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# Processing by controlled mechanical milling of nanocomposite powders Mg + X (X = Co, Cr, Mo, V, Y, Zr) and their hydrogenation properties

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## Abstract

Controlled mechanical milling under high-energy impact (impact 2) mode in the magneto-mill Uni-Ball-Mill 5 was applied for processing of nanocomposite powders Mg + X (X = Co, Cr, Mo, V, Y, Zr) in order to develop novel nanoscale Mg-based materials with improved hydrogen storage properties through nanostructurization and possible catalytic effect of additive metal. No mechanical alloying has occurred between Mg and the catalytic metals after milling for 20 h. Catalytic metals such as Co, Cr, V, Y and Zr improve the absorption kinetics very substantially. Only the nanocomposite Mg/Mo has the hydrogenation kinetics much worse than that of a single-phase Mg. No correlation between the crystallite (nanograin) size of catalytic metals and the hydrogen absorption kinetics is observed.

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**Keywords:** Controlled mechanical milling; Nanocomposite materials; Hydrogen sorption

## 1. Introduction

Commercializing fuel cell vehicles requires a viable solution to the major bottleneck which is hydrogen storage [1,2]. The most effective for such mobile applications is the method of solid state hydrogen storage where hydrogen is stored in the form of metal, intermetallic and/or non-metallic hydrides [1,2]. Magnesium has long been considered as a potential material for solid state hydrogen storage in the form of magnesium hydride (MgH<sub>2</sub>). Mg is abundant, inexpensive and the theoretical hydrogen storage capacity of MgH<sub>2</sub> is ~7.6 wt.% [2–5] which is quite adequate for commercial applications as a hydrogen fuel source [4–6]. However, the slow sorption/desorption kinetics and high dissociation temperature of MgH<sub>2</sub> limit its practical application. Therefore, a research effort has been underway in the last 10 years to develop novel nanoscale Mg-based materials with improved hydrogen storage properties [7,8]. As pointed out by Bobet et al. [8] the hydrogen diffusion is controlled by the number of crystal-

lites (nanograins) per powder particle of hydrogen absorbing material. In turn, application of mechanical (ball) milling reduces substantially crystallite (nanograin) size and increases the number of nanograins in the average powder particle. In addition, various catalysts can be added to improve the sorption/desorption kinetics [8,9].

In this paper we report the application of controlled mechanical milling in a unique magneto-mill to produce nanocomposites of Mg and various additive metals which would possibly provide catalytic effect with the objective of achieving a high dispersion of nanocrystalline catalytic metal in the nanocrystalline magnesium matrix and resulting improvement of hydrogen storage properties. The results of microstructural analysis and studies on the hydrogenation properties of these nanocomposites will be presented and discussed.

## 2. Experimental

Pure elemental powders of Mg (325 mesh), Zr (625 mesh), V (400 mesh), Cr (50 mesh), Mo (1250 mesh), Y (40 mesh)

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and Co (1250 mesh) were used as starting materials. The elemental powders were weighed under a high purity argon flux to obtain Mg-based mixtures containing 10 wt.% of each catalyst metal. The ball milling of Mg/metal mixtures with the initial ball-to-powder mass ratio of 10:1 was performed in an argon atmosphere under controlled high-energy impact mode (impact 2) in the magneto-mill Uni-Ball-Mill 5 (A.O.C. Scientific Engineering, Australia) for 20 h. The samples were handled in a glove box under argon and the vials were sealed under the same atmosphere. The microstructure was analyzed by X-ray diffraction (XRD) with Seifert C3000 and Philips PW1830 diffractometers using Cu  $K\alpha$  radiation at operating parameters of 30 mA, 50 kV and step size  $0.02^\circ$  per 3 s. The nanograin (crystallite) size and lattice strain of phases residing in the milled powders were estimated from the broadening of their respective XRD peaks by the linear regression plot of Cauchy/Gaussian approximation [10,11]. The morphology and chemical composition of powders were investigated

by SEM using a Philips XL30 (LaB<sub>6</sub>) equipped with an automatic image analyzer, backscatter electron detector (BSE) and energy dispersive X-ray spectroscopy system (EDAX). The hydriding properties of the milled nanocomposite powders were evaluated by volumetric method using an automated Sieverts apparatus at 573 K under 1.0 MPa hydrogen pressure. All powder handlings during hydriding experiments were performed in air. An activation procedure was applied to all samples before conducting the sorption kinetics experiments. This procedure consisted of three cycles of hydrogen absorption and desorption at 623 K and a hydrogen pressure of 1.0 MPa for absorption and 0.1 MPa for desorption.

