

# Synthesis and Electrode Characteristics of $Mg_{(2-x)}Al_xNi$ Alloys by Combustion Synthesis

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**Abstract:** The Mg-based hydrogen storage alloy  $Mg_{2-x}Al_xNi$  ( $x=0.1-0.5$ ) was synthesized by combustion synthesis. XRD indicates that a new phase with the cubic  $Ti_2Ni$  structure appears in the product, and SEM shows that there are a large number of defects on the alloy surface. The effect of partial substitution of Al for Mg on the electrochemical performances of  $Mg_2Ni$  was investigated. The results show that Al addition affects its electrode characteristics strongly. The electrochemical capacity and cycle lives of Al containing alloys increase strongly compared to the Al-free alloy. This is attributed to the structure of a new phase ( $Mg_3AlNi_2$ ), and the formation of the protect layer of  $Al_2O_3$ . In addition, the results reveal that mechanical grinding is beneficial to improve activation behavior and the maximum electrode capacity, but can not improve the cyclic stability due to breaking of  $Al_2O_3$  protect layer.

**Key words:** ternary hydrogen storage alloys;  $Mg_{2-x}Al_xNi$ ; combustion synthesis; mechanical grinding; electrode characteristics

$Mg_2Ni$  type metal hydride electrodes have been studied extensively in the recent years because of their large hydrogen capacity, low cost, light weight and non-toxicity etc. However, there are some difficulties of the conventional arc-melting process for synthesizing the  $Mg_2Ni$  phase due to the large difference in the melting points of the two elements, and segregation problems. Some researchers have tried to overcome these drawbacks by employing a combustion synthesis process<sup>[1,2]</sup>. In our previous work<sup>[3]</sup>, the  $Mg_2Ni$  phase was successfully synthesized by the thermal explosion mode of the self-propagating high-temperature synthesis. As a rule, the polycrystalline  $Mg_2Ni$  phase forms a stable hydride,  $Mg_2NiH_4$ , which is unable to desorb hydrogen at room temperature and shows a very low electrochemical discharge capacity<sup>[4]</sup>. In order to improve the electrochemical properties of the Mg-Ni-H system, the partial substitution of several foreign elements for Ni has been studied<sup>[5-7]</sup>. The results show that the partial replacement of Ni by V, Cr, Fe, Co, Cu or Zn weakens the Mg-Ni bond strength and makes the hydride unstable. Kohno et al<sup>[8]</sup> also reported that the partial replacement of Mg by a more electronegative element (Al or Mn) could decrease significantly the hydrogen absorption temperature. It is possible to improve the reversibility and increase the cycle life due to

the formation of  $Al_2O_3$  on the surface of this alloy. In the present work, Al is added to the Mg-Ni system by the thermal explosion in order to improve electrochemical performance. Moreover, the alloy structure and electrochemical characteristics are investigated. The parent alloy  $Mg_2Ni$  is also characterized for comparison.

## 1 Experiment

Pure Mg, Al and Ni powders were mixed with a composition  $Mg_{2-x}Al_xNi$  ( $x=0, 0.1, 0.2, 0.3, 0.4, 0.5$ ), and ground uniformly in a ball mill for 2 h. The ratio of ball and material was 5:1. The revolution was 150 r/min. Then the mixture was pressed into pellets with 20 mm in diameter and 25 mm in length under a pressure of 159 MPa. A W-3 % Re/W-25 %Re thermocouple inserted in the bottom of the sample was used to measure the temperature profile during the thermal explosion. The obtained compact was put in a reaction chamber with 0.1 MPa argon. Rapid heating of the compact resulted in the ignition of the self-sustained  $2Mg + Ni \rightarrow Mg_2Ni$  reaction in thermal explosion mode. Then the reaction chamber was cooled to room temperature, the sample was removed and crushed to the powder with -200 mesh in air. The phase constituents of these alloys were examined by XRD using  $Cu K\alpha$

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radiation.

