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Properties of $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy ball-milled with nanocrystalline $LaNi_5$ powder

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Abstract

A type of composite powder was prepared by ball-milling $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy with a small amount of (2 wt%) nanocrystalline $LaNi_5$ which was synthesized by mechanical alloying. SEM and EDX results show that the surface of $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy was coated with fine nanocrystalline $LaNi_5$ particles after ball-milling. Electrochemical measurement revealed that electrochemical activity of this composite powder was higher than that of as-cast $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ powder. The mechanism of this improvement was also discussed.

Keywords: Zr-Based alloy; AB_2 Laves phase; Nanocrystalline; $LaNi_5$; Electrochemical property

1. Introduction

In recent years, Zr-based AB_2 type Laves phase alloys have been of great interest. They are thought to be the second generation promising electrode materials for nickel–metal hydride batteries because they can potentially offer higher capacities and longer cycle lifetimes [1]. However, their electrochemical activation behavior is very poor because of the thin but dense and passive oxide films on the surfaces of alloys. In order to solve this problem, many efforts have been focused on surface modification of the alloys [2–5].

Very recently, mechanical milling was employed to modify the surface of Zr-based Laves alloys. Chen et al., reported that the $Zr_{0.5}Ti_{0.5}(V_{0.25}Mn_{0.15}Ni_{0.6})_2$ alloy ball-milled with 10 wt% Ni powder for 8 h in high-energy planetary mill exhibited rapid activation, good high-rate dischargeability and long cycle life [6]. Sun et al., also found that the activation process for the $Zr(Cr_{0.4}Ni_{0.6})_2$ alloy electrode was apparently shortened when coated with nickel particles on its surface by high-energy ball-milling [7].

In previous work [8], we found that the nanocrystalline $LaNi_5$ synthesized by mechanical alloying was of high electrochemical activity. In this study, the as-cast $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy was ball-milled with this nanocrystalline $LaNi_5$ powder. The electrochemical activation behavior of the composite powder prepared by this method was investigated.

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2. Experimental details

The $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy was prepared in an arc-melting furnace under argon atmosphere on a water-chilled copper hearth. The purity of the metals was above 99 wt%. The ingot (about 20 g) was turned over and remelted four times. The as-cast alloy was mechanically pulverized into small particles (about 1 mm in size) in atmosphere. The preparation of nanocrystalline $LaNi_5$ was the same as described in previous study [8].

Two types of electrode powders were prepared in this study. For convenience, the powders are respectively named powder A and powder B. Powder A was prepared by grinding $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy particles under protection of argon using a planetary mill with ball-to-powder ratio of 10:1, at a speed of 150 rev/min for 0.5 h. Powder B was prepared by grinding the mixture of $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy particles and 2 wt% nanocrystalline $LaNi_5$ powder. The grinding condition is the same as described above.

For preparation a negative electrode, approximately 0.8 g alloy powder was mixed with 1 wt% carbon black, about 0.08 g 3 wt% polyvinyl alcohol solution and then compacted into a porous nickel substrate. After being dried, the substrate was pressed under a pressure of 5 MPa.

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The properties of the as-prepared negative electrode were examined at room temperature (20°C) using a sintered nickel electrode with a large capacity as the counter electrode and a Hg/HgO electrode as the reference electrode. The electrolyte was a 6 M KOH solution. The electrode was charged at 30 mA g^{-1} for 12 h and discharged at 30 mA g^{-1} after 5 min resting time. The end discharging was set to −0.74 V with respect to the reference electrode.

Phase analysis of the powders was performed by X-ray diffraction (XRD). Transmission electron microscope (TEM) and scanning electron microscope (SEM) were employed to characterize the microstructure of the powders.

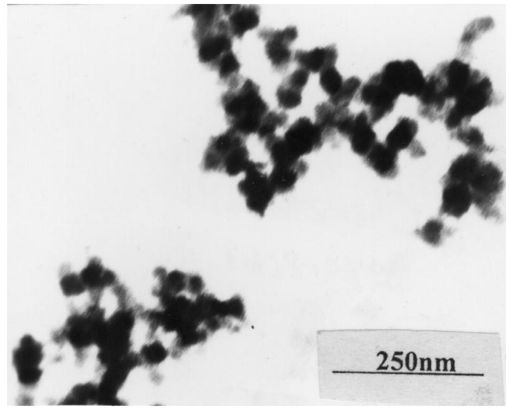

Fig. 2. TEM image of nanocrystalline $LaNi_5$.

3. Results

3.1. Characterization of nanocrystalline $LaNi_5$

After ball-milling for 8 h, the mixture of nickel powder and lanthanum powder was characterized by XRD and TEM. As shown in Fig. 1(a), the XRD pattern shows the clear and prominent peaks of $LaNi_5$, and exhibits broadening of the peaks which is a characteristic of nanocrystalline materials. In many cases, the materials produced by mechanical alloying are amorphous. However, in this study, crystalline $LaNi_5$ was formed directly from La and Ni in mechanical alloying process. This indicates that $LaNi_5$ tends to crystallize.

