# Effect of sintering conditions on the formation of single-phase NdMgNi$_4$ compound and its hydrogen storage properties

Z.M. Wang [a,*], Huaiying Zhou [a], R.P. Zou [b], Qingrong Yao [a]

[a] *Department of Information Material Science and Engineering, Guilin University of Electronic Technology, Guilin, Guangxi 541004, PR China*
[b] *School of Material Science and Engineering, University of New South Wales, Sydney, NSW 2052, Australia*

## Abstract

Effects of different sintering conditions on the formation of single-phase NdMgNi$_4$ compound and its electrochemical properties have been investigated. XRD analysis shows that an ideal single-phase compound of NdMgNi$_4$ can be synthesized by sintering the pressed tablets of mixture of Mg, Ni and NdNi powders under 973 K for 5 h; single-phase compounds of REMgNi$_4$ (RE = La, Ce, Pr) can be synthesized in this way as well. The electrochemical properties were measured by simulated battery tests. The maximum discharge capacity of NdMgNi$_4$ compound was about 200 mAh/g, and just 78 mAh/g for CeMgNi$_4$ compound. NdMgNi$_4$ compound could store 3.5 H/M of hydrogen under 2.5 MPa at 298 K, whilst it is difficult to absorb hydrogen at a higher temperature (473 K).
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*Keywords:* REMgNi$_4$; Ball milling; Sintering; Discharge capacity; Hydrogenation

## 1. Introduction

Recently, much work was focused on Mg–Ni based hydrogen storage alloys. The theoretical discharge capacity of Mg$_2$Ni electrode is about 1000 mAh/g, which is about three times that of LaNi$_5$-based alloys. Therefore, they have a large potential for application in rechargeable batteries and fuel cells [1,2]. The major limitation to the application of Mg-Ni based alloys is their poor hydrogen absorption/desorption kinetics and poor corrosion resistance in alkaline aqueous solution. For a better hydrogen storage capacity, other compound in Mg–Ni-RE systems are regarded as the most promising candidates. For example, La$_{1-x}$Mg$_x$Ni$_2$ compound is superior to LaNi$_5$ type or Laves-phase compounds in hydrogen absorbing capacity [3]. REMgNi$_4$ (RE = Ca, La, Ce, Pr, Nd and Y) is also a very promising ternary compound with a cubic SnMgCu$_4$ structure [4]. Aono et al. [5] reported synthesis of YMgNi$_4$ and its hydriding properties, and observed 1.05 wt.% of reversible hydrogen capacity to YMgNi$_4$ compound with an enthalpy of hydride formation of −35.8 kJ/mol H$_2$, which is comparable to that of LaNi$_5$-H

system, indicating this compound can also be of interest for hydrogen storage.

Recently we have carried out studies on the synthesis and electrode properties of amorphous REMgNi$_4$ (RE = La, Ce, Pr, Nd) [6–8]. This paper is an extension to previous papers in which heavy emphasis is placed on the synthesis, characterization, hydrogenation behavior and electrode properties of NdMgNi$_4$ as well as other REMgNi$_4$ compounds.

## 2. Experimental details

REMgNi$_4$ compounds were synthesized by the following procedures. Firstly, RENi (RE = La, Ce, Pr, Nd) alloy were synthesized by melting Ni and RE in a vacuum melting furnace, turned over and remelted 3 times to assure homogeneity; then crushed and grounded mechanically to powders (about 200 mesch). Secondly, the mixed powders of Mg, Ni and RENi were milled for 7 h, and then pressed into tablets. The milling process was performed under the protection of pure argon in a QM-1SP planetary ball mill. The weight ratio of steel ball to powder was 10:1, and the rotational speed was 150 rpm. Finally, the pressed tablets were sealed in quartz tube with 0.8 MPa Ar gas and heat-treated at 973 K for 5 h, then cooled to room temperature for use.