### 3. Results and discussion

Fig. 1 shows the microstructure on the cross-section of nanocomposite powders after controlled ball milling for 20 h.

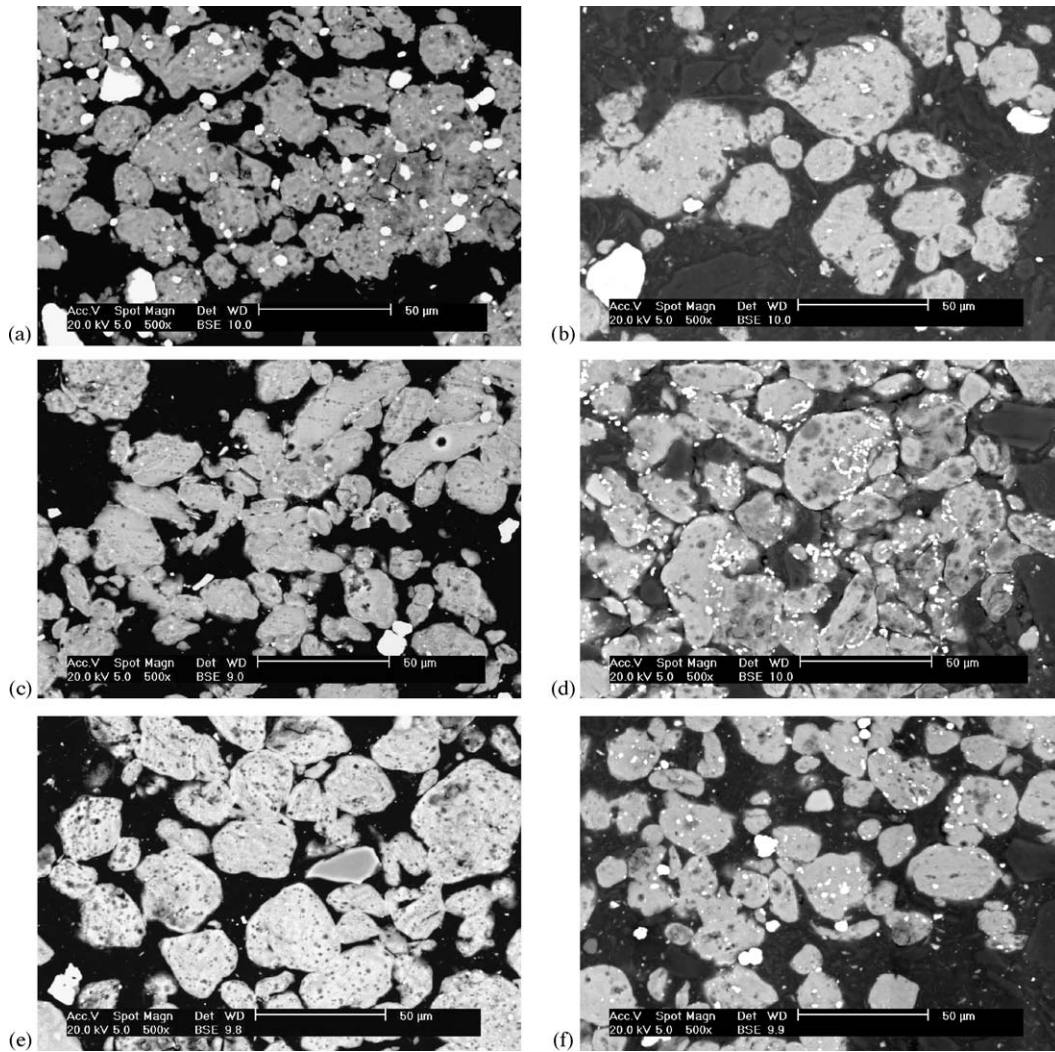


Fig. 1. Backscattered electron (BSE) micrographs of the cross-section of Mg + 10 wt.% X (where X = Zr, V, Y, Co, Cr, Mo) nanocomposite particles processed by milling for 20 h in the magneto-mill Uni-Ball-Mill 5 under high-energy impact (impact 2) mode: (a) Mg + 10 wt.% Zr; (b) Mg + 10 wt.% V; (c) Mg + 10 wt.% Y; (d) Mg + 10 wt.% Co; (e) Mg + 10 wt.% Cr and (f) Mg + 10 wt.% Mo.

