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Hydrogenation properties of mechanically milled $Mg_2Ni_{0.8}Cr_{0.2}$-CoO/Al_2O_3 composites*

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Abstract: $Mg_2Ni_{0.8}Cr_{0.2}$-x wt.% CoO/Al_2O_3 (x=0.5, 1, 2 and 3) composites were prepared by mechanically milling sintered $Mg_2Ni_{0.8}Cr_{0.2}$ alloy and CoO/Al_2O_3 compound for 45 h. The addition of CoO/Al_2O_3 compound resulted in the good kinetics properties of hydriding/dehydriding reaction of the composites. The composite with 1.0 wt.% CoO/Al_2O_3 catalyst could reach the maximum hydrogen absorption capacity (2.9 wt.%) within 5 min at 393 K under H_2 pressure of 4 MPa, and can desorb rapidly at 493 K. The decomposition and synthesis of hydrogen molecule on $Mg_2Ni_{0.8}Cr_{0.2}$ alloy surface was promoted by addition of CoO/Al_2O_3 catalyst. In addition, the formation of metallic Ni particles, strain and defects during the ball milling process also resulted in the improved hydrogenation performance of Mg_2Ni-based alloys.

Key words: Mg_2Ni-based composite, Hydrogen storage, Ball milling, Catalyst, Hydriding/dehydriding kinetics
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INTRODUCTION

Mg-based alloys are considered as potential candidates for hydrogen storage materials because of their large hydrogen capacity (Reilly and Wiswall, 1968; Pedersen and Larsen, 1993). However, as Mg-based alloys desorb hydrogen at temperatures higher than 600 K, they are not applicable to practical use. Many researches have studied to improve hydriding/dehydriding kinetics and to lower the working temperature (Wang *et al*., 2002; Tsushio *et al*., 1998; Spassov and Köster, 1998; Orimo *et al*., 1997). Among various methods, ranging from element substitution, addition of a catalytic component, and surface treatment to the introduction of non-conventional fabrication methods, composite formation has been generally accepted as a simple and effective method. The addition of some metal oxides could bring about a favorable change in the hydrogenation performance of the material. Wang *et al*.(2000) found that the addition of nanostructure TiO_2 powder resulted in markedly improved hydrogenation performance of Mg. Oelerich *et al*.(2001) investigated the influence of cheap metal oxides (Sc_2O, TiO_2, V_2O_5, Cr_2O_3, Mn_2O_3, Fe_3O_4, CuO, Al_2O_3, SiO_2) on the sorption behavior of nanocrystalline Mg-based systems, and found that in absorption, the catalytic effect of TiO_2, V_2O_5, Cr_2O_3, Mn_2O_3, Fe_3O_4, and CuO was comparable; and that concerning desorption, composite material containing Fe_3O_4 showed faster kinetics, followed by V_2O_5, Mn_2O_3, Cr_2O_3 and TiO_2. Song *et al*.(2002) showed the effects of the addition of Cr_2O_3, Al_2O_3, CeO_2 on the hydrogenation properties of Mg powder.

All the above researches showed that metal oxides could improve hydriding/dehydriding properties by accelerating the decomposing/composing of hydrogen molecule on the alloy surface. Many researches in the chemical industry showed compounds consisting of more than one metal oxide could im-

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prove the catalytic effect in the hydriding/dehydriding reaction markedly (Liu *et al.*, 2002; Chen *et al.*, 2000; Zhu *et al.*, 2002; Cong *et al.*, 2000). However, the hydrding/dehydriding properties of hydrogen storage alloy with complex metal oxide as catalyst have not been reported before. In the present work, CoO/Al_2O_3 compound was prepared by chemical method, and the hydriding/dehydriding properties of Mg_2Ni-based alloy with CoO/Al_2O_3 catalyst were investigated.

EXPERIMENTAL DETAILS

In this work, CoO/Al_2O_3 catalyst was prepared by the following impregnation procedure. Cobalt nitrate $[Co(NO_3)_2]$ was utilized as the CoO precursor. An aqueous solution of cobalt nitrate was heated slowly until all of the precursors were completely dissolved. This solution was then added to aqueous γ-Al_2O_3 slurry. The resulting solution was stirred for 24 h, and then a 0.1 mol/L aqueous solution of ammonia $(NH_3{\cdot}H_2O)$ was poured into the stirred slowly solution. During the process, excessive ammonia was introduced to ensure Co^{2+} precipitated completely in the form of cobalt hydroxide $[Co(OH)_2]$. After complete precipitation, the final solution was dried at 383 K. Samples thus obtained were calcined at 723 K for 3 h in the flow of hydrogen flux (80 ml/min) in order to avoid oxidation of CoO. During the calcinations the cobalt hydroxide was decomposed to yield cobalt oxide.