X-ray diffractometer (D8 Advance) using Cu Kα radiation was used to determine the phase structure and phase component of the compounds. The electrode properties of the synthesis compounds were measured by simulated battery tests with the REMgNi$_4$ compounds as negative electrodes. The negative electrodes were fabricated by the following procedures: Firstly, the alloy powder (0.6 g) were mixed with fine Copper powder (1.2 g) and a small amount

of polytetrafluoroethylene (PTFE). Secondly, the mixture was pasted onto both sides of a Nickel foam sheet (2.5 cm × 2.5 cm). Finally, the Nickel sheets pasted with alloy powder were cold pressed to a pellet at a compacting pressure of 155–175 MPa. Commercial Nickel hydroxide $Ni(OH)_2$ were used as the counter electrode (positive). The negative electrode was separated from the counter electrode $(Ni(OH)_2)$ by a porous frit in 6 M KOH electrolyte. This type of test battery construction was designed for a negative capacity-limited system, i.e. the capacity of the negative electrode was much less than that of positive electrode. Electrochemical properties of test battery were measured at 298 K using a computer-controlled battery testing instrument (PCBT-138-8D-A). In the charge–discharge measurement, negative electrodes were charged at 150 mA/g for 3.5 h and discharged at 50 mA/g to the cut-off potential of 0.9 V. The P-C isotherms were measured using a gas reaction controller. About 1 g powder sample was taken for each test. The measurement was carried out at a constant temperature of 298 and 473 K, respectively to investigate the absorption and desorption equilibrium pressure.

## 3. Results and discussion

### 3.1. Preparation of single-phase NdMgNi₄ compound and REMgNi₄ (RE = La, Ce, Pr) compounds

The XRD patterns of $NdMgNi_4$ synthesized by the above-mentioned method are shown in Fig. 1(b). Fig. 1(a) presents the diffraction peaks of the mixed powders of Mg, Ni and RENi milled for 7 h. It can be clearly seen that no solid reaction took place during the ball milling process. The $NdMgNi_4$ phase was produced in the subsequent sintering procedure—heat-treated at 973 K for 5 h. So the formation of $NdMgNi_4$ phase may be described by the following reactions:

$$Mg + 3Ni + NdNi \rightarrow NdMgNi_4.$$

Furthermore, effects of different sintering temperature on the formation of $NdMgNi_4$ phase have been studied. The XRD patterns of $NdMgNi_4$ sample prepared under different sintering conditions are given in Fig. 2. It can be seen that the single-phase compound of $NdMgNi_4$ phase were formed after sintering at 873 K for 5 h, or sintering at 973 K for 5 h, and the $Nd_2Ni_7$ phase emerged when the sintering temperature was increased to 1173 K. It is suggested that an ideal single-phase compound of $NdMgNi_4$ phase can be synthesized by sintering at the tempera-
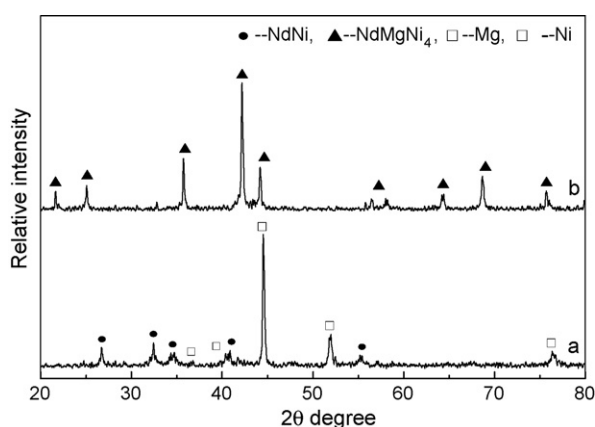


Fig. 2. XRD patterns of $NdMgNi_4$ sample sintered under different sintering conditions: line a, sintered at 873 K for 5 h; line b, sintered at 973 K for 5 h and line c, sintered at 1173 K for 5 h.

ture ranging from 873 to 973 K. To compare with the reference data [4], the observed and calculated $2\theta$, $d$-values and intensities of $NdMgNi_4$ phase formed under different sintering conditions are listed in Table 1, respectively.

A series of $REMgNi_4$ (where RE = La, Ce, Pr) compounds have also been synthesized in the same way. The XRD spectra of $REMgNi_4$ compounds are shown in Fig. 3. It reveals that these compounds are all single-phase with the same cubic structure as $SnMgCu_4$ [4].

