Effect of Milling and Heat treatment on the Microstructure of 38%wtTiO_2-36%wtNiO-26%wtC Powder Mixtures and the Influence of Produced Nanostructured Compounds on the Hydrogen Desorption from MgH_2

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1- Introduction

Storage of hydrogen in magnesium hydride is one of hydrogen storage mechanisms in materials. This hydride has high storage capacity (MgH_2, up to 7.6wt %). The major challenges in hydrogen storage in this material are high desorption temperature (more than 400°C) and very slow reaction kinetics. In recent years a large number of studies have been done to decrease the desorption temperature of hydrogen and increase the adsorption/desorption rate of hydrogen from magnesium hydride by decreasing the particle size of hydride and addition of catalysts. The main goal of this research is to study the effects of ball milling and heat treatment on the phase constituent of TiO_2-NiO-C powder mixture and subsequently investigating the effect of produced nanostructured catalyst on the hydrogen desorption temperatue and capacity from MgH_2.

2-Experimental

High purity laboratory grade materials were used in this study. Ball milling of powder mixtures was done in a planetary ball mill under argon atmosphere. The pills produced from milled powders were heat treated at various temperatures under flowing argon atmosphere inside a tube furnace. In the next step, 10 wt.% of four 20h milled and heat treated samples was added to MgH_2 and then milled under argon atmosphere. X-ray diffraction method and field emission scanning electron microscopy were used to evaluate the phase constituent and particle size of milled powders. Then, the powder mixture was heated to 450°C under flowing argon atmosphere to determine the temperature and the amount of hydrogen desorption in a TGA machine.

3- Results and Discussions

The XRD patterns of milled powder mixtures showed that even after 20h of milling, only graphate was transformed to amourphous state. Increasing milling time from 5 to 20 hours led to a decrease in the average size of particles and agglomerates from 60 to 30 and from 220 to 120 nanometers, respectively.

Heat treatment at 300°C led to transform the carbon structure from amourphous to crystalline state in 5 and 10 hour milled samples but new phases did not form in this condition (Fig. 1). Partial reduction of NiO occurred due to the heating of milled powder at 600°C (Fig. 2). NiO was reduced completely and anatase transformed to rutile after heat treatment at 900°C (Fig. 3). Heat treatment at 1200°C led to appearance of $NiTiO_3$ phase (Fig. 4).

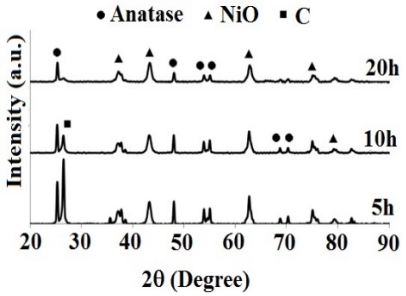

Fig. 1 XRD patterns of milled powders and then heat treated at 300°C

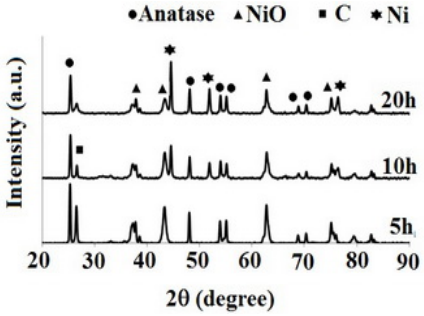

Fig. 2 XRD patterns of milled powders and then heat treated at 600°C

In the next step 10 wt.% of 20h milled samples heat treated at various temperatures were added to MgH_2 as catalyst and then ball milled for 20h. The results of TGA analysis showed that magnesium hydride did not desorb any hydrogen at 350°C.

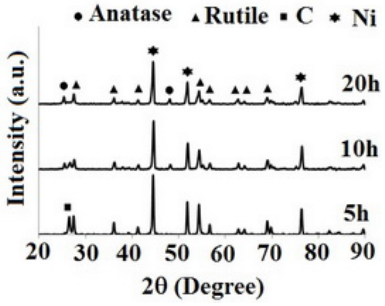

Fig. 3 XRD patterns of milled powders and then heat treated at 900°C

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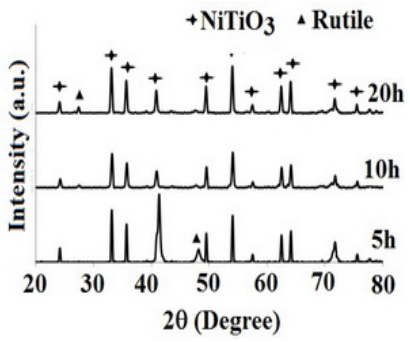

Fig. 4 XRD patterns of milled powders and then heat treated at 1200°C

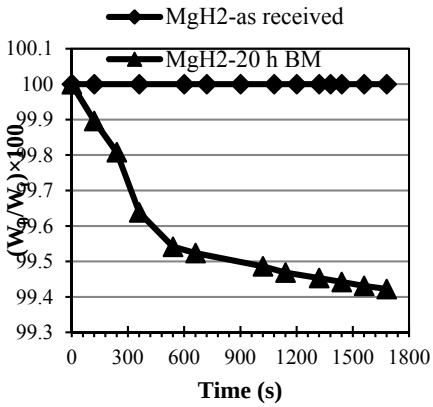

Fig. 5 TG curves of MgH_2 and 20h milled MgH_2 powder at 350°C

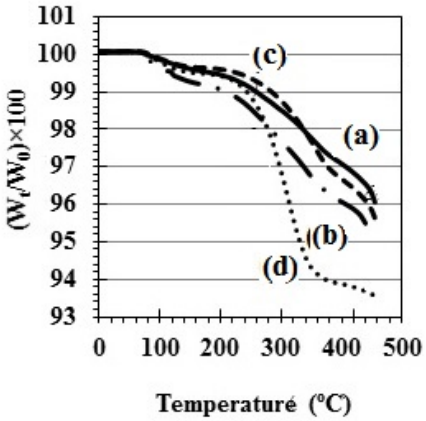

Fig. 6 TG curves of samples milled with catalysts produced at a) 300 b) 600 c) 900 d) 1200°C

Meanwhile MgH_2 desorbs 0.6 wt.% hydrogen after 20h of ball milling. Results showed that adding catalyst had a major effect on the hydrogen desorption of MgH_2. Catalyst produced at 1200°C had the best performance among produced powders. Adding catalysts to MgH_2 and ball milling for 20h led to hydrogen desorption from at least 5.4 to maximum 6.45 wt.% from room temperature to 455°C (Fig. 6). The important point was the improved performance of catalyst produced at 1200°C which contained $NiTiO_3$ phase. The reason for this improvement in hydrogen desorption properties was related to the catalytic effect of $NiTiO_3$ phase.

4- Conclusions

Increaing ball milling times had no effect on the phase constituent of the powder mixture before and after heat treatment at 300°C. Heat treatment at 600°C led to partial reduction of NiO. This phase was completely reduced and anatase phase partially transformed to rutile after heat treatment at 900°C. $NiTiO_3$ phase was formed during heat treatment at 1200°C. Ball milling without adding catalyst did not significantly affect the hydrogen desorption of MgH_2. Adding produced catalysts to MgH_2 and 20h ball milling led to hydrogen desorption from at least 5.4 to maximum 6.45 wt.%. The reason for maximum increase was related to the presence of $NiTiO_3$ phase due to the heat treatment at 1200°C.