The TEM result also manifests its nanocrystalline structure, as shown in Fig. 2. The average grain size is about 50 nm.

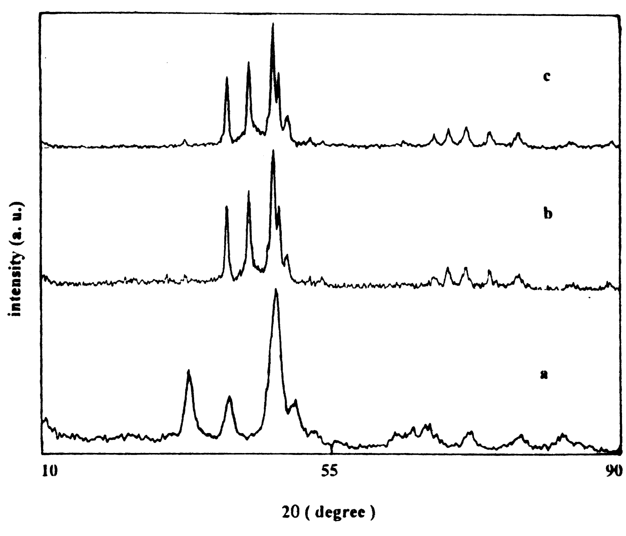

Fig. 1. XRD pattern of nanocrystalline $LaNi_5$ (a), powder A (b), and powder B (c).

3.2. Characterization of $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy powders

Fig. 1(b) shows that the as-cast $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy has hexagonal C_{14} type Laves phase structure. Fig. 1(c) is the XRD pattern of the $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy ball-milled with 2 wt% nanocrystalline $LaNi_5$ for 0.5 h. It can be seen that $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy still maintains its crystalline state. Because the amount of $LaNi_5$ added is very small (2 wt%), the peaks of $LaNi_5$ cannot be seen in this diffraction pattern.

Fig. 3 shows the SEM images of powder A and powder B. It demonstrates that the surface of the as-cast $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy particle is relatively smooth and there are a few small particles on it. After ball-milling with 2 wt% nanocrystalline $LaNi_5$, the surface of alloy became rougher and there were a large amount of very fine particles (below 500 nm) evenly coated on its surface. These particles are so fine that it is difficult to analyze their composition.

Fig. 4 gives the SEM micrograph and EDX image of powder B after being mixed with 1 wt% carbon black. The alloy surface was also coated with fine carbon particles and became more complex, as shown in Fig. 4(a). From Fig. 4(b) we can see that the element lanthanum was very evenly dispersed on the surface of $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy. This indicates that nanocrystalline $LaNi_5$ was very evenly coated on the surface of $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy.

3.3. Activation behavior of the electrodes

The discharge capacity of the electrode vs. cycle number is shown in Fig. 5, it can be seen that the capacity of powder A slowly increased with cycling, eventually giving a capacity of 305 mAh/g after 10 charge–discharge cycles. However, the electrode prepared with powder B shows rapid activation and reaches its highest capacity of 303 mAh/g at the sixth charge–discharge cycle. So ball-mil-

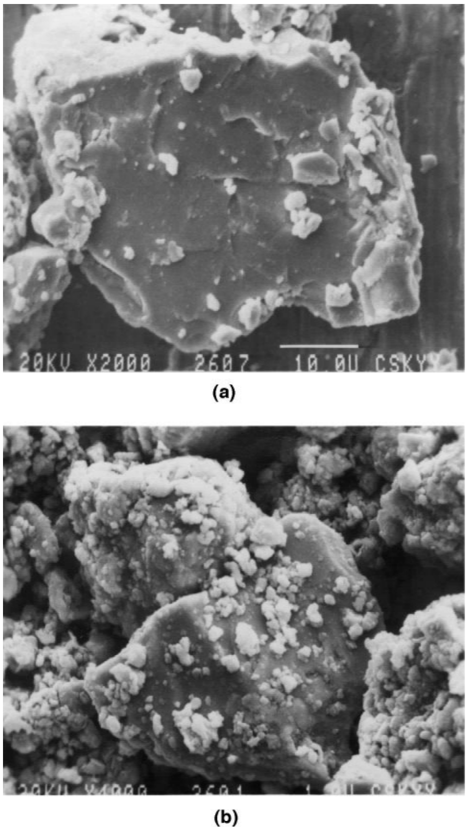

Fig. 3. SEM image of powder A (a), powder B (b).