### 3.2. Effect of sintering condition on electrochemical properties of NdMgNi₄ compounds

As above mentioned, formation of $NdMgNi_4$ phase was significantly influenced by the sintering temperature. Effects of sintering temperature on the electrochemical properties of $NdMgNi_4$ compound were investigated. Fig. 4 shows the dependence of the discharge capacity of $NdMgNi_4$ compound synthesized at different sintering temperatures on the number of charge/discharge cycles. It can be seen that good electrochemical property was observed in $NdMgNi_4$ compound synthesized



Fig. 1. XRD patterns of $NdMgNi_4$ sample: line a, the mixed powders of Mg, Ni and NdNi alloy milled for 7 h under the protection of pure argon; line b, the pressed tablets sintered at 973 K for 5 h.
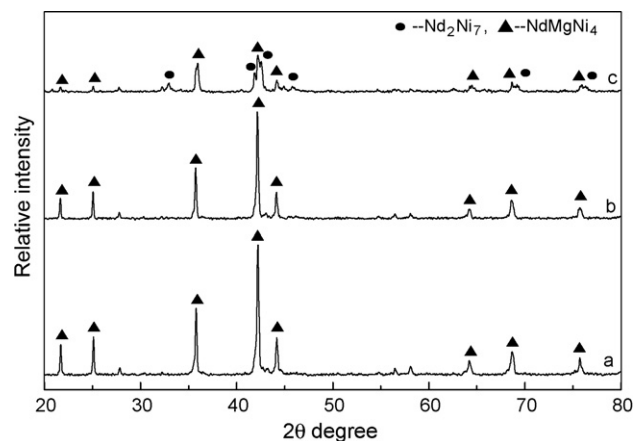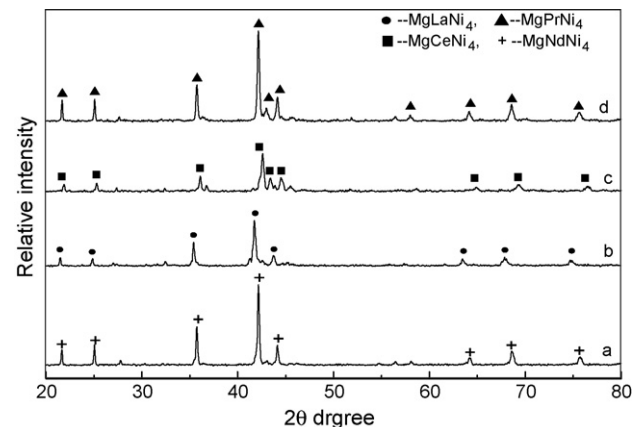


Fig. 3. XRD patterns of $REMgNi_4$ (RE = La, Ce, Pr, Nd) synthesized by sintering at 973 K for 5 h, respectively: line a, $NdMgNi_4$; line b, $LaMgNi_4$; line c, $CeMgNi_4$ and line d, $PrMgNi_4$.

Table 1
Observed and calculated 2θ, d-values and intensities of NdMgNi$_4$ phase with Si as the internal standard at 293 K

| H k l | $2\theta_{cal}$ | | | | $d_{obs}$ | | | | $I_{obs}$ | | | |
|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| | 0[#] | a[#] | b[#] | c[#] | 0[#] | a[#] | b[#] | c[#] | 0[#] | a[#] | b[#] | c[#] |
| 1 1 1 | 21.589 | 21.679 | 21.646 | 21.652 | 4.1134 | 4.096 | 4.102 | 4.101 | 14 | 19.6 | 17.3 | 14.6 |
| 2 0 0 | 24.980 | 25.081 | 25.049 | 25.054 | 3.5623 | 3.548 | 3.552 | 3.551 | 18 | 24.3 | 22.4 | 14.4 |
| 2 2 0 | 35.618 | 35.749 | 35.730 | 35.899 | 2.5196 | 2.510 | 2.511 | 2.500 | 44 | 47.8 | 46.6 | 75.4 |
| 3 1 1 | 42.033 | 42.185 | 42.171 | 42.201 | 2.1488 | 2.141 | 2.141 | 2.140 | 100 | 100 | 100 | 100 |
| 2 2 2 | 43.997 | 44.154 | 44.131 | 44.155 | 2.0569 | 2.050 | 2.050 | 2.050 | 34 | 29.2 | 25.6 | 33.4 |
| 4 2 2 | 63.976 | 64.190 | 64.208 | 64.469 | 1.4545 | 1.450 | 1.449 | 1.444 | 16 | 12.8 | 11.5 | 22.3 |
| 5 1 1 | 68.371 | 68.646 | 68.612 | 68.650 | 1.3709 | 1.366 | 1.367 | 1.366 | 33 | 20.1 | 22.5 | 18.2 |
| 4 4 0 | 75.424 | 75.705 | 75.671 | 75.832 | 1.2593 | 1.222 | 1.256 | 1.254 | 22 | 16.3 | 12.4 | 20.9 |

Note: 0[#] are the data of NdMgNi$_4$ phase reported in reference, [4] and a[#], b[#], c[#] are observed and calculated data of the sample under different sintering conditions (please refer to Fig. 2).

by being sintered at 873 K for 5 h. The increase of sintering temperature leads to the decrease of discharge capacity. It is likely that an ideal single-phase compound of NdMgNi$_4$ with good electrochemical properties can be synthesized by lower sintering temperature (873 K).

