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Effect of nanosized oxides on MgH_2 (de)hydriding kinetics

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Abstract

The kinetics of hydrogen absorption and desorption (H-sorption) in magnesium have been improved by mechanically milling magnesium hydride (MgH_2) with metal oxides (M_xO_y). Here, we investigate the effect of initial particle size of the oxides on the H-sorption properties of magnesium. As mechanical milling is regarded as an efficient method to break and disperse catalytic particles of M_xO_y, nanosized M_xO_y should allow shorter milling times and improved hydrogen kinetics (H-kinetics) compared to microsized M_xO_y. Our results show that the fastest kinetics can mostly be achieved, independent of initial particle size of the oxides. In some cases, milling time can be shortened to achieve this, while in other cases, nanosized M_xO_y does not lead to the expected improvement of magnesium H-sorption properties. The results are rationalised in a new frame considering M_xO_y as process controlling agent helping to refine MgH_2 particle size during milling.

Keywords: Metal hydride; Mechanical alloying; Kinetic; DSC

1. Introduction

Several materials have been examined to store hydrogen and at present magnesium is the only one that is low cost and has a high storage capacity (7.6 wt.%). Nevertheless, practical application of magnesium for hydrogen storage is hindered by slow hydrogen kinetics and the high thermodynamic stability of its hydride [1]. It was found that H-sorption in magnesium could be improved by mechanically milling MgH_2 [2]. Further improvement was gained by milling MgH_2 with 3d transition metals (TM) or transition metal oxides (TMO) [3,4]. The TM or TMO used are believed to facilitate the dissociation/recombination of hydrogen on magnesium surface and therefore catalyse H-sorption in magnesium [5–7]. In this regard, mechanical milling is regarded as a method to break and homogeneously disperse particles of TM or TMO on magnesium surface [7]. Nevertheless, recent work indicates that non-TMO, such as MgO or Al_2O_3, can also be used to significantly improve magnesium H-sorption properties [8,9]. Beyond any potential catalytic effect, it appears that milling MgH_2 is a complex process during which M_xO_y also act as a refinement agent for MgH_2 powder and thus, facilitate the formation of nanoparticles of MgH_2 [8,10], which exhibit faster hydrogen sorption behaviour.

In this study, we investigate the influence of the initial particle size of the oxides on the reaction kinetics by using nanosized or microsized M_xO_y particles. In addition to TMOs, which are considered to have a catalytic effect on H-sorption in magnesium, microsized and nanosized non-TMO were also used, which are unable to catalyse H-sorption of magnesium. Thus, a separation of the catalytic and the particle refining effect should be achieved.

2. Experimental

MgH_2 powder (95% hydrided, 20–60 μm) was purchased from Goldschmidt AG. The metal oxides were purchased from Sigma–Aldrich. Their particle size is given Table 1. A Fritsch P5 planetary ball mill installed in a glove-box under Ar was used. MgH_2 was milled with 10 wt.% of metal oxides in ceramic vials with 100 g zirconium oxide balls (Ø 10 mm). The ball to powder weight ratio was 10:1.

Samples morphology was characterised by SEM with a Zeiss DSM 962 apparatus. Structural characterization of the samples was carried out with a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation. Calorimetric measurements were performed with a DSC 404 C Pegasus from Netzsch. The measurements were carried out under a flow of high purity Ar ($50\,mL\,min^{-1}$) with a heating rate of 5 K/min from 25 to 500 °C. Hydrogen titration measurements were made with a Sievert apparatus designed by HERA Hydrogen Storage Systems. The measurements were performed at 300 °C at 1 MPa of hydrogen for absorption and 0.1 kPa for desorption.

