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Journal of Alloys and Compounds 356–357 (2003) 649–653

Journal of ALLOYS AND COMPOUNDS

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# The absorption and desorption properties of nanocrystalline $Mg_2Ni_{0.75}Cr_{0.25}$ alloy containing $TiO_2$ nanoparticles

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Received 10 June 2002; accepted 25 October 2002

**Abstract**

A type of nanocrystalline $Mg_2Ni_{0.75}Cr_{0.25}/TiO_2$ composite was prepared by ball-milling alloy with different amounts of (0.5, 1.5, 2.5 wt%) $TiO_2$ nanoparticles. The microstructures of the nanocomposites were examined by XRD and TEM. The effects of the addition of transition metal oxide $TiO_2$ nanoparticles on the absorption and desorption properties of the nanocrystalline $Mg_2Ni_{0.75}Cr_{0.25}$ alloy were investigated. The $TiO_2$ nanoparticles could act as catalyst and the nanocomposites showed rapid absorption and desorption kinetics and good thermodynamic properties. The absorption temperatures of the nanocomposites were greatly decreased and the rates of hydriding were increased. In comparison with the nanocrystalline $Mg_2Ni_{0.75}Cr_{0.25}$ alloy, the enthalpy of hydride formation for the nanocomposite was small, but the absorption capacity was reduced.


*Keywords:* Hydrogen storage materials; Mechanical milling; Nanocrystalline; $TiO_2$ nanoparticles

## 1. Introduction

Magnesium-based hydrogen storage alloys have been considered to be one important hydrogen storage material, due to their safety, extremely high storage capacity and rich natural resources [1,2]. Nevertheless, the crystalline $Mg_2Ni$ alloy can reversibly absorb and desorb hydrogen only at high temperatures (i.e. ~300 °C). Therefore, the research activities have concentrated on improving the absorption and desorption behavior of the material.

Many attempts have been made to improve the absorption and desorption properties of the $Mg_2Ni$ hydrogen storage alloys. A lot of works show that substitution of the third element [3–6] and mechanical alloying [7–9] can decrease the temperature of the alloy–hydrogen reaction. Tsushio et al. [10] found that Cr-substituted alloy $MgNi_{0.86}Cr_{0.03}$ prepared by mechanical alloying could desorb hydrogen at 423 K, but the desorption capacity was small (0.4 wt%). As shown in the past researches, $Mg_2Ni$-based alloy can attain rapid absorption and desorption kinetics and low absorption temperature by addition of catalysts Ni, Co, Pt and Zr–Ni–Cr, etc. [11–14]. Recently, the transition metal (V, Cr, Mn) oxides and chlorides have been used as catalysts [15,16]. The results showed that Mg powder milled with 1 wt% $Cr_2O_3$ could absorb 6.7 wt% of hydrogen at 573 K within 2 min and Mg–3Ni–1$CrCl_3$ could absorb hydrogen to 5.8 wt% at 433 K. In this work, the effect of $TiO_2$ nanoparticles on absorption and desorption properties of nanocrystalline $Mg_2Ni$-based alloys were investigated.

## 2. Experimental details

The magnesium, nickel and chromium powder, with purity of 99.9% and 200 mesh, corresponding to a composition $Mg_2Ni_{0.75}Cr_{0.25}$ were mechanically mixed under an argon atmosphere in a planetary mill machine for 1 h with a ball-to-powder weight ratio of 5:1. After milling, the mixture was cold pressed into pellets under a pressure of 1000 MPa. The pellets were sintered at 743 K under argon atmosphere in a furnace for 4.5 h, and were then crushed to produce powders below 200 mesh in air. The powders mixed with a composition of 0, 0.5, 1.5, 2.5 wt% $TiO_2$ (tetragonal, average size: 40 nm). Nanoparticles were mechanical milled under an argon atmosphere (2 MPa) for 40 h with a ball-to-powder weight ratio of 10:1. After being ball milled, the composites were annealed at 473 K for 1 h in vacuum.