In comparison, Fig. 5 shows the dependence of discharge capacity of REMgNi$_4$ (where RE = La, Ce, Pr, Nd) compounds synthesized by sintering at 973 K for 5 h on the charge/discharge cycle number. It can be clearly seen that the maximum values of discharge capacity of these compounds were obtained after 2–5 charge–discharge cycles, and then slightly decreased with increasing number of cycles. This phenomenon has also been observed in LaNi$_5$ -based hydrogen storage alloys [9]. As to REMgNi$_4$ compounds, a slight increase in discharge capacity was observed in this order: NdMgNi$_4$ > PrMgNi$_4$ > LaMgNi$_4$ > CeMgNi$_4$. The maximum discharge capacity was about 200 mAh/g for NdMgNi$_4$ compound, and 78 mAh/g for CeMgNi$_4$ compound. It is suggested that CeMgNi$_4$ compound is much easier to oxidize in alkaline solution than other compounds. Thus, increase in cycle numbers may result in serious decrease in capacity as active materials were lost in oxidation.

### 3.3. The pressure-composition-isotherm curves of NdMgNi$_4$ compound

Usually, the gaseous hydrogen storage capacity of an alloy is known as the indicator of the upper electrochemical energy density limit in an electrochemical cell. The P-C-I curves (pressure-composition-isotherm) of NdMgNi$_4$ compound at 298 K and 473 K are shown in Fig. 6, respectively. It clearly shows that a plateau pressure was around 0.38 MPa in the absorbing process at 298 K, and the value of H/M could reach up to 3.0 in this plateau region, and 3.5 H/M obtained under 2.5 MPa. As to the reversibility of the hydrogen absorption/desorption reaction, single-phase compound of NdMgNi$_4$ released about 80% $(((3.2 - 0.7)/3.5) \times 100\%)$ of stored hydrogen under 0.01 MPa. When increases the experimental temperature to 473 K (Fig. 7), no clear plateau pressure could be observed under 4.0 MPa of hydrogen pressure, and the maximum value of H/M was only
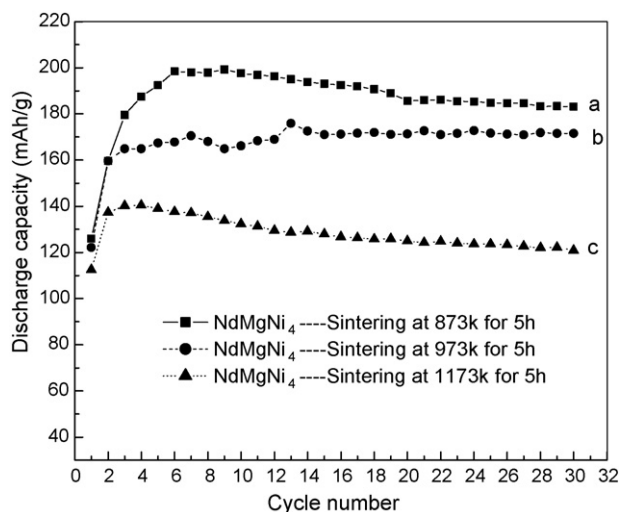


Fig. 4. The variation of discharge capacity with cycle number in the charge/discharge cycle process of NdMgNi$_4$ compound synthesized under different sintering conditions: line a, sintered at 873 K for 5 h; line b, sintered at 973 K for 5 h and line c, sintered at 1173 K for 5 h.
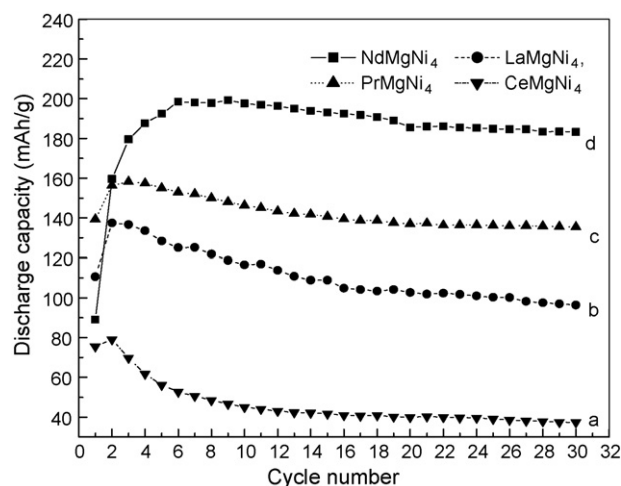


