Influence of Ball-milling with Ni Powder on the Phase Structure and Electrochemical Hydrogen Storage Properties of $Mg_{17}Al_{12}$ Alloy

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Abstract: The phase structures and electrochemical properties of the as-cast $Mg_{17}Al_{12}$ alloy and ball-milled $Mg_{17}Al_{12}$ + x% Ni composites (x = 50, 100, 150, 200) have been investigated. The results show that the phase structures and discharge capacities of the $Mg_{17}Al_{12}$-Ni composites depend greatly on the amount of Ni powder. The more Ni powder introduced, the more advantageous for the formation of amorphous structure, and the larger discharge capacity obtained. After ball-milling for 120 h, the $Mg_{17}Al_{12}$ + 200% Ni composite exhibits a high discharge capacity of 658.2 mAh·g^{-1} (barring the weight of Ni powder) at 303 K.

Key words: hydrogen storage alloy; $mg_{17}Al_{12}$; ball-milling; electrochemical properties; phase structure
CLC number: TG139 **Document code:** A **Article ID:** 0529-6579 (2007) S1-0086-03

Bouaricha et al[1] reported that $Mg_{17}Al_{12}$ could dehydrogenate and rehydrogenate reversibly, hydrogenation led to the formation of MgH_2 and Al, and $Mg_{17}Al_{12}$ was formed back again upon dehydrogenation. The theoretical hydrogen storage capacity of $Mg_{17}Al_{12}$-H system is higher than that of Mg_2NiH_4. Moreover, it was found that the electrochemical cycle life was improved by the substitution of Al for Mg in Mg_2Ni alloy[2]. However, the electrochemical properties of $Mg_{17}Al_{12}$ have not been reported heretofore. In the present study, $Mg_{17}Al_{12}$ + x% Ni composites (x = 50 ~ 200) were prepared by ball-milling of as-cast $Mg_{17}Al_{12}$ alloy with different amounts of Ni powder. Their phase structures and electrochemical properties were investigated.

1 Experiment

The as-cast $Mg_{17}Al_{12}$ was prepared by induction melting method. The ingot was mechanically pulverized to less than 74 μm in diameter. Then, the powders were mixed with x% (x = 50, 100, 150, 200) metallic Ni powder, and milled with stainless steel balls (Ø = 10 mm) in a stainless steel vessel under the argon atmosphere by using planetary ball-miller at a speed of 350 rpm for 120 h. The ball-to-powder weight ratio was 30:1. The phase structure of the samples was identified by XRD with Cu Kα radiation. The electrochemical measurements were the same as our previous paper[3].

2 Results and discussion

The XRD patterns of the as-cast $Mg_{17}Al_{12}$ alloy and $Mg_{17}Al_{12}$ + x% Ni (x = 50 ~ 200) composites are shown in Fig. 1. The result shows that the as-cast $Mg_{17}Al_{12}$ alloy has a single $Mg_{17}Al_{12}$ phase. The diffraction peaks of the ball-milled $Mg_{17}Al_{12}$ + x wt.% Ni composites become weakened and broadened as x increases from 50 to 200, reflecting a decrement of average crystallite size and an increment of atomic disordering. For the ball-milled composite with x = 50 and 100, all of the peaks corresponding to $Mg_{17}Al_{12}$ have almost disappeared, and some broadened Mg peaks appeared. It indicates that there is a phase transformation from polycrystalline to amorphous or nanocrystalline structure. When x reaches 150, the main phase of composite is amorphous AlNi with Ni as a minor phase[4]. All the diffraction peaks become more weakened and broadened as x = 200, we can come to the conclusion that the more Ni powders added, the easier to form the amorphous structure for the $Mg_{17}Al_{12}$-Ni composite. However, some small Ni peaks still remain as x increases from 50 to 200. It is probably due to the small Ni particles

①收稿日期：2007-01-10
基金项目：国家高技术研究发展计划资助项目（2006AA05Z144）；国家自然科学基金资助项目（50571089，50471042）
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are present on the amorphous Mg-based composite during the ball-milling process[3].

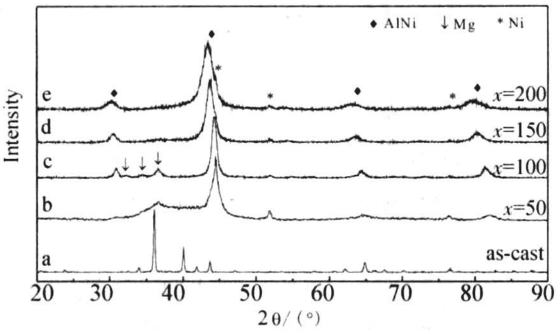

Fig.1 XRD patterns of the as-cast $Mg_{17}Al_{12}$ alloy and $Mg_{17}Al_{12}$ + x wt.% Ni composites