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0925-8388/02/$ – see front matter 
doi:10.1016/S0925-8388(02)01287-2

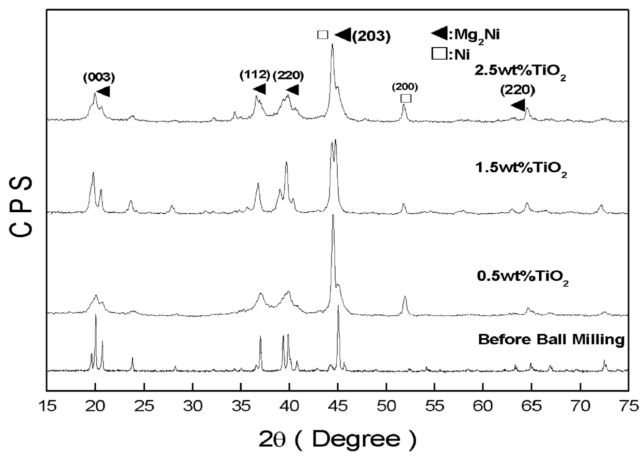


Fig. 1. XRD patterns of $Mg_2Ni_{0.75}Cr_{0.25}$ alloy before and after milling with $TiO_2$ nanoparticles.

The apparatus employed for hydriding and dehydriding measurements are similar to the equipment described in Ref. [17]. In the present work, the hydrogen absorption behavior of the $Mg_2Ni_{0.75}Cr_{0.25}/TiO_2$ nanocomposites were measured at 373, 413, 433 and 483 K, respectively. The measurements were carried out as follows. After being activated for one to two cycles at higher temperature (473 K), the vessel filled with powder samples was evacuated to vacuum ($10^{-2}$ Pa) by a rotary vacuum pump. Then the vessel was heated to 373 K, and hydrogen was introduced at a pressure of 4 MPa at 373 K in order to reach complete hydrogenation. After measurements of the hydrogen absorbing behavior at 373 K, the vessel was evacuated to 0.1 MPa and heated to 463 K to desorb the hydrogen in the nanocomposites, and the capacity of the dehydriding was determined at this temperature. This procedure was repeated for the other three samples at different temperatures. The pressure–composition ($P$–$C$) isotherms were measured by an AMC gas reaction controller at 523 K. The plateau pressures on the $P$–$C$ isotherms for the composites were examined and used to estimate the enthalpy of formation of hydrides from the nanocrystalline $Mg_2Ni_{0.75}Cr_{0.25}/TiO_2$ composites. The microstructure of the nanocomposites was examined by X-ray diffraction (Cu K$\alpha_1$, Philips X'Pert-MPD) and transmission electron microscopy (Philips C200UT).

## 3. Results and discussion

### *3.1. Microstructure of nanocomposites*

Fig. 1 shows XRD patterns of $Mg_2Ni_{0.75}Cr_{0.25}$ alloys before and after milling with $TiO_2$ nanoparticles. In the case of the $Mg_2Ni_{0.75}Cr_{0.25}$ alloy before milling, only the $Mg_2Ni$ phase was formed after sintering and the element chromium was in solid solution. But in the case of $Mg_2Ni_{0.75}Cr_{0.25}$ alloy after milling with $TiO_2$ nanoparticles, the diffraction peaks of the Ni appeared. It shows that little single Ni was precipitated from $Mg_2Ni_{0.75}Cr_{0.25}$ alloys by ball milling and formed the $Mg_2Ni$–Ni complex phase. The broadened peaks of the XRD patterns indicate that the nanocrystalline structure of the $Mg_2Ni_{0.75}Cr_{0.25}$ alloys formed during 40 h of ball milling. According to the Scherrer formula, the average sizes of the nanocomposites were estimated to be about 24–40 nm (Table 1).

Fig. 2 shows the TEM image and electron diffraction pattern of the $Mg_2Ni_{0.75}Cr_{0.25}+2.5$ wt% $TiO_2$ nanocomposite. TEM observation indicated that some $TiO_2$ nanoparticles or precipitated single Ni particles are present in the composite. The electron diffraction pattern shown separately in Fig. 2 indicates that the $Mg_2Ni$ is the main phase, which is the same as the result examined by XRD analysis.