$Mg_2Ni_{0.8}Cr_{0.2}$ primary alloy was prepared by the conventional powder metallurgical technique. The Mg, Ni, Cr powders with purity of 99.9% and 200 mesh were thoroughly mixed by the milling process according to the required stoichiometric ratios, coldly pressed into pellets (ϕ 25 mm) at pressure of 800 MPa and then sintered at 823 K for 3 h under high purity argon. The primary pellets obtained were mechanically pulverized into particles smaller than 100 mesh for further modification. The mixtures of sintered $Mg_2Ni_{0.8}Cr_{0.2}$ powder and as-prepared CoO/Al_2O_3 catalyst powder in different content of 0.5 wt.%, 1.0 wt.%, 2.0 wt.% and 5.0 wt.% were introduced into a cylindrical stainless steel 100 ml capacity container. The sealed container was pumped and filled with high purity argon to prevent oxidation of the magnesium-based alloy. Ball milling (BM) process was carried out by Fritsch planetary BM equipment with a ball to powder weight ratio of 20:1. The planetary rotation speed was 400 rpm for 45 h. The microstructure of the as-milled powders and catalyst was examined by X-ray diffraction (Cu K_α, Philips X'Pert-MPD) and transmission electron microscopy (Philips C200UT).

The hydrogen absorption behaviors of $Mg_2Ni_{0.8}Cr_{0.2}$-CoO/Al_2O_3 composites were measured at 373 K, 393 K, 413 K, 423 K and 473 K, respectively. The measurements were carried out as follows. The as-milled sample was introduced into the reactor, sealed and pumped for 30 min, then brought into contact with high purity hydrogen (99.99999%) under 4.0 MPa at 473 K. The pressure change, which was continuously monitored by a sensitive pressure transducer and automatically recorded by a computer, was used to determine the rate of hydrogen absorption during the hydriding process. After measurement of the hydrogen absorbing behavior at 473 K, the vessel was evacuated to 0.1 MPa and heated to above 493 K to desorb the hydrogen. This procedure was repeated for the other three samples at different temperatures.

RESULTS AND DISCUSSION

Structural characteristics

The X-ray diffraction pattern of CoO/Al_2O_3 catalyst shown in Fig.1 reveals the existence of two phases: CoO and Al_2O_3. It can be seen clearly that the diffraction peaks broadened and their amplitudes decreased. Fig.1 reveals that the amplitudes of CoO diffraction peaks are higher than these of the Al_2O_3

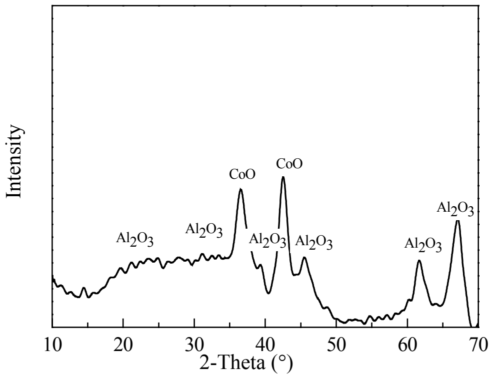

Fig.1 X-ray diffraction spectrum of CoO/Al_2O_3 catalyst

diffraction peaks. XRD quantitative analysis showed that the weight content of CoO in the total catalyst was higher than that of Al_2O_3. However, the content of CoO was only 11 wt.% in the end product due to the preparation process, which indicated that during the preparation, Co^{2+} was deposited on the surface of the Al_2O_3 powder so that part of the Al_2O_3 particle surface was covered by CoO, which resulted in the higher amplitudes of CoO diffraction peaks and the lower amplitudes of Al_2O_3 diffraction peaks.

The X-ray diffraction patterns of $Mg_2Ni_{0.8}Cr_{0.2}$ alloy with different contents of CoO/Al_2O_3 compound are shown in Fig.2 showing that only one crystal structure as Mg_2Ni phase existed before ball milling. No evidence of new phases was observed in Fig.2 (A), which suggests that the sites of Ni in the Mg_2Ni lattice might be substituted by element Cr during the sintering process. After ball milling, the diffraction peaks of the composites were broadened and the amplitudes of the peaks decreased due to the fine grain, inter-stress and defects. In addition, it can be seen clearly that Ni diffraction peaks are strongly strengthened, which indicates Ni precipitated in the alloy and Mg_2Ni+Ni complex phase formed during ball milling. No diffraction peaks of CoO or Al_2O_3 in the XRD spectra of as-milled composites were found because the content of catalyst was too small.

