Effect of Milling and Heat treatment on the Microstructure of 38\%wtTiO₂-36\%wtNiO-26\%wtC Powder Mixtures and the Influence of Produced Nanostructured Compounds on the Hydrogen Desorption from MgH₂

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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 (MgH₂, 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 TiO₂-NiO-C powder mixture and subsequently investigating the effect of produced nanostructured catalyst on the hydrogen desorption temperature and capacity from MgH₂.

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 MgH₂ 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 graphite was transformed to amorphous 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 amorphous 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 NiTiO₃ phase (Fig. 4).

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Meanwhile MgH₂ desorbs 0.6 wt.% hydrogen after 20h of ball milling. Results showed that adding catalyst had a major effect on the hydrogen desorption of MgH₂. Catalyst produced at 1200°C had the best performance among produced powders. Adding catalysts to MgH₂ 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 NiTiO₃ phase. The reason for this improvement in hydrogen desorption properties was related to the catalytic effect of NiTiO₃ phase.

4- Conclusions
Increasing 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. NiTiO₃ phase was formed during heat treatment at 1200°C. Ball milling without adding catalyst did not significantly affect the hydrogen desorption of MgH₂. Adding produced catalysts to MgH₂ and 20h ball milling led to hydrogen desorption from at least 5.4 to maximum 6.45 wt.% at 1200°C.