### *3.2. Hydrogen storage properties*

Fig. 3 shows the absorption curve of the nanocrystalline $Mg_2Ni_{0.75}Cr_{0.25}$ alloy milling with 1.5 wt% $TiO_2$ nanoparticles after two absorption–desorption cycles. After the nanocomposites were fully activated, the absorption was almost finished within 2 min at 373 K under a hydrogen pressure of 4 MPa. As a comparison, the original nanocrystalline $Mg_2Ni_{0.75}Cr_{0.25}$ alloy did not absorb hydrogen at 373 K. These results showed that the hydriding kinetics of the nanocomposites was obviously improved by mechanical milling with $TiO_2$ nanoparticles. But the absorption capacity of the composite is decreased to only 2.2 wt% because of the precipitation of single Ni and the low absorption temperature.

Fig. 4 presents the hydrogen absorption curves of $Mg_2Ni_{0.75}Cr_{0.25}/TiO_2$ nanocomposites under a hydrogen pressure of 4 MPa at 453 K. As shown in Fig. 4, each nanocomposite has achieved its rapid absorption rate of the

Table 1
The average crystalline size of the composites after mechanical milling

| Sample | $Mg_2Ni_{0.75}Cr_{0.25}$ | Alloy + 0.5 wt% $TiO_2$ | Alloy + 1.5 wt% $TiO_2$ | Alloy + 2.5 wt% $TiO_2$ |
|---|---|---|---|---|
| Average size (nm) | 40 | 33 | 35 | 24 |

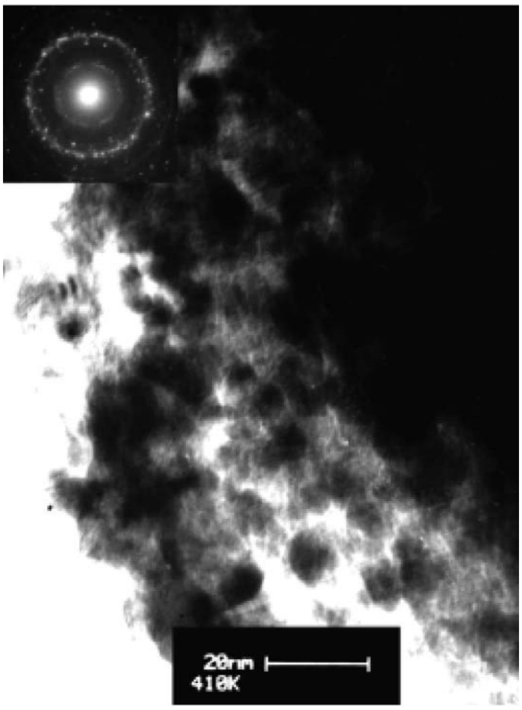


Fig. 2. TEM image and electron diffraction patterns of the $Mg_2Ni_{0.75}Cr_{0.25}$/2.5 wt% $TiO_2$ nanocomposite.

hydrogen. In comparison with nanocrystalline $Mg_2Ni_{0.75}Cr_{0.25}$ alloy, the $Mg_2Ni_{0.75}Cr_{0.25}/TiO_2$ nanocomposites achieved a faster absorption hydrogen rate, which indicated that the $TiO_2$ nanoparticles improved the absorption kinetic properties of the nanocomposites. With increasing the amount of $TiO_2$ nanoparticles, the

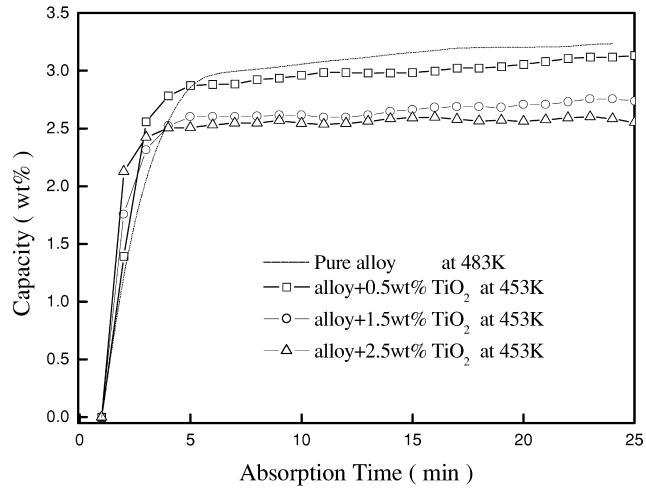


Fig. 4. Hydrogen absorption curves of the nanocomposites with different content of $TiO_2$ nanoparticles at 453 K.

decrease in the absorption hydrogen capacity of the nanocomposites is small.