Fig. 5. The variation of discharge capacities of REMgNi$_4$ compounds with the cycle number in the charge/discharge cycle process: line a, CeMgNi$_4$; line b, LaMgNi$_4$; line c, PrMgNi$_4$ and line d, NdMgNi$_4$.
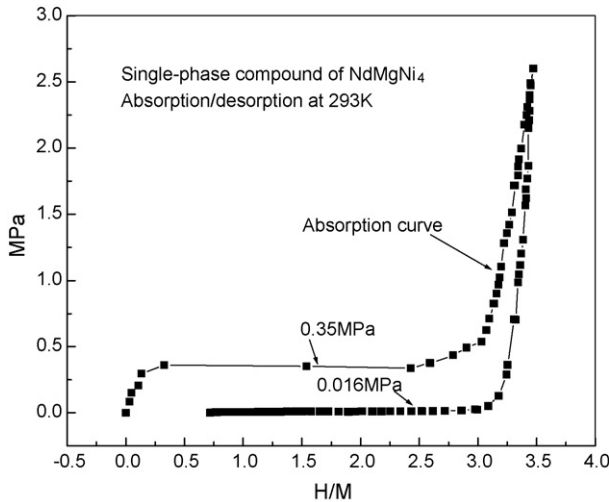
Fig. 6. Pressure-composition isotherms for NdMgNi$_4$ compound (H/M is the hydrogen-to-metal ratio) tested at 298 K.
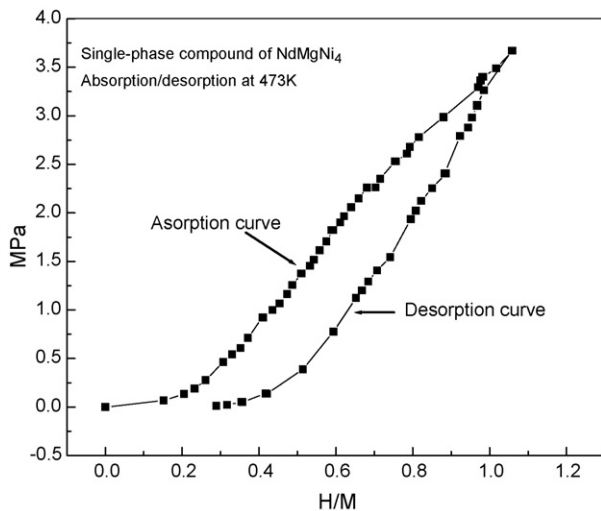


Fig. 7. Pressure-composition isotherms for NdMgNi$_4$ compound (H/M is the hydrogen-to-metal ratio) tested at 473 K.

about 1.1 under 3.75 MPa. As illustrated by Figs. 6 and 7, it is likely that synthesized NdMgNi$_4$ compound is easier to absorb/desorb hydrogen at low temperature (298 K), but difficult to absorb/desorb at higher temperature (473 K).

## 4. Conclusions

Single-phase compound NdMgNi$_4$ has been synthesized by sintering the pressed tablets of the mixture of Mg, Ni and NdNi powders under 973 K for 5 h, and other single-phase compounds of REMgNi$_4$ (RE = La, Ce, Pr) were made in the same way as well. NdMgNi$_4$ compound was able to store 3.5 H/M of hydrogen under 2.5 MPa at 298 K and release about 80% ($((3.2 - 0.7)/3.5) \times 100\%$) of the stored hydrogen under 0.01 MPa, but difficult to absorb hydrogen at a higher temperature (473 K). As to REMgNi$_4$ compounds in general, a slight increase in discharge capacity was observed in this order: NdMgNi$_4$ > PrMgNi$_4$ > LaMgNi$_4$ > CeMgNi$_4$. The maximum discharge capacity was about 200 mAh/g for NdMgNi$_4$ compound, and 78 mAh/g for CeMgNi$_4$ compound.

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