To investigate the effect of mechanical grinding on the electrochemical properties of  $\text{Mg}_{1.5}\text{Al}_{0.5}\text{Ni}$  alloy, the following experimental procedure was designed. The combustion-synthesized ternary  $\text{Mg}_{1.5}\text{Al}_{0.5}\text{Ni}$  alloy was mechanically crushed and charged into Cr-Ni steel vials. The mechanical grinding was performed under an Ar atmosphere in a planetary ball mill (Fritsch, pulverisette P5). The milling speed of 250 r/min, and the ratio of ball to powder weight of 30:1 were chosen. To minimize temperature rising during ball milling, the milling period of 20 min was alternated with an equal rest time. Total milling time was 5 h. After finishing the grinding process, the milled powders was divided into two portions, one was used for XRD measurement and the other was used for charge-discharge tests.

The test electrodes were fabricated according to the following procedures: the alloy powder was mixed with fine Ni powder in a massratio of 1:3, and pressed into a pellet of 1.0 cm in diameter under a pressure of 50 MPa. Both sides of the pellet were coated with a foam nickel sheet and pressed at 30 MPa. Subsequently, as current conductor, a nickel lead wire was attached to the pressed foam nickel sheet by spot welding. The test electrode properties were measured at 298 K using a computer-controlled battery testing instrument (PCBT-110-3D- A).  $\text{NiOOH}/\text{Ni}(\text{OH})_2$  and  $\text{Hg}/\text{HgO}$  were used as the counter electrode and the reference electrode, respectively. In charge-discharge cycle tests, each negative electrode was charged at 50 mA/g for 3 h and discharged to 0.65 V vs.  $\text{Hg}/\text{HgO}$  at 100 mA/g in a 5 mol/L KOH aqueous solution. The resting time between charge and discharge was 10 min. When the capacity was calculated, the weight of the mixed Ni powder in the electrode was subtracted.

## 2 Results and Discussion

### 2.1 Effect of Al content on the temperature-time curves of combustion synthesis

Fig.1 shows the effect of Al content on the reaction temperature and adiabatic temperature under the thermal explosion of Mg and Ni. It can be seen that the reaction temperature of the compact increase slowly with increasing of Al content (Fig.1a), while the adiabatic temperature increases strongly (Fig.1b). When the Al content reaches  $x=0.5$ , the adiabatic temperature is even over 1000 °C. This is because melting of Mg and Al takes place first in the sample. With an increase in flow ability of the liquid, the contact area of the initial reactants becomes larger and larger, accelerating the reacting rate of the compact. This demonstrates that the reaction is much more drastic between Ni and Mg with the addition of Al.

### 2.2 Structure of $\text{Mg}_{2-x}\text{Al}_x\text{Ni}$ ( $x=0.1-0.5$ ) alloys

The XRD patterns of  $\text{Mg}_{2-x}\text{Al}_x\text{Ni}$  ( $x=0.1-0.5$ ) alloys are shown in Fig.2. A new phase appears in the product when Al is added to Mg-Ni system, and the relative amount of the new phase increases with increasing of Al content. The combustion-

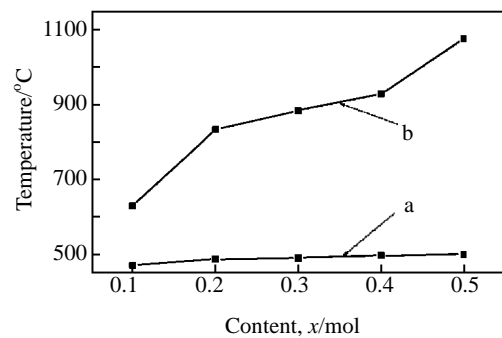


Fig.1 Effect of Al content on (a) reaction temperature and (b) adiabatic temperature