The discharge curves at first cycle for the as-cast $Mg_{17}Al_{12}$ and $Mg_{17}Al_{12}$ + x% Ni (x = 50~200) composites are shown in Fig.2. The result shows that the as-cast $Mg_{17}Al_{12}$ has a low discharge capacity of about 10 mAh·g^{-1}. In contrast, the discharge capacities of $Mg_{17}Al_{12}$ ball-milled with Ni powder are high. With increasing x from 50 to 200, the discharge capacity increases from 41.3 mAh·g^{-1} to 658.2 mAh·g^{-1}. The amorphous structure of the $Mg_{17}Al_{12}$-Ni composites is the main reason to obtain high discharge capacities[3]. The Ni particles are beneficial for the formation of amorphous Mg-Al-Ni composite and have good electro-catalytic activity, resulting in a significant increase of the electrochemical capacity[5]. Moreover, the average crystallite size decreases gradually with the increase of Ni content in the ball-milling process. Thus can increase the specific surface area and improve the diffusion of hydrogen in the composite.

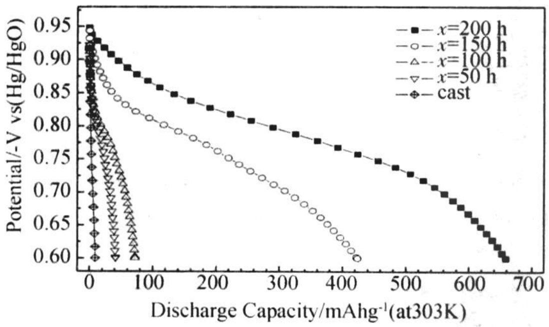

Fig.2 The discharge curves at first cycle for the as-cast $Mg_{17}Al_{12}$ and $Mg_{17}Al_{12}$ + x% Ni composites

Fig.3 shows the cycling stabilities of the $Mg_{17}Al_{12}$ + x% Ni (x = 50~200) composites. It can be seen that all the composites ball-milled with Ni powder reach the maximum discharge capacities at the first cycle, indicating a high electrochemical activity caused by ball-milling with Ni powders. However, the discharge capacities of all the electrodes decrease with cycling going on. The capacity retention rates after 10 cycles for the $Mg_{17}Al_{12}$ + x% Ni (x = 50, 100, 150, 200) composites are 47.0, 56.0, 42.4 and 50.7%, respectively. The bad cycling life of the ball-milling composites is attributed to their amorphous structure and high surface-to-volume ratio, which accelerate the corrosion rate of Mg-based composite by electrolyte solution[6].

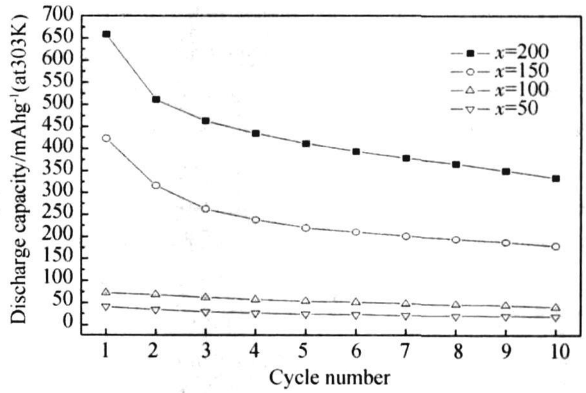

Fig.3 Cycling stabilities of $Mg_{17}Al_{12}$ + x wt.% Ni composites

3 Conclusion

The amorphous $Mg_{17}Al_{12}$ + x% Ni electrode composites can be synthesized by mechanical ball-milling with Ni powder. The more Ni powders added, the more advantageous for the formation of $Mg_{17}Al_{12}$-Ni amorphous structure. With increasing the Ni content from 50 to 200, the discharge capacity increases from 41.3 to 658.2 mAh·g^{-1}.

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硅提纯的热力学基础

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摘 要：随着光伏产业的发展，硅作为生产晶体硅片太阳电池的基础材料，其应用已经超过了 90%。从热力学基础对提纯硅的冶金过程进行讨论，其中包括酸浸、真空精炼和定向凝固，并基于热力学相图对这一过程的可行性进行了讨论。除此之外，通过金相分析对过程可行性进行证明。目的在于寻找一种区别于西门子法的低成本的生产太阳能级硅的工艺过程。

关键词：硅提纯；太阳能级硅；热力学
中图分类号：O613.72; TF114

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添加镍粉球磨对 $Mg_{17}Al_{12}$ 合金相结构及电化学储氢性能的影响

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摘 要：研究了 $Mg_{17}Al_{12}$ 铸态合金和 $Mg_{17}Al_{12}$ + x% Ni (x = 50 ~ 200) 球磨复合物的相结构和电化学性能。结果表明，$Mg_{17}Al_{12}$-Ni 复合物的相结构和放电容量主要取决于复合物中镍粉的加入量。加入的镍粉越多，越利于非晶结构的形成，其放电容量就越大。球磨 120 h的 $Mg_{17}Al_{12}$ + 200% Ni复合物在 303 K的放电容量高达 658.2 mAh·g^{-1} (除去镍粉的质量)。

关键词：储氢合金；$Mg_{17}Al_{12}$；球磨；电化学性能；相结构
中图分类号：TG139