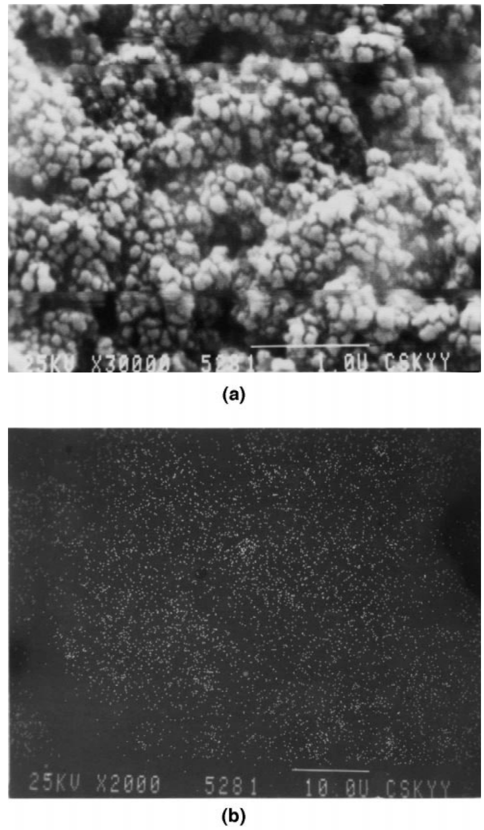

Fig. 4. SEM micrograph (a) and EDX image of Lanthanum (b) of powder B.

ling of $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy with nanocrystalline $LaNi_5$ powder greatly improves the activation behavior of $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy.

4. Discussion

XRD reveals that $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy maintains its crystalline state after ball-milling with 2 wt% nanocrystalline $LaNi_5$ powder for 0.5 h. The amount of nanocrystalline $LaNi_5$ is so small that no $LaNi_5$ peaks appear in XRD pattern of powder B. But because $LaNi_5$ shows a marked tendency to crystallize in the process of mechanical alloying, we think nanocrystalline $LaNi_5$ maintains its crystalline state too after this medium speed ball-milling (150 rev/min) for 0.5 h.

Further SEM observation shows that along with the formation of fresh surface, a large amount of very fine particles coated on the surface of alloy after ball-milling. EDX result shows that lanthanum metal was evenly dispersed on the surface of $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy. We conclude that $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy was evenly coated with very fine nanocrystalline $LaNi_5$ particles after ball-milling.

After removal from the steel container of planetary mill, the ball-milled powder was exposed to atmosphere. Because the surface of powder B was coated with nanocrystalline $LaNi_5$, the $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy was prevent from being oxidized somewhat. On the contrary, the surface of powder A was oxidized and covered by the passive oxide film after exposure to atmosphere. In a word,

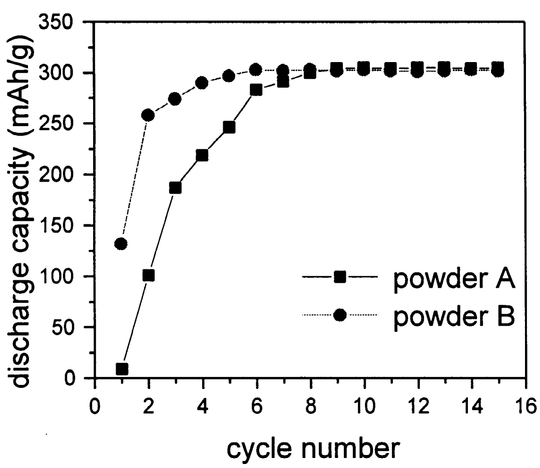

Fig. 5. The capacity of electrode vs. cycle number (20°C).

$Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy obtained a relatively active surface state after ball-milling with nanocrystalline $LaNi_5$.

In the literature, the improvements of the activation of the Zr-based Laves alloys were explained on the basis of the model that the nickel-rich surface not only hinders the accumulation of Zr on the alloy surface, but also catalyzes the electrode reaction. In this study, the activation behavior was improved after ball-milling with nanocrystalline $LaNi_5$. Because nanocrystalline $LaNi_5$ is of very high electrochemical activity [8], we assume that the fine nanocrystalline $LaNi_5$ particles adhered to the surface of $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy work as active site in the electrochemical reaction. During charge–discharge cycles, *H* atoms and $LaNi_5$ can easily react. Because there is no passive oxide film on interface of nanocrystalline $LaNi_5$ and $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy, *H* atoms can pass through it and enter or exit $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy rather than overcome the passive oxide film. So the activation behavior is greatly improved.

5. Conclusion

By means of ball-milling with a small amount of nanocrystalline $LaNi_5$ for 0.5 h, $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy was successfully coated with fine nanocrystalline $LaNi_5$ particles. The electrochemical activation of this composite is much higher than that of the $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy powder without nanocrystalline $LaNi_5$. The nanocrystalline $LaNi_5$ on the surface was thought to work as active site which caused the improvement of activation behavior of the alloy.

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