sion-synthesized  $\text{Mg}_{2-x}\text{Al}_x\text{Ni}$  alloy with  $x=0.5$  is composed of the new phase and elemental Mg, and the  $\text{Mg}_2\text{Ni}$  phase disappears entirely. Fig.3 shows the surface structure of the  $\text{Mg}_2\text{Ni}$  and  $\text{Mg}_{1.5}\text{Al}_{0.5}\text{Ni}$  alloys. It can be seen that there are a large number of defects on the surfaces of the alloys. The surface of  $\text{Mg}_{1.5}\text{Al}_{0.5}\text{Ni}$  alloy is smoother than that of  $\text{Mg}_2\text{Ni}$ . These features clearly give an evidence of eutectic reaction with liquid phase which happened in the combustion synthesis. The  $\text{Mg}_{1.5}\text{Al}_{0.5}\text{Ni}$  alloy phase has the cubic  $\text{Ti}_2\text{Ni}$  structure<sup>[9]</sup>. The bond lengths of Mg-Ni in  $\text{Mg}_{1.5}\text{Al}_{0.5}\text{Ni}$  are slightly longer than that in hexagonal  $\text{Mg}_2\text{Ni}$ , so the instability of its hydride is higher than  $\text{Mg}_2\text{Ni}$ .

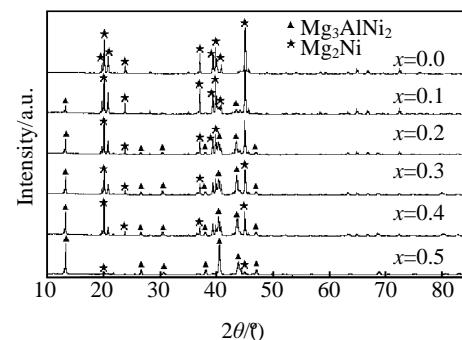


Fig.2 XRD patterns of  $\text{Mg}_{2-x}\text{Al}_x\text{Ni}$  ( $x=0.1-0.5$ ) alloys

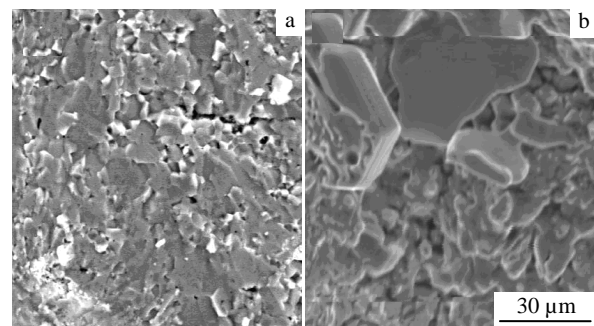


Fig.3 SEM images of  $\text{Mg}_{2-x}\text{Al}_x\text{Ni}$  alloy : (a)  $x=0$  and (b)  $x=0.5$

### 2.3 Discharge capacity and cycle lifetime

Electrochemical cycle data for  $Mg_{2-x}Al_xNi$  ( $x=0.1-0.5$ ) electrodes with various Al contents within 50 cycles are shown in Fig.4. The discharge current density was 100 mA/g. The discharge capacities of electrodes with compositions  $x=0.5$  is greatly increased, exceeding the results reported in Refs [9], and the  $Mg_{1.9}Al_{0.1}Ni$  electrode with  $x=0.1$  displays the poorest discharge capacity, which is still higher than that of the Al-free alloy (20 mAh/g). From the charging/discharging curves shown in Fig.4, it can be seen that the electrochemical capacities of the alloys decrease gradually. The degradation in the discharge capacity of  $Mg_{2-x}Al_xNi$  electrodes is so weak that about 10% of the maximum capacity is lost within 20 cycles; the loss of the capacity is far lower than that of the addition of  $Zr^{[10]}$ . After the addition of Al, the electrochemical capacity and cycle life increase strongly. On the one hand, owing to the high cooling rate in the combustion synthesis, high defect concentration and non-equilibrium structure exist in the alloys which has more activation<sup>[11]</sup>, as shown in Fig3, accelerating the hydrogen diffusion in and out the alloys and promoting the charge transfer reaction. At the same time, as mentioned above, the bond lengths of Mg-Ni in the new phase are larger, the unit cell volume is increased, indicating a larger hole size where hydrogen can be accommodated<sup>[12]</sup>. On the other hand, the addition of Al improves the anti-corrosion behavior to a certain extent due to the formation of an oxide layer of  $Al_2O_3$ , which prevents further oxidizing of Mg on the surface of alloys in alkaline solution. These results suggest that the addition of Al improves greatly the performance of alloys and promotes the practical application of these type alloys in a Ni-MH battery.