In order to evaluate the effect of the $TiO_2$ content on the thermodynamics properties of nanocrystalline $Mg_2Ni_{0.75}Cr_{0.25}$ alloy, the pressure–composition isotherms of the nanocomposites were measured. The $P$–$C$–$T$ curves of desorption for the $Mg_2Ni_{0.75}Cr_{0.25}/TiO_2$ nanocomposites at 523 K after full activation are shown in Fig. 5. The results show that the equilibrium hydrogen pressure differed in accordance with the amounts of $TiO_2$ nanoparticles. Table 2 summarizes the desorption temperatures of the nanocomposites. With increasing of the amount of $TiO_2$ nanoparticles, the hydrogen pressure of the desorption equilibrium plateau was also increased.

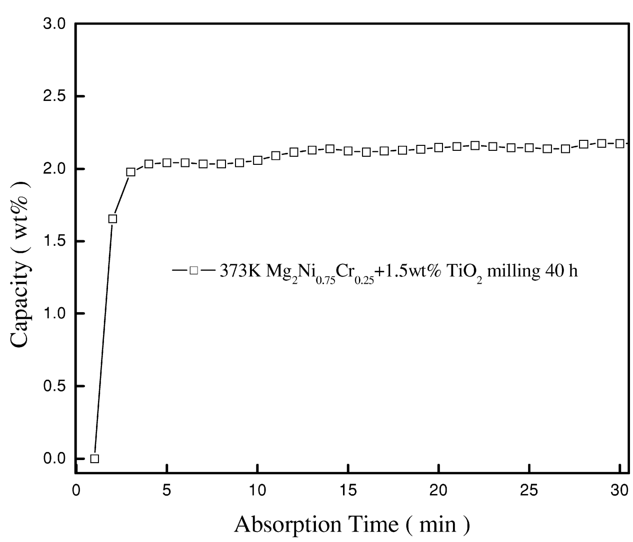


Fig. 3. Absorption curve of the nanocrystalline $Mg_2Ni_{0.75}Cr_{0.25}$/1.5 wt% $TiO_2$ nanocomposite at 373 K.

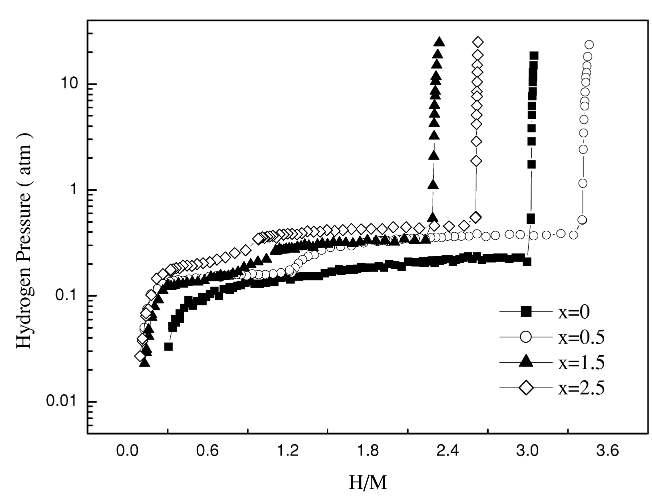


Fig. 5. Pressure–composition isotherms of the desorption for $Mg_2Ni_{0.75}Cr_{0.25}/TiO_2$ nanocomposites at 523 K.