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Table 1
Particle size of the metal oxides

	MgO	Al_2O_3	SiO_2	Fe_2O_3	Cr_2O_3	TiO_2
Microsized (μm)	50	≤10	0.5–10	<5	50	<5
Nanosized (nm)	12	40	10	15	50	47

3. Results and discussion

3.1. Effect of nanosized transition metal oxide Cr_2O_3

Fig. 1a shows the evolution of pure MgH_2 decomposition temperature (T_d) with milling time. Before milling, the starting material MgH_2 exhibits a single endothermic peak at 414 °C corresponding to the release of hydrogen with an enthalpy of 2.34 ± 0.3 kJ/g, i.e. 61.6 ± 7.9 kJ/mol-H_2. After milling, two endothermic peaks with equivalent enthalpy energy are obtained [11,12]. Fig. 1b shows the evolution of T_d during milling, for MgH_2 milled with microsized Cr_2O_3 ($Cr_2O_3^{micro}$) and MgH_2 milled with nanosized Cr_2O_3 ($Cr_2O_3^{nano}$). Similar endothermic peaks to the one obtained for pure MgH_2 are observed. Milling MgH_2 with Cr_2O_3 allows a faster decrease of T_d than for pure MgH_2 (Fig. 1a and b). After 50 h of milling, pure MgH_2 decomposes at 344 °C whereas $Cr_2O_3^{micro}$ and $Cr_2O_3^{nano}$ decompose at 288 and 284 °C, respectively. Further improvement is gained by continuing the milling. After 200 h of milling, $Cr_2O_3^{micro}$ and $Cr_2O_3^{nano}$ decompose at 279 and 270 °C, respectively, and the onset is shifted from 250 to 200 °C. The enthalpy of decomposition remains constant (2.13 ± 0.3 kJ/g) for all milling times, and agrees with the value for pure MgH_2, if the additional 10 wt.% Cr_2O_3 is taken into account. Thus, Cr_2O_3 does neither affect MgH_2 thermodynamic properties, nor does any desorption take place during milling.

Fig. 2 presents the morphology of $Cr_2O_3^{micro}$ and $Cr_2O_3^{nano}$ after 200 h of milling. Besides nanosized particles of MgH_2, agglomerates and microsized particles can be observed. $Cr_2O_3^{micro}$ and $Cr_2O_3^{nano}$ have similar average particle sizes, 0.60 ± 0.40 and 0.55 ± 0.40 μm, respectively.

$Cr_2O_3^{micro}$ and $Cr_2O_3^{nano}$ also show similar XRD patterns, as shown Fig. 3. After 200 h of milling, Cr_2O_3 is still present and no reaction is observed during milling between Cr_2O_3 and MgH_2 [4]. Nevertheless, as expected, β-MgH_2 peaks are broadened upon milling and the metastable phase γ-MgH_2 is formed [11]. The crystallite size of β-MgH_2, as determined by the Rietveld-method, is the same for $Cr_2O_3^{micro}$ and $Cr_2O_3^{nano}$ (12 ± 2 nm).

The lower T_d obtained for $Cr_2O_3^{nano}$ by DSC characterisation, is confirmed by hydrogen titration measurements (Fig. 4). While $Cr_2O_3^{micro}$ desorbs in 600 s, $Cr_2O_3^{nano}$ desorbs

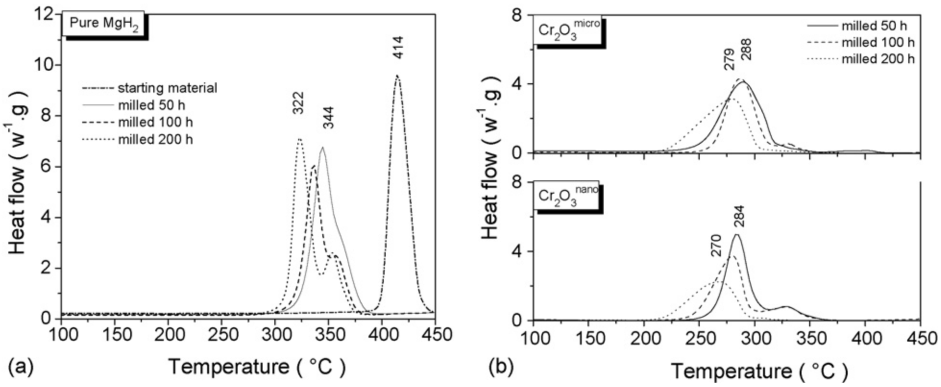

Fig. 1. (a) Evolution of MgH_2 decomposition with milling time. (b) Evolution of $Cr_2O_3^{micro}$ and $Cr_2O_3^{nano}$ decomposition with milling time. DSC measurements.