Table 1

Regression grain size and lattice strain of the nanocrystalline magnesium and catalyst metal in Mg + 10 wt.%X (where X = Zr, V, Y, Co, Cr, Mo) nanocomposites

Nanocomposite	Mg-matrix				Catalyst metal			
	Grain size (nm)	Strain ( $\times 10^{-6}$ )	$R^2$	No. of peaks	Grain size (nm)	Strain	$R^2$	No. of peaks
Mg	44	6	0.973	9	–	–	–	–
Mg + 10 wt.% Mo	64	3	0.946	4	44	$7 \times 10^{-6}$	0.994	4
Mg + 10 wt.% Co	40	9	0.932	9	18	$4 \times 10^{-5}$	0.997	3
Mg + 10 wt.% Cr	102	1	0.992	4	25	$2 \times 10^{-5}$	0.939	3
Mg + 10 wt.% Y	45	4	0.964	6	4	$6 \times 10^{-4}$	0.987	5
Mg + 10 wt.% Zr	62	4	0.979	10	70	$9 \times 10^{-7}$	0.947	8
Mg + 10 wt.% V	62	5	0.939	6	19	$4 \times 10^{-5}$	0.999	3

The average Mg powder particle size is within the 20–30  $\mu\text{m}$  range. Light specks visible within the Mg particles correspond to the particles of catalytic metal which seem to be quite substantially refined to the submicrometer size. The highest dispersion and homogeneity of catalytic metal particles is observed for Co (Fig. 1d). The XRD analysis of milled powders (not shown here) revealed that no mechanical alloying occurred and only the diffraction peaks from the metallic phases could be detected. Only a minimal amount of MgO was detected in all powders.

Table 1 shows the nanograin (crystallite) size of the Mg matrix and catalyst metal in the nanocomposite Mg + 10 wt.%X estimated from the broadening of their respective XRD peaks [10,11]. It can be seen that Mg has relatively large nanograin size on the order of a few tens of nanometers. The nanograin size of catalytic metals seems to be more refined than that of Mg. For instance, the nanograin (crystallite) size of Y is refined down to barely  $\sim 4$  nm and the crystallite size of Co, V and Cr is 18, 19 and 25 nm, respectively. Only the nanograin size of Mo and Zr is large being equal to 44 and 70 nm, respectively, which is comparable to that of Mg. Lattice strains are negligible for both Mg and the catalytic metals.

XRD analysis revealed that after hydrogenation the major hydride phase formed was  $\text{MgH}_2$  in almost all powders except Mg/V in which a small amount of  $\text{VH}_2$  hydride was also detected. A few powder samples of each composition Mg + 10 wt.% X were investigated for the hydrogen absorption kinetics in a Sieverts apparatus. It has been confirmed that the absorption curves for the samples of the same composition Mg + 10 wt.% X do not differ in any practical way from one another. Fig. 2 shows selected examples of the absorption curves which illustrate the rate of absorption kinetics for the processed nanocomposites as compared to a single-phase Mg sample taken as a reference. It is obvious that only one nanocomposite containing Mo has the kinetics much worse than that of Mg. All the other catalytic metals improve the absorption kinetics very substantially. In the beginning up to  $\sim 900$  s the fastest kinetics is exhibited by Mg/Co nanocomposite. However, for longer absorption times Mg/Y, Mg/V and Mg/Zr show better kinetics and larger final hydrogen storage capacity.

However, it must be pointed out that for all the catalytic mixtures investigated in the present work, the absorption ki-

netics in Fig. 2 is definitely slower than that reported by Zaluska et al. [12] for the ball-milled Mg + X mixtures. They reported that at 300 °C the Mg + 8 wt.%V mixture reached the hydrogen capacity of  $\sim 6$  wt.% after  $\sim 960$  s. Even more effective was the addition of 5 wt.% Zr which resulted in the hydrogen capacity of  $\sim 6$  wt.% achieved after only 480 s exposure at lower temperature of 280 °C. In contrast, as observed in Fig. 2 during hydrogen absorption at 300 °C the Mg + 10 wt.% V and Mg + 10 wt.% Zr mixtures reach  $\sim 5$  wt.% after  $\sim 4000$  s which is much longer absorption time than that reported by Zaluska et al. [12]. Since Zaluska et al. did not report any details of microstructural analysis of ball milled powders it is impossible to comment on the origin of the differences in the kinetics of hydrogen absorption between their and the present work.

