

## Hydriding/dehydriding properties of NdMgNi alloy with catalyst CeO<sub>2</sub>

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**Abstract:** Hydrogen storage composites Nd<sub>2</sub>Mg<sub>17</sub>-50 wt.%Ni-*x* wt.%CeO<sub>2</sub> (*x*=0, 0.5, 1.0, 1.5, 2.0) were obtained by induction-ball milling method. The catalytic effect of CeO<sub>2</sub> on hydriding kinetics of Nd<sub>2</sub>Mg<sub>17</sub>-50 wt.%Ni composite was investigated. X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) analyses showed that Nd<sub>2</sub>Mg<sub>17</sub>-50 wt.%Ni alloy had a multiphase structure, consisting of NdMg<sub>12</sub>, NdMg<sub>2</sub>Ni, Mg<sub>2</sub>Ni and Ni phases and the addition of catalyst CeO<sub>2</sub> prompted the composites to be partly transformed into amorphous structure. The CeO<sub>2</sub> improved the maximum hydrogen capacity of Nd<sub>2</sub>Mg<sub>17</sub>-50 wt.%Ni alloy from 3.192 wt.% to 3.376 wt.% (*x*=1.0). What's more, the increment of diffusion coefficient *D* led to the faster hydriding kinetics, which was calculated by Avrami-Erofeev equation. The dehydrogenation temperature reduced from 515.54 to 504.72 K was mainly caused by the decrease of activation energy from 93.28 to 69.36 kJ/mol, which was proved by the Kissinger equation.

**Keywords:** Nd-Mg-Ni alloy; ball milling; hydriding/dehydriding; catalysis; rare earths

The successful application of hydrogen energy technology in emission-free hydrogen vehicles is widely considered to depend on the availability of an economical, safe and efficient storage of hydrogen<sup>[1]</sup>. Hydrogen storage in metal hydrides is considered as one of the future power sources to meet the requirements<sup>[2]</sup>.

Mg and Mg-based alloys are particularly attractive for the solid-state storage of hydrogen largely due to their high theoretical storage capacity of up to 7.6 wt.% H (in the case of pure MgH<sub>2</sub>), light weight, low cost and cycle stability. It was documented that the hydriding and dehydriding kinetics of the Mg and Mg based alloys are very sensitive to their structures<sup>[3]</sup>. Especially, the hydrogen storage properties strongly rely on the phase structure, crystal defect, alloy components, and stability of hydride. In order to overcome the slow hydrogen sorption kinetics and high desorption temperature of Mg-based alloys, many strategies for improvements have been taken. In recent years, Duarte et al.<sup>[4]</sup> found that Nd-Mg(Al)-Ni alloy presented a reasonably fast hydrogen desorption rate, approximately 97% of the hydrogen stored was released in the first 5 min at 673 K. Yin et al.<sup>[5]</sup> found that the addition of Nd in Mg-Ni alloy showed better desorption kinetics than original alloy, releasing up to 4.5 wt.% H<sub>2</sub> at 573 K. Our previous work<sup>[6,7]</sup> have proved that addition of Nd on Mg-Ni system improved the kinetics of absorption rate. Specifically, the desorbed capacity in 100 min is enhanced from 0.301 wt.% to

1.232 wt.%. Furthermore, the amount of the first absorbed hydrogen of Mg<sub>1.9</sub>Nd<sub>0.1</sub>Ni at 573 K and 4 MPa is 2.86% in mass fraction, which is higher than that of as-cast Mg<sub>2</sub>Ni. Therefore, in this study, we examined the effect of catalyst on Nd-Mg-Ni alloy. The hydrogen storage properties and the microstructure of a novel Nd-Mg-Ni alloy with catalyst CeO<sub>2</sub> were reported. Finally, the catalyst effect of CeO<sub>2</sub> on hydriding/dehydriding kinetics was calculated by Avrami-Erofeev equation and Kissinger equation.