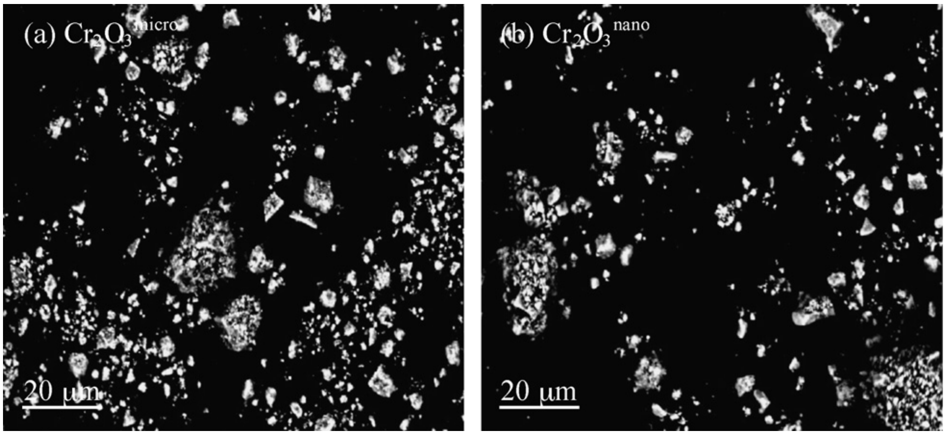

Fig. 2. SEM backscattered electron images of (a) $Cr_2O_3^{micro}$ and (b) $Cr_2O_3^{nano}$ after 200 h of milling.

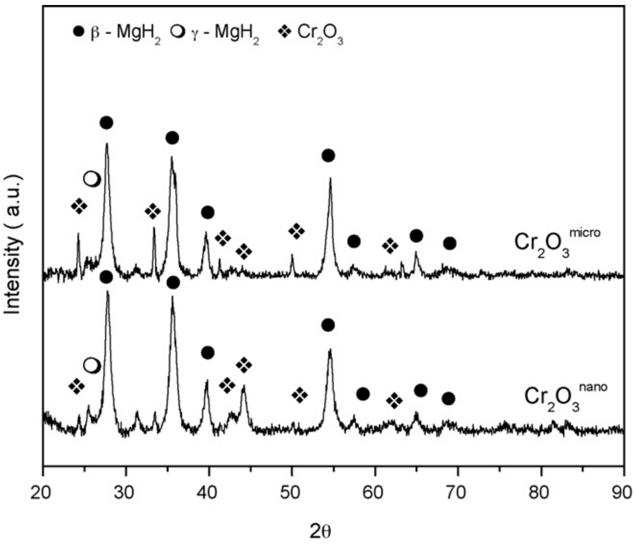

Fig. 3. XRD patterns of $Cr_2O_3^{micro}$ and $Cr_2O_3^{nano}$ after 200 h of milling.

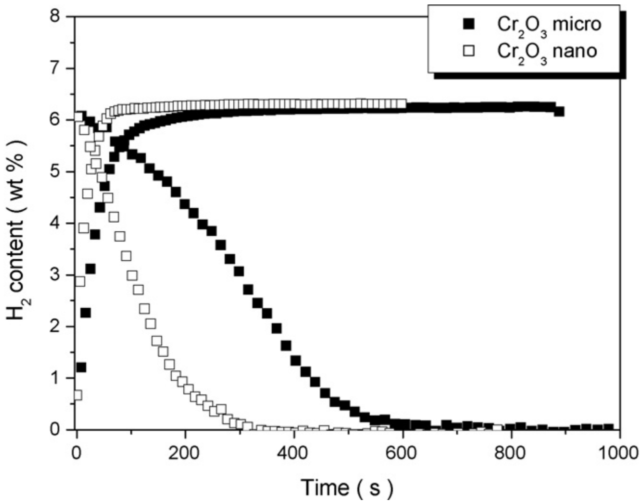

Fig. 4. Hydrogen kinetic curves of $Cr_2O_3^{micro}$ and $Cr_2O_3^{nano}$ after 200 h of milling.

in 300 s. Hydrogen absorption is also faster for $Cr_2O_3^{nano}$ than for $Cr_2O_3^{micro}$. Therefore, even if milling with nanosized Cr_2O_3 does not reduce milling time, faster H-kinetics is obtained.