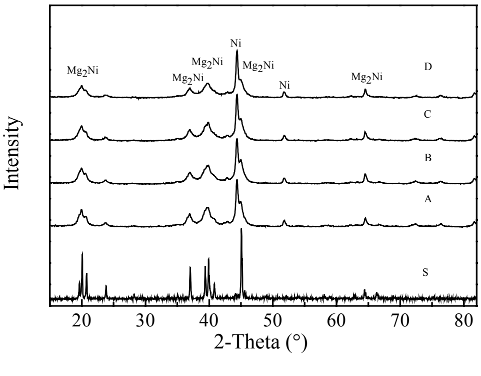

Fig.2 XRD patterns of $Mg_2Ni_{0.8}Cr_{0.2}$ alloy with different contents of CoO/Al_2O_3 catalyst after ball 45 h milling

S: Sintered $Mg_2Ni_{0.8}Cr_{0.2}$ alloy before ball milling; A: $Mg_2Ni_{0.8}Cr_{0.2}$+0.5 wt.% CoO/Al_2O_3; B: $Mg_2Ni_{0.8}Cr_{0.2}$+1.0 wt.% CoO/Al_2O_3; C: $Mg_2Ni_{0.8}Cr_{0.2}$+2.0 wt.% CoO/Al_2O_3; D: $Mg_2Ni_{0.8}Cr_{0.2}$+5.0 wt.% CoO/Al_2O_3

Hydrogen storage properties

Fig.3 shows the hydrogen absorption curves of the $Mg_2Ni_{0.8}Cr_{0.2}$ alloy with different contents of CoO/Al_2O_3 catalyst at 393 K under 4.0 MPa H_2. The activity of the composites was very good. The as-milled samples needed no activation for rapid H-absorption. It can be seen that the absorption kinetics properties of $Mg_2Ni_{0.8}Cr_{0.2}$ alloy were strongly improved with the addition of CoO/Al_2O_3 catalyst compared with $Mg_2Ni_{0.8}Cr_{0.2}$ alloy studied before (Wang *et al.*, 2002). However, the maximum hydrogen absorption capacity decreased with the increasing content of catalyst in the composites. The composite with 1.0 wt.% CoO/Al_2O_3 could absorb 2.5 wt.% H_2 in 33 s, and complete the absorption (hydrogen capacity 2.9 wt.%) in 5 min. Composites with 2.0 wt.% and 5.0 wt.% CoO/Al_2O_3, could also rapidly absorb hydrogen, but the full hydrogen absorption capacity reduced markedly. The absorption kinetics of $Mg_2Ni_{0.8}Cr_{0.2}$-1.0 wt.% CoO/Al_2O_3 composite at different temperatures under 4.0 MPa H_2 is shown in Fig.4. The composite could reach the full hydrogen absorption capacity at 393 K with the good absorption kinetics. Increasing temperature resulted in few changes on the absorption kinetics properties.

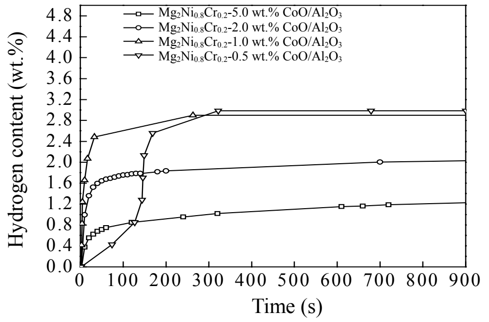

Fig.3 Hydrogen absorption kinetics of $Mg_2Ni_{0.8}Cr_{0.2}$-x wt.% CoO/Al_2O_3 composites at 393 K under hydrogen pressure of 4.0 MPa

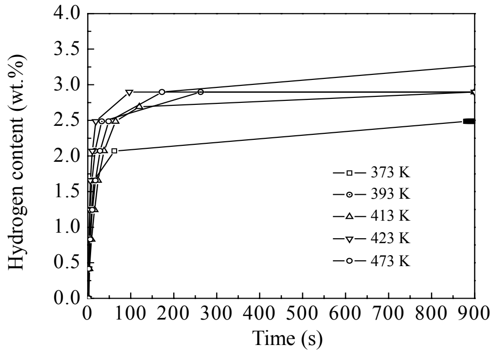

Fig.4 Hydrogen absorption kinetics of $Mg_2Ni_{0.8}Cr_{0.2}$-1.0 wt.% CoO/Al_2O_3 composite at different temperatures under hydrogen pressure of 4.0 MPa