### 1 Experimental

The Nd<sub>2</sub>Mg<sub>17</sub> alloy ingot was prepared in a low frequency induction furnace with purity above 99.8% under helium atmosphere. A slight excess of magnesium was used to compensate for evaporative Mg loss. The nickel powders and proportional amounts of CeO<sub>2</sub> were added to the Nd<sub>2</sub>Mg<sub>17</sub> alloy by ball milling process, while the ball to powder mass ratio was 20:1, the rotating speed of the vial was 450 r/min and ball milling time was 40 h for all the experiments.

X-ray diffraction (XRD) analysis was carried out for hydriding/dehydriding Nd<sub>2</sub>Mg<sub>17</sub>-50 wt.%Ni-*x* wt.%CeO<sub>2</sub> (*x*=0, 0.5, 1.0, 1.5, 2.0) by a Germany D8-ADVANCE model diffractometer using Cu K $\alpha$  (40 KV and 40 mA) radiation. These patterns were scanned by steps of 0.02° (2 $\theta$ ) from 10° to 90°. For the TEM study, the ball milled

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alloys were ground into fine powders with diameters less than 1  $\mu\text{m}$  in acetone, dispersed on a carbon micro-grid, and inserted into the TEM sample chamber for observation.

The kinetics of hydrogen absorption/desorption of the ball-milling  $\text{Nd}_2\text{Mg}_{17-50}$  wt.%Ni-CeO<sub>2</sub> composite were measured by an automatically controlled Sieverts apparatus under 3 MPa and at 473 K. The results have been calculated only according to the mass of  $\text{Nd}_2\text{Mg}_{17-50}$  wt.%Ni, which can illustrate the effect of catalyst CeO<sub>2</sub>.

Peak temperatures of hydrogenated alloys were evaluated by a differential scanning calorimeter (DSC) of type SDT Q600 instrument (TA Company) at the heating rates of 5, 10, 15 and 20 K/min respectively, where the sample was heated from room temperature to 773 K with flowing argon environment.

## 2 Results and discussion

### 2.1 Phase structure of composites

Fig. 1 exhibits the XRD patterns of  $\text{Nd}_2\text{Mg}_{17-50}$  wt.% Ni- $x$  wt.%CeO<sub>2</sub> ( $x=0, 1.0$ ) composite. As shown in Fig. 1, the diffraction peaks of the composites widen via ball milling process.

It is shown that  $\text{Nd}_2\text{Mg}_{17-50}$  wt.%Ni alloy had a multiphase structure, consisting of  $\text{NdMg}_{12}$ ,  $\text{NdMg}_2\text{Ni}$ ,  $\text{Mg}_2\text{Ni}$  and Ni phases, however, the addition of CeO<sub>2</sub>, did not change the phase structure, but doped in the phase inter-space, and leading to the exacerbation of amorphous structure.

HRTEM images and SAED patterns for ball milled

$\text{Nd}_2\text{Mg}_{17-50}$  wt.%Ni- $x$ CeO<sub>2</sub> ( $x=0, 1.0$ ) composites are shown in Fig. 2. The HRTEM image of  $\text{Nd}_2\text{Mg}_{17-50}$  wt.%Ni shows the crystal structure of  $\text{Mg}_2\text{Ni}$  and Ni particles clearly, the SAED pattern confirmed that the structure partly transferred to amorphous structure which shows the broad and dull multi-circles. However, the SAED patterns of  $\text{Nd}_2\text{Mg}_{17-50}$  wt.%Ni-1.0 wt.%CeO<sub>2</sub> present the more multi-circles and spots, which indicated that the addition of CeO<sub>2</sub> was beneficial for amorphization.