3.2. Effect of nanosized non-transition metal oxide MgO

Fig. 5 presents the evolution of T_d for MgH_2 milled with microsized MgO (MgO^{micro}) and nanosized MgO (MgO^{nano}) with milling time. Once more, single or double endothermic peaks corresponding to the release of hydrogen are observed. The enthalpy of the reaction is equivalent to the one of pure MgH_2 decomposition, if the additional MgO is deduced [13]. For MgO^{micro}, a fast decrease of T_d from 414 to 262 °C is observed, while for MgO^{nano} T_d remains at 364 °C after 50 h of milling. T_d measured for MgO^{nano} is in fact higher than T_d obtained for pure MgH_2 milled 200 h (322 °C, Fig. 1b). Nevertheless, by continuing the milling for 500 h it is eventually possible to decrease T_d to 273 °C (Fig. 5a). Therefore, using nanosized MgO does not present any advantages compared to microsized MgO. This is reflected by hydrogen titration measurements (Fig. 5b). While MgO^{micro} desorbs in 150 s, it takes more than 3500 s to fully release hydrogen from MgO^{nano}. Hydrogen adsorption is also faster for MgO^{micro} compared to MgO^{nano}.

The morphological analysis by SEM of MgO^{micro} and MgO^{nano} reveals that smaller particles of MgH_2 are formed for MgO^{micro} than for MgO^{nano} (Fig. 6). MgO^{micro} and MgO^{nano} have average particle sizes of 0.44 ± 0.40 and 0.90 ± 0.60 μm, respectively. Apart from these nanoparticles, agglomerates are also observed.

MgO^{micro} and MgO^{nano} have similar crystalline structure after 200 h of milling (Fig. 7). Once again, milling results in a decrease of β-MgH_2 crystallite size to 12 ± 2 nm for both samples and formation of γ-MgH_2.

3.3. Comparison of different oxides

Some tendencies observed for Cr_2O_3 and MgO are representative for other oxides. Two groups can be distinguished: (a) transition metal oxides (TMO) with a potential catalytic effect on chemisorption and (b) non-TMO without any catalytic potential. As shown in Fig. 8, all investigated nanoparticle TMO yield fast magnesium H-sorption properties already after 50 h. In contrast, nanosized non-TMO SiO_2 and MgO do not facilitate a similar

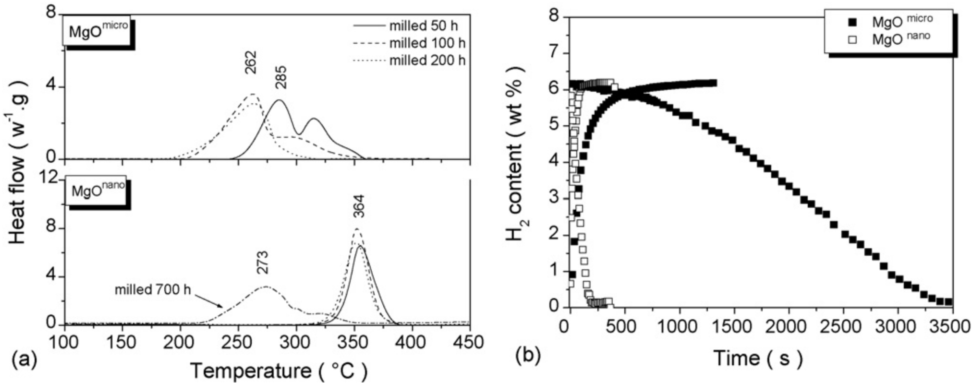

Fig. 5. (a) Evolution of MgO^{micro} and MgO^{nano} decomposition measured by DSC, with milling time. (b) Hydrogen kinetic curves of MgO^{micro} and MgO^{nano} after 200 h of milling.

