samples are similar and they look like exponential growth curves, slightly faster at the beginning for the composite. On the other hand, the desorption curves for both samples look quite different, both in shape and rate constant. The desorption curve of the untreated Mg corresponds to a typical nucleation and growth process [10], while it looks like an exponential growth curve for the composite. The dehydriding of the composite is completed in less than half an hour, while for the untreated Mg it takes more than 4 h. We note, also, that only a modest fraction of the whole composite, ~0.3, takes part in the hydriding/dehydriding process, compared to the 0.6 value reached by the untreated Mg in a similar time. This could be related to the larger size of the composite particles (~200 μm) compared with those of Mg (~45 μm), which means longer diffusion paths for hydrogen.

The influence of temperature on the hydriding/dehydriding of the composite can be seen in Fig. 4a and b, respectively. Hydriding curves were obtained at temperatures from 411 to 607 K, while dehydriding curves were obtained from 539 to 606 K. The shape of the curves are similar to those in Fig. 3a and b. They show smaller reaction rates when the temperature is decreased. Partial hydrogenation of the composites occurs at temperatures as low as 411 K, where the hydrogenation of untreated Mg proceeds very slowly. As a practical conclusion, the reacted fraction at a given time, let us say 5 h, changes drastically with temperature from 0.3 at 606 K to 0.1 at 411 K. At temperatures of ~530 K, the composite absorbs hydrogen up to a reacted fraction of 0.2 (1.5 wt% of hydrogen) in less than 1 h and desorbs it in 30 min.

The low equilibrium H-pressure of the composite at temperatures below 540 K makes it very difficult to obtain desorption data by the volumetric method. On the other hand, it is possible to obtain such information from the thermal desorption technique (TDS). The inset in Fig. 4b shows the TDS spectrum of a hydrogenated composite linearly heated at 5 K min^{-1} in vacuum from RT to 650 K. The desorption rate is maximum at 525 K and is still certainly noticeable at temperatures as low as 450 K. For similar heating rates, untreated Mg starts to release hydrogen at a temperature of ~630 K, being its maximum desorption rate at a temperature of 680 K [11].

4. Conclusions

Mg–ZrCr$_2$ composites were prepared by mechanical alloying. The milling time is a key parameter to produce composites with different morphologies. At short milling times, the IMC is mainly attached to the near surface region of Mg particles, while by increasing the milling time, an irregular distribution of the IMC in the Mg bulk is produced. From XRD analysis we have concluded that no alloy formation takes place during milling.

Composites with an irregular distribution of the IMC in the Mg bulk show improved hydriding/dehydriding

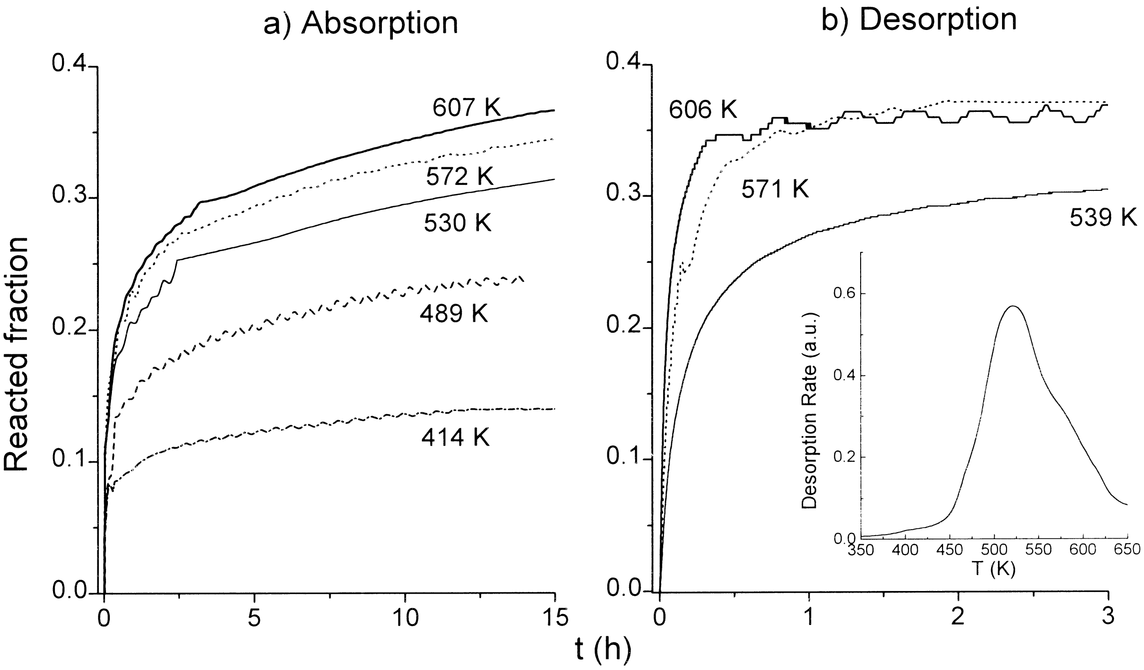

Fig. 4. Hydriding (a) and dehydriding (b) reactions of Mg–$ZrCr_2$ composite at different temperatures. The inset in (b) is the TDS spectra of the composite linearly heated at 5 K min^{-1}.

characteristics compared to untreated Mg. They do not need any activation treatment and their hydriding/dehydriding processes are faster than those of untreated Mg. At temperatures of ~530 K, the composites absorb hydrogen up to 1.5 wt% in less than 1 h and desorb it in 30 min.

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