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Effect of Tantalum Oxide Addition on Hydrogen Treatment of Magnesium Hydride Nano-Composite Produced by Mechanical Alloying

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1. Introduction

In recent years the Hydrogen was considered as fuel by many researchers and scientists. Given that solid mode storage of Hydrogen is the safest and the most productive mode, many projects have been defined in the field of improving Hydrogen properties of the metals with the most capacity of Hydrogen Storage. The compositions of materials contain Niobium were used in many researches and the desired results were presented in multiple articles. According to the similarities of Tantalum to Niobium in chemical and physical properties, and by considering that there are rare researches about the effect of compositions of Ta on Hydrogen properties of metals, the decision of studying effects of Tantalum Oxide on MgH_2 as base metal was made after reading many articles about the compositions of Tantalum. In this research, two compositions of Tantalum Oxide with Magnesium Hydride were prepared and the effect of additives and ball milling time as the preparation method on physical properties and also dehydrogenation properties, were evaluated and were compared with ball milled pure Magnesium Hydride.

2. Experimental

Two compositions of MgH_2-10%wt Ta_2O_5, MT1 samples; and MgH_2-20%wt Ta_2O_5, MT2 samples; were prepared by ball milling of Magnesium Hydride and tantalum oxide powders under Argon atmosphere for 3, 8 and 15 hours. As noted before for comparison, the pure Magnesium Hydride powders were ball milled at the same conditions.

Phase transformations of pure Magnesium Hydride and Composites Compounds were determined by X-Ray Diffraction equipment (XRD). Grain size (d) and Lattice Strain (ε) evaluated by Williamson-Hall equation:

$$\beta\ \mathrm{Cos}\,\theta = \frac{0.9\lambda}{d} + 2\mathrm{A}\varepsilon\,\mathrm{Sin}\,\theta$$

Where β is full width at half of maximum height of peak, λ is the wavelength of x-rays, θ is Bragg angle and A is constant value.

Transformation morphology of powder particles were studied by Field Emission Scanning Electron Microscope (FE-SEM). Average of powder particle size were evaluated by MIP Image Analyzer on Electron Microscope Images.

Finally, to define dehydrogenation temperature, the Differential Scanning Calorimetry Analysis (DSC) were used under pure Nitrogen atmosphere.

3. Results and Discussions

3.1. Pure Magnesium Hydride

By increasing the Ball Milling time the Beta-Magnesium Hydride phase peaks became Wider but the intensity of the peaks were decreased. The Gama- Magnesium Hydride that is a semi-stable kind of Beta phase, was created after 3 hours ball milling. By increasing the Ball Milling time the amount of Gama phase will be increased but many fewer than Beta phase. The Gama phase have effect on decreasing of dehydrogenation temperature but according to the insignificant amount of this phase, it is not the main reason for this temperature decreasing. Although the Argon atmosphere were used, but the MgO phase were created because of reactivity and sensitivity of MgH to Oxygen. As the peaks became wider due to increasing the Ball Milling time, the Grain Size and Lattice strain have decreasing and increasing trend, respectively. In early hours of ball milling, the decrease in particle sizes are noticeable but in the following, the reduction in particle size will show reduction in the intensity of decreasing.The dehydrogenation temperature of MgH was 431 Degrees of Centigrade before ball milling, this temperature reduce to 405, 396 and 390 Degrees of Centigrade respectively after 3, 8 and 15 hours ball milling.

Table 1. Average particle size (D), grain size (d), lattice strain (ε) and desorption temperature (T) of pure milled and un-milled MgH_2 after mechanical alloying for different times

Time h	Phase	D µm	d nm	ε %	T °C
0	β	35	48	0	431
3	β, γ, MgO	10.6	27	0.6	405
8	β, γ, MgO	3.1	22	0.8	396
15	β, γ, MgO	1.4	13	0.85	390

3.2. Composite Compounds

Addition of 10 % wt Ta_2O_5 to magnesium hydride as well as its mechanical alloying at different times of milling process reduced the dehydrogenation temperature in comparison with the pure magnesium hydride in the same times. The temperature changes from 405 to 382 °C in MT1-3, from 396 to 385 °C in MT1-8 and from 390 to 389 °C in MT1-15 composites. The temperature reduction trend in MT2-3, MT2-8 and MT2-15 samples with a greater intensity than MT1 composites show 370, 369 and 360 °C

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temperatures, respectively; at 3, 8 and 15 hours of ball milling. X-ray diffraction and scanning electron microscopy analyses were used in order to determine the causes of this temperature reduction.