Table 2
Desorption temperature of the $Mg_2Ni_{0.75}Cr_{0.25}/TiO_2$ nanocomposites

| Sample | $Mg_2Ni_{0.75}Cr_{0.25}$ | Alloy + 0.5 wt% $TiO_2$ | Alloy + 1.5 wt% $TiO_2$ | Alloy + 2.5 wt% $TiO_2$ |
|---|---|---|---|---|
| Temperature of desorption (K) | 523 | 498 | 470 | 470 |

The $P$–$C$–$T$ curves of the $Mg_2Ni_{0.75}Cr_{0.25}/1.5$ wt% $TiO_2$ nanocomposite at different temperatures are shown in Fig. 6. According to the van't Hoff equation [18], the value of absorption enthalpy for hydride formation of the nanocomposite is estimated to be $-58$ kJ (mol $H_2)^{-1}$. With respect to the value of enthalpy for hydride formation of standard $Mg_2Ni$ alloy ($-64.5$ kJ $mol^{-1}$ $H_2^{-1}$), the value of absorption enthalpy for the $Mg_2Ni_{0.75}Cr_{0.25}+1.5$ wt% $TiO_2$ nanocomposite was decreased.

In general, the key step in the absorption process is the diffusion of hydrogen in the hydride $Mg_2NiH_x$. The diffusion coefficient of hydrogen in this hydride layer is very small [16]. When the alloy particles are wrapped by this hydride layer during the absorption process, $H_2$ must obtain enough energy to cross this energy barrier. Zhenxing et al. [16] have reported that if ignition takes place during the absorption process, the rate of absorption will be increased. The catalysts can be used to increase the effect of the ignition. For catalysts, before the diffusion of the hydrogen can take place, it must absorb hydrogen at the surface. But the perfect $TiO_2$ single-crystal surfaces are inert towards reactions with $H_2$. However, the $TiO_2$ nanoparticle contains a higher density of defects in the crystal structure after mechanical alloying can absorb $H_2$ and act as catalyst to improve the hydriding alloys gas reaction properties [15]. Therefore, the absorption properties of the $Mg_2Ni_{0.75}Cr_{0.25}/TiO_2$ nanocomposites are improved by $TiO_2$ nanoparticles being ball milled. During the hydrogen desorption process, the addition of the $TiO_2$ nanoparticles also decreases the stability of the hydride, indicating that the alloy can release $H_2$ at lower temperature.

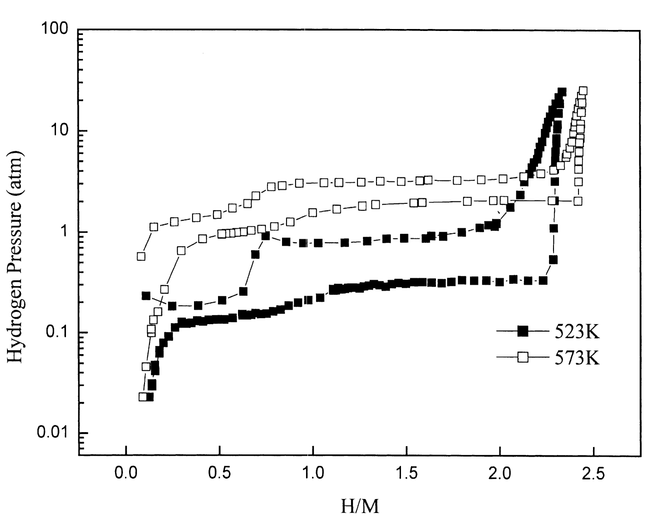


Fig. 6. PCT curves of the $Mg_2Ni_{0.75}Cr_{0.25}/1.5$ wt% $TiO_2$ nanocomposite at different temperatures.

## 4. Conclusions

The $Mg_2Ni_{0.75}Cr_{0.25}/TiO_2$ nanocomposites are synthesized by sintering and mechanical milling with different content of $TiO_2$ nanoparticles. The $TiO_2$ nanoparticles could act as catalyst and the nanocomposites showed rapid absorption–desorption kinetics and good thermodynamics properties. With increasing the amount of $TiO_2$ nanoparticles, however, the absorption hydrogen capacity of the nanocomposites was decreased. In the case when the content of $TiO_2$ was 1.5 wt%, the nanocomposite could absorb 2.2 wt% hydrogen under $H_2$ pressure of 4 MPa at 373 K. The value of enthalpy for the nanocomposite was decreased compared to nanocrystalline $Mg_2Ni_{0.75}Cr_{0.25}$ alloy.

## Acknowledgements

This work was supported by the special Funds for Major States Basic Research Project (No. G20000264-06) of MOST, China.

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