Rather surprisingly, if one compares the nanograin size of the catalytic metals from Table 1 with their effect on the acceleration of absorption kinetics, there is no clear correlation between them. Y has the finest nanograin size of  $\sim 4$  nm and indeed, Mg/Y has rapid kinetics and the largest maximum hydrogen capacity. However, the other two nanocomposites Mg/V and Mg/Zr exhibit almost identical maximum capacities which are very close to that of Mg/Y but the corre-

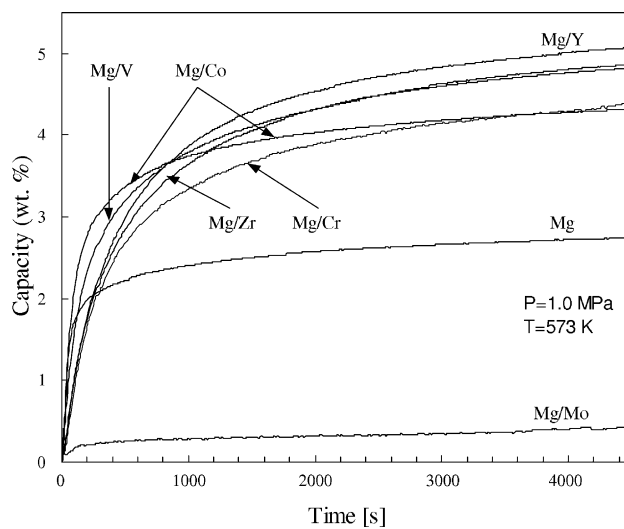


Fig. 2. Rate of hydrogen absorption by nanocrystalline magnesium and Mg + 10 wt.% X (where X = Zr, V, Y, Co, Cr, Mo) nanocomposites at 573 K under 1.0 MPa hydrogen pressure.

sponding nanograin size of V and Zr is 19 and 70 nm, respectively. Apparently, the nanograin size of the catalytic metal does not seem to be a primary factor governing the hydrogen absorption kinetics and maximum capacity. Most likely, the chemical nature of the catalytic metal is more important.

#### 4. Conclusions

More important conclusions are listed below.

1. After controlled mechanical milling for 20 h no mechanical alloying has occurred between Mg and the catalytic metals.
2. The average powder particle size of the Mg + X mixture is approximately within the 20–30  $\mu\text{m}$  range after controlled mechanical milling for 20 h.
3. The crystallite (nanograin) size of Mg phase remains within the 40–60 nm range for almost all powder mixtures except the Mg + 10 wt.% Cr mixture in which the Mg crystallite size is on the order of  $\sim 100$  nm.
4. The highest dispersion and homogeneity of the catalytic metal particles is observed for Co.
5. The most extensive nanograin (crystallite) refinement of  $\sim 4$  nm is observed for Y. The crystallite size of Co, V and Cr is 18, 19 and 25 nm, respectively, and that of Mo and Zr is 44 and 70 nm, respectively.
6. The major hydride phase formed during hydrogen absorption in almost all powders is  $\text{MgH}_2$  except the Mg/V nanocomposite in which a small amount of  $\text{VH}_2$  hydride is also detected.
7. Only one nanocomposite Mg/Mo has the hydrogen absorption kinetics much worse than that of a single-phase Mg. All the other catalytic metals improve the absorption kinetics very substantially.
8. There is correlation between the nanograin size of catalytic metals and the acceleration of absorption kinetics.

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#### References

- [1] J.A. Ritter, A.D. Ebner, J. Wang, R. Zidan, *Mater. Today* (September 2003) 18–23.
- [2] A. Züttel, *Mater. Today* (September 2003) 24–33.
- [3] A. Züttel, P. Wenger, S. Rentsch, P. Sudan, Ph. Mauron, Ch. Emmenegger, *J. Power Sources* 118 (2003) 1–7.
- [4] L. Schlapbach, A. Züttel, *Nature* 414 (2001) 353–358.
- [5] L. Schlapbach, *MRS Bull.* 27 (2002) 675–676.
- [6] R. Schulz, J. Huot, G. Liang, S. Boily, G. Lalande, M.C. Denis, J.P. Dodelet, *Mater. Sci. Eng. A* 267 (1999) 240–245.
- [7] A. Zaluska, L. Zaluski, J.O. Ström-Olsen, *Appl. Phys.*, a 72 (2001) 157–165.
- [8] J.-L. Bobet, B. Chevalier, M.Y. Song, B. Darriet, J. Etourneau, *J. Alloys Compd.* 336 (2002) 292–296.
- [9] G. Liang, J. Huot, S. Boily, A. Van Neste, R. Schulz, *J. Alloys Compd.* 292 (1999) 247–252.
- [10] R.A. Varin, T. Czujko, J. Mizera, *J. Alloys Compd.* 354 (2003) 281–295.
- [11] R.A. Varin, S. Li, A. Calka, D. Wexler, *J. Alloys Compd.* 373 (2004) 270–286.
- [12] A. Zaluska, L. Zaluski, J.O. Ström-Olsen, *J. Alloys Compd.* 288 (1999) 217–225.