### 2.4 Effect of mechanical grinding on electrochemical properties of $Mg_{1.5}Al_{0.5}Ni$ alloy

Fig.5 shows the XRD patterns of combustion-synthesized  $Mg_{1.5}Al_{0.5}Ni$  alloys before and after 5 h ball milling. The results show that the width of the diffraction peaks of the powders increases after mechanical milling. The peak broadening means a refinement of the average crystallite size and an increase in the internal strain by mechanical deformation

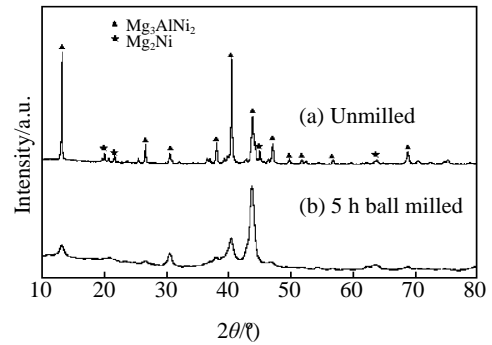


Fig.5 XRD patterns of  $Mg_{1.5}Al_{0.5}Ni$  alloys before and after mechanical grinding

during ball-milling. The electrochemical properties of the  $Mg_{1.5}Al_{0.5}Ni$  alloy before and after mechanical grinding are shown in Fig.6. It can be seen that the unmilled  $Mg_{1.5}Al_{0.5}Ni$  alloy electrodes can be only activated after twenty charge/discharge cycles, whose maximum discharge capacity is 88.7 mAh/g. However, the ball milled  $Mg_{1.5}Al_{0.5}Ni$  alloy electrodes can be fully activated within three cycles, whose maximum discharge capacity reaches 151.3 mAh/g. This is because the mechanical grinding results in the decrease of the particle size and the augmentation of the defect density of the materials. The refinement of the crystallite size causes an increase of the grain boundaries that facilitate hydrogen diffusion in the matrix, and an abundance of defects act as nucleation sites for the hydride phase, which may considerably improve the diffusion of hydrogen atoms in the electrode materials<sup>[13]</sup>. Although the maximum capacity of the milled alloy electrodes increases strongly, it only maintains at 40% of the maximum capacity after 40 cycles, and that of the unmilled alloy electrodes is 60%. The ball-milling raises the maximum electrode capacity, but does not improve the cyclic stability. The reason is that the cyclic stability in milled alloy electrodes is lower than that in unmilled because mechanical

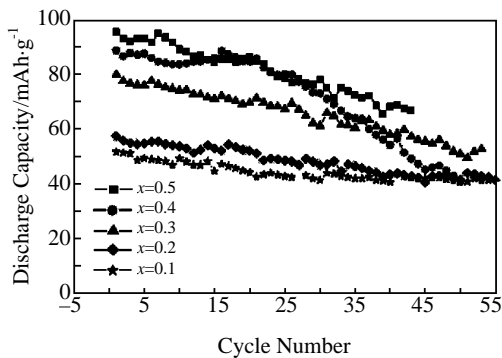


Fig.4 Relationship between discharge capacity and cycle number for  $Mg_{2-x}Al_xNi$  ( $x=0.1-0.5$ ) alloys