The quasi-stable gamma-magnesium hydride phase is visible in both nanocomposites groups after 3 hours milling process. This phase can affect the hydrogen properties of magnesium hydride, due to its quasi-stability which has lower desorption temperature than magnesium beta-hydride phase. Volume contraction and stresses applied on the mass of β-magnesium hydride are the reasons for effect of gamma phase on β phase desorption temperature. The applied strain caused by the gamma phase reduces the beta stability. Therefore it improves absorption and desorption kinetics. The quasi-stable gamma-magnesium hydride phase has lower desorption hydrogen enthalpy than magnesium hydride that can affect hydrogen desorption thermodynamics, it can't be considered as the main factor to improve the hydrogen properties of magnesium hydride, due to its low value. The magnesium oxide phase is observed in the X-ray diffraction results of both composite specimens. This phase forms some layers by forming oxide layers on surface that prevent release of oxygen and magnesium nucleation from magnesium hydride and affects the hydrogen desorption properties negatively. By comparing diffraction patterns, it is observed that the intensity of MgO peaks in 10 wt% Ta_2O_5 samples are greater than that of 20 wt% Ta_2O_5 samples at similar milling time which could be due to higher percentage of Ta_2O_5 that is because of its catalytic properties preventing intensive oxidation of newly created magnesium levels causes from milling process. According to XRD analysis, in magnesium hydride samples containing 10 wt% Ta_2O_5 have not been observed any other intermetallic compound that the low amount of additive (10% by weight) can be attributed as the main factor. However, relatively poor peaks of $TaH_{0.48}$ hydride compound were observed after 3 hours milling time in the results of magnesium hydride samples containing 20 wt% Ta_2O_5, which do not show a significant change in their peaks with increasing milling time. Tantalum hydride is an amorphous compound that improves dehydrogenation temperature.

By adding the catalyst to pure magnesium hydride, intensity of the peaks in all specimens has decreased indicating a reduction in the grain size due to addition of the catalyst. Peak intensity in MT2 decreased more than MT1 samples at the same time of milling process. These results indicate a reduction in the grain size of the synthesized samples compared to pure magnesium hydride and also a further decrease in MT2 compared to MT1 samples. Oxide catalysts act as small balls in milling process which lead to a further reduction in grain size and particle size. Ta_2O_5 is a brittle and fragile oxide catalyst, therefore it can help magnesium hydride to grind further. For this reason, grain size in pure composite samples was reduced relative to pure hydride. On the other hand, it seems that in MT2 samples, the grain size is reduced further due to the higher percentage of Ta_2O_5. The grain size and lattice strain calculated by Williamson-Hall method confirms a further reduction in grain size of MT2 samples. It can be seen in both composite samples, by increasing milling time, grain size shows a decreasing trend. Regarding to the strain values obtained in this study, it can be claimed that lattice strain with higher values in MT1 samples can play an important role to improve the hydrogen properties. The numerical results of particle size parameters obtained from the MIP Image Analyzer software show a sharp decrease in particle size in both composite samples after 3 hours milling. It seems that small amount of both catalysts has a significant effect on mechanical milling process. The morphological study of powders shows that there is no significant change in particle size with increasing milling time from 3 to 8 hours. Furthermore, as milling time increases in MT1 and MT2 samples, the particle size increases, too, due to the agglomeration phenomenon which can have a negative effect on the dehydrogenation temperature. However, this negative effect is very low, due to a slight increase in particle size.

Table 2. Average particle size (D), grain size (d), lattice strain (ε) and desorption temperature (T) of composite compounds after mechanical alloying.

composites-Time, h	D µm	d nm	ε %	T °C
MT1-3	0.27	13.3	2	382
MT1-8	0.31	12.6	1.5	385
MT1-15	0.36	12.27	1.8	389
MT2-3	0.25	10.83	1.2	370
MT2-8	0.34	10.74	1.74	369
MT2-15	0.38	8.61	0.91	360

4. Conclusion

1. The greatest changes in grain size and particle size are observed in the initial milling time.
2. The catalytic compounds containing Ta_2O_5 has led to a significant reduction in the grain size and particle size due to its high brittleness.
3. MT2 nanocomposites with a higher percentage of oxidized and brittle Ta_2O_5 catalysts have lower grain size and dehydrogenation temperatures than MT1 samples.