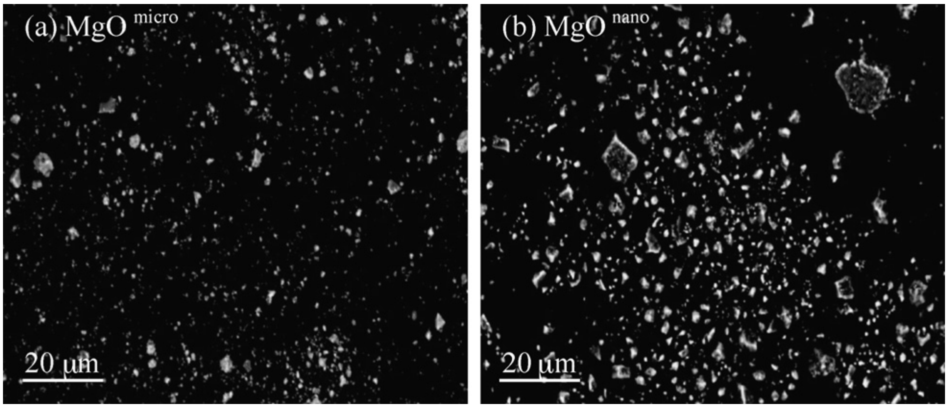

Fig. 6. SEM backscattered electron images of (a) MgO^{micro} and (b) MgO^{nano} after 200 h of milling.

improvement even after 200 h of milling, with the exception of Al_2O_3, which yields similar kinetics as the nanoparticle TMO. Using micro particle size oxides, sorption properties are generally improved with increasing milling time for all investigated oxides and similar kinetics are obtained after 200 h of milling. The resulting kinetic rates are comparable to the fastest rates or the lowest T_d of MgH_2 (∼270 °C at a heating rate of 5 K/min) as achieved in previous investigations, using various catalysts or extended milling time. The only exception is SiO_2, where even after 200 h, T_d still remains above 300 °C.

4. Discussion

There are different potential effects of oxide particles on the sorption behaviour of MgH_2. As previously reported, TMO may have a catalytic function due to a partial or total reduction of TMO to native metal during mechanical milling [4]. Nanoparticle oxides can be more easily distributed and lead to a high interface area with MgH_2 even after short milling times. In addition, only TMO with multiple valencies are expected to have a catalytic effect [4]. Therefore, catalysis cannot explain the improvement obtained using MgO, SiO_2, or Al_2O_3 in the present investigation.

Another effect may be the incorporation of particles into the microstructure of MgH_2, thus pinning grain boundaries and stabilizing the microstructure. Furthermore, these particulates may support nucleation processes during the phase transformations. However, if the microstructure dimensions are below a critical size, these processes are obviously not rate-limiting anymore. Therefore, within the grain size regime of the present study, the different coarsening behaviour with or without particles will not have any influence.

TMO reduction during milling with MgH_2 could also give rise to a catalytic native metal and MgO. Partially or totally reduced metal could have catalytic effects on H_2 absorption/desorption and MgO could also contribute in improving magnesium H-kinetics as observed above. Nevertheless, as shown by XRD nanosized TMO are not reduced during milling with MgH_2. Therefore, such hypothesis is not valid.

The results can be rationalised by considering the process of repeated agglomeration, cold welding and fracturing that is taking place during milling [14]. The oxide additions may change the milling behaviour of the powder blend, resulting in smaller particle sizes [8,13]. Smaller particles of magnesium will absorb

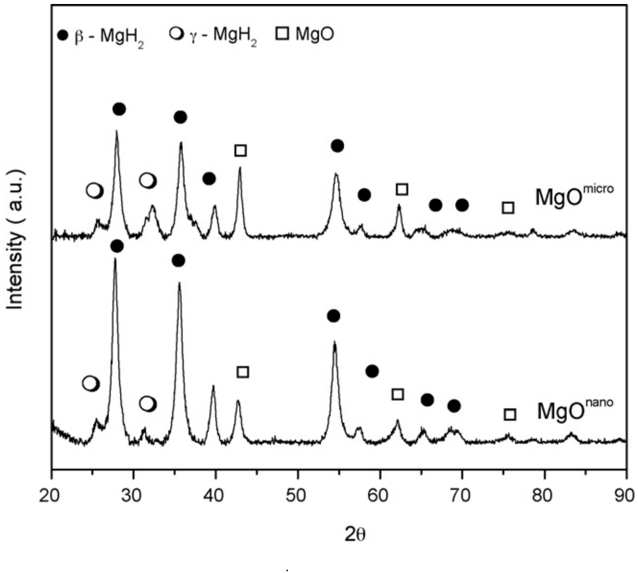

Fig. 7. XRD patterns of MgO^{micro} and MgO^{nano} after 200 h of milling.