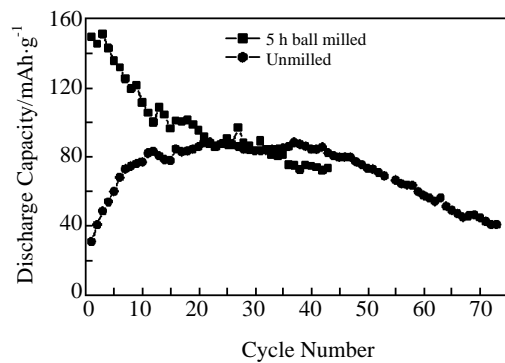


Fig.6 Electrochemical capacity of  $Mg_{1.5}Al_{0.5}Ni$  alloy before and after mechanical grinding

grinding will break the surface protective layer of  $\text{Al}_2\text{O}_3$ . A new metal hydride surface appears and is then rapidly oxidized, so it is not effective to protect the master alloy resulting in a progressive decrease in the cycle life. Sakai et al<sup>[14]</sup> pointed out that Al could precipitate at the grain boundary in the form of  $\text{AlNi}_3$  preferentially for a Mm-deficient  $\text{AB}_5$  alloy. This compound is easily dissolved in 6 mol/L KOH solution, breaking the protective layer and degrading the cyclic stability. X-ray diffraction pattern confirms that  $\text{Al}_2\text{O}_3$  does exist on the surface of unmilled  $\text{Mg}_{1.5}\text{Al}_{0.5}\text{Ni}$  after 50 charge-discharge cycles (Fig7).

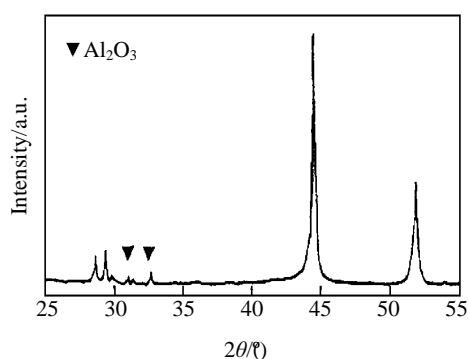


Fig.7 XRD pattern of unmilled  $\text{Mg}_{1.5}\text{Al}_{0.5}\text{Ni}$  after 50 cycles at discharge current density of 100 mA/g.

### 3 Conclusion

1) The pure Mg-Al-Ni ternary hydrogen-storage alloys can be synthesized by combustion synthesis method.

2) With increasing of Al addition, the adiabatic temperature of the reaction increases greatly, and the reaction becomes very drastic.

3) A new phase  $\text{Mg}_3\text{AlNi}_2$  appears in the product, and the relative amount of the new phase increases as increasing of Al content. The new phase has excellent electrochemical properties, the capacity of the alloys increases with the increase of

the amount of the new phase.

4) There are a large number of defects formed on the surface of the alloys.

5) Addition of Al not only increases the electrochemical capacity, but also prevents the alloys electrode from being further oxidized, and prolongs the cycle life of the alloy to a great extent.

6) The mechanical grinding is beneficial to improve activation behavior and the maximum electrode capacity, but does not improve the cyclic stability.

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## $\text{Mg}_{(2-x)}\text{Al}_x\text{Ni}$ 的燃烧合成及其电极性能

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**摘要:**采用燃烧合成法合成了三元镁基储氢合金  $\text{Mg}_{2-x}\text{Al}_x\text{Ni}$  ( $x=0.1\sim 0.5$ ), XRD 衍射研究表明合成产物中出现了具有  $\text{Ti}_2\text{Ni}$  型立方结构的新相, SEM 结果显示合金表面存在大量缺陷。Al 元素部分替代 Mg 对  $\text{Mg}_2\text{Ni}$  电化学性能影响的研究表明:  $\text{Mg}_{2-x}\text{Al}_x\text{Ni}$  合金的电化学容量和循环寿命明显优于无 Al 的  $\text{Mg}_2\text{Ni}$ , 这归因于新相  $\text{Mg}_3\text{AlNi}_2$  的结构特点及形成的  $\text{Al}_2\text{O}_3$  保护层。此外, 对合成产物的进一步的机械研磨有助于改进合金的活化行为及电极容量, 但无助于循环能力的提高。

**关键词:**三元储氢合金;  $\text{Mg}_{2-x}\text{Al}_x\text{Ni}$  燃烧合成; 机械研磨; 电极性能

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