### 2.2 Hydrogen absorption kinetics of composites

Typical hydriding kinetic curves of  $\text{Nd}_2\text{Mg}_{17-50}$  wt.% Ni- $x$  wt.%CeO<sub>2</sub> ( $x=0, 0.5, 1.0, 1.5, 2.0$ ) alloys at 473 K

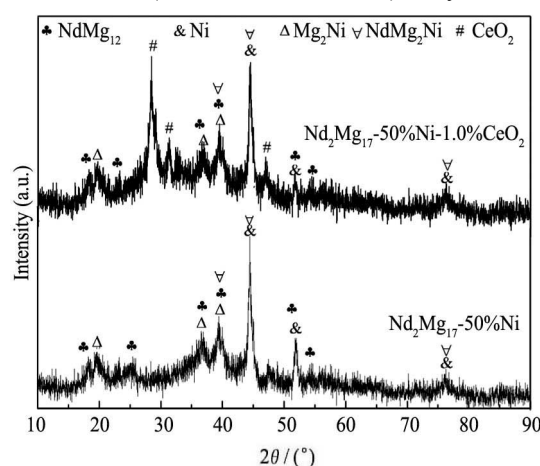


Fig. 1 XRD patterns of  $\text{Nd}_2\text{Mg}_{17-50}$  wt.%Ni- $x$ CeO<sub>2</sub> ( $x=0, 1.0$ ) composites

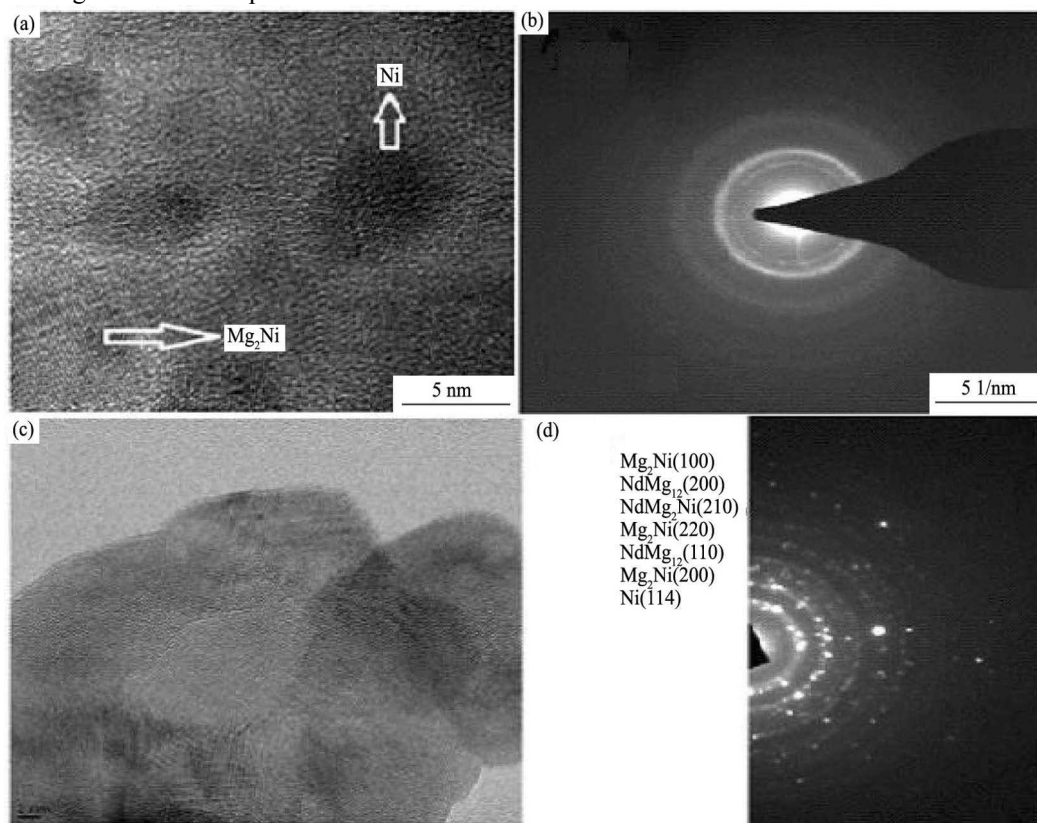


Fig. 2 HRTEM images and SAED patterns for alloys  
(a), (b)  $\text{Nd}_2\text{Mg}_{17-50}$  wt.%Ni; (c), (d)  $\text{Nd}_2\text{Mg}_{17-50}$  wt.%Ni-1.0 wt.%CeO<sub>2</sub>

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