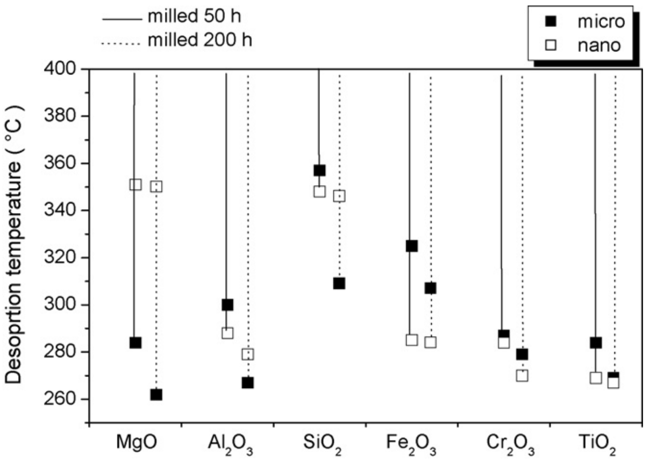

Fig. 8. Decomposition temperature obtained by DSC of MgH_2 milled 200 h with different metal oxides.

hydrogen faster because diffusion paths in the solid are shorter and chemisorption may be enhanced by the higher surface to volume ratio. Therefore, smaller particles are expected to show decomposition at a lower temperature as compared to larger particles.

Firstly, by embedding oxide particles into the matrix phase, the mechanical properties may be modified. The hardness and brittleness of MgH_2 will continuously increase with the fraction of embedded oxide particles, shifting the balance between fracturing and agglomeration to smaller particle sizes. However, this argument is not able to explain the superior effect of micro particles over nanoparticles in case of MgO or SiO_2, because it should be faster and easier to embed nanoparticles.

Secondly, the surface properties may be modified, leading to less agglomeration and smaller particle sizes as well. Oxides with a more ionic than covalent metal–oxygen bond such as TiO_2 or MgO compared to SiO_2, can easily build up charges on the surfaces upon milling and balance the surface forces generated by electrostatic charges on MgH_2 particles during milling. Oxides may thus prevent agglomeration and coldwelding of MgH_2 particles by stabilising MgH_2 nanoparticles through repulsive and/or attractive forces and consequently facilitate the reduction of MgH_2 particle size. Due to its more pronounced ionic character, a larger improvement of magnesium H-kinetics is expected and obtained if MgO is used than SiO_2. The use of oxide nanoparticles quickly dispersed on MgH_2 particle surface from the very start of the milling may result in a fast decrease of MgH_2 particle size and thus quick improvement of MgH_2 H-sorption properties. On the contrary, using microsized oxides, which have to be broken during milling to fully cover MgH_2 particles and compensate surface charges, will lead to longer milling time. The difference of MgH_2 particle size for MgO^{micro} compared to MgO^{nano} could explain the lower T_d and faster H-sorption kinetics obtained for MgO^{micro}. Concomitant with the reduction of MgH_2 particle size, oxide particles may be progressively embedded into the softer MgH_2 particles with increasing milling time. Thus, the positive effect of hindering agglomeration would cease continuously. It is expected that this effect is more pronounced for nanoparticles, which would explain the low efficiency of nano MgO and nano SiO_2. Finally, a steady state is reached, in which the fraction of particles embedded and particles active at the surface remains constant. Then, no further reduction of MgH_2 particle size is achieved.

Further investigations of the microstructural development aim at a better understanding of the phenomena occurring during milling of MgH_2 with oxides and focus on short milling times, when the oxide particles should still be on the surfaces rather than being embedded.

5. Conclusion

Aside any catalytic function, the improvements of magnesium H-kinetics with oxides addition could be explained in a new frame considering the ability of M_xO_y to help refining MgH_2 powder particle sizes during milling by modifying the surface properties. The delicate control of the surface forces generated on MgH_2 particles during milling may be a key parameter to stabilise MgH_2 nanoparticles and to prevent agglomeration and cold welding. Furthermore, adding nanosized TMO to MgH_2 does not allow the reduction of TMO during milling and therefore, the formation of catalytic native metal or MgO, which could explain the results obtained. The improvement of magnesium H-sorption properties by milling with oxide additions seems to be a complex process and further work is needed to clarify the role of the oxides.

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