The desorption kinetic properties of $Mg_2Ni_{0.8}Cr_{0.2}$-x wt.% CoO/Al_2O_3 composites at 493 K were also investigated. As shown in Fig.5, the composites could rapidly desorb hydrogen at 493 K under 0.1 MPa H_2. The composite with 0.5 wt.% CoO/Al_2O_3 could desorb 2.48 wt.% H_2 in less than 25 min. It is noteworthy that all the composites could desorb completely in 30 min. However, with increasing the content of CoO/Al_2O_3 catalyst, the dehydriding properties of the composites became worse.

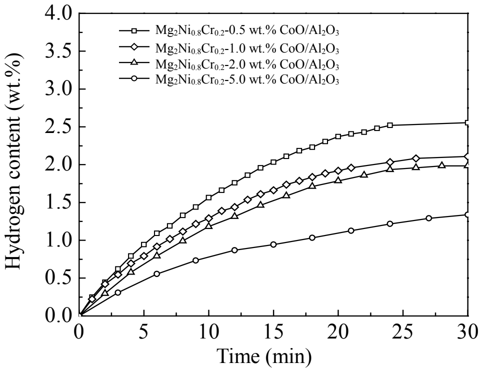

Fig.5 Hydrogen desorption kinetics of $Mg_2Ni_{0.8}Cr_{0.2}$-x wt.% CoO/Al_2O_3 composites at 493 K

Compared with what was reported (Wang *et al.*, 2002) before, that $Mg_2Ni_{0.8}Cr_{0.2}$ alloy completed the hydrogen absorption in 5 min at 483 K with good kinetics and could desorb at 523 K, the hydrding/dehydriding properties of the composites with CoO/Al_2O_3 catalyst were strongly improved. $Mg_2Ni_{0.8}Cr_{0.2}$ alloy without CoO/Al_2O_3 catalyst could not react with hydrogen at 393 K. According to Song *et al.*(2002), the oxides on the surface of the alloy could react at lower reacting temperature by accelerating the composing/decomposing of H_2 molecule. It was reported that ball-milled Mg with CoO addition need more than 60 min to finish the hydriding process at 598 K (Lee *et al.*, 2004) and Mg with Al_2O_3 addition could absorb 5.66 wt.% in 60 min at 573 K with bad dehydriding properties (Song *et al.*, 2002). The compound composed of two oxides can improve its catalytic capacity markedly due to the interaction of two oxides. Besides, Ni particles precipitated during the high energy ball milling of the Mg-based alloy may act as the active sites for the redox reaction of hydrogen and at the same time have "bypass effect" on hydrogen diffusion. Furthermore, mechanical milling can facilitate nucleation by creating many defects on the surface and/or in the interior of Mg-based alloy, or have an additive effect by serving as active sites for the nucleation, and shorten the diffusion distance by reducing the effective particle sizes of Mg-based alloy (Lee *et al.*, 2004). All the conditions discussed above improved the hydrogenation properties of $Mg_2Ni_{0.8}Cr_{0.2}$-CoO/Al_2O_3 composites.

CONCLUSION

$Mg_2Ni_{0.8}Cr_{0.2}$-x wt.% CoO/Al_2O_3 (x=0.5, 1, 2 and 3) composites were prepared by mechanically milling sintered $Mg_2Ni_{0.8}Cr_{0.2}$ alloy and CoO/Al_2O_3 compound. The addition of CoO/Al_2O_3 catalyst resulted in the good kinetics properties of hydriding/dehydriding reaction. $Mg_2Ni_{0.8}Cr_{0.2}$-x wt.% CoO/Al_2O_3 composites can reach the maximum hydrogen storage content during the hydriding without any activation. In the case when CoO/Al_2O_3 content was 1.0 wt.%, the composite could absorb 2.9 wt.% hydrogen within 5 min at 393 K under H_2 pressure of 4 MPa, and could rapidly desorb at 493 K. The maximum absorption hydrogen capacity decreased with further increasing of the content of the CoO/Al_2O_3 catalyst in the composites. The improvement of hydriding/dehydriging kinetics properties of the composite was attributed to the combined effects of the catalyst of CoO/Al_2O_3, Ni particles precipitated and the mechanical driving force.

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