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Modification of a rapidly solidified hydrogen storage electrode alloy by ball-milling with Co_3Mo ☆

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Abstract

Rapidly solidified hydrogen storage alloys were reported to have good cycle life, but they are very difficult to activate, especially for AB_2 type alloys. In this study, a $Zr_{0.9}Ti_{0.1}(Ni_{0.57}V_{0.1}Mn_{0.28}Co_{0.05})_{2.1}$ alloy was prepared by melt-spinning followed by ball-milling with Co_3Mo additive in order to improve its kinetic characteristics. The experimental results showed that the alloy exhibited a much improved activation performance as well as electrochemical capacity after 2 hours milling. Cyclic voltammetry and electrochemical impedance experiments also showed that ball-milling of the alloy with Co_3Mo could improve the surface activation property to a great extent. This can be attributed to the catalytic effect of Co_3Mo, which had a much closer contact to the alloy powders after ball-milling, on the hydrogen oxidation. However, long time milling could decrease the capacity gradually due to the further amorphization of the alloy.

Keywords: Metal–hydride electrodes; Ni–MH batteries; Ball-milling treatment

1. Introduction

One of the effective ways to enhance the kinetic property, discharge capacity and cycle life of hydrogen storage electrode alloys is to make the electrode by mixing the alloy powders with some pure metal or metal oxide additives. Normally there are two ways to make it:

1. Directly mixing the alloy with the metal or metal oxide powders to make the electrode [1–3];
2. Milling the above mixed powders under protective atmosphere for some time and then making the electrode [4,5].

Since it can make a much closer contact between the alloy and the additive and some new metallic compounds may be formed at the same time, the second way mentioned above is more effective than the first one.

Rapidly solidified hydrogen storage alloy has the advantage of fine grains, homogeneous composition and long cycle life. However, the lower initial electrochemical activity is a deficiency of this technique, especially for the AB_2 type alloys which are intrinsically difficult to be activated. The reason for low activity could be the high amorphous extent and internal stress on the alloy surface caused by rapid solidification, which results in a bad electrochemical activity of the alloy and difficulty for activation [6]. Therefore, the key to improve the kinetic property of the alloy is to modify its surface. Good results have been reported to activate the rapidly solidified AB_5 type alloys by chemical treatment [7,8]. In the present work, Co_3Mo, an excellent electrocatalytic material [9], was used as an additive to ball-mill with rapidly solidified $Zr_{0.9}Ti_{0.1}(Ni_{0.57}V_{0.1}Mn_{0.28}Co_{0.05})_{2.1}$, an AB_2 type alloy, in order to improve the kinetic property of this hydrogen storage electrode alloy.

2. Experimental details

2.1. Preparation and ball-milling of Co_3Mo with $Zr_{0.9}Ti_{0.1}(Ni_{0.57}V_{0.1}Mn_{0.28}Co_{0.05})_{2.1}$

Co_3Mo alloy was prepared in a vacuum arc melting furnace and poured into a water-cooled copper crucible by using pure Co and Mo (purity above 99%) with atomic ratio of 3:1. The as-cast alloy was annealed at 880°C for 4 hours in a vacuum condition of 10^{-2}–10^{-3} Pa. The ingot was crushed into about 1 mm particles and then ball-milled into powders less than 20 μm.

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Host $Zr_{0.9}Ti_{0.1}(Ni_{0.57}V_{0.1}Mn_{0.28}Co_{0.05})_{2.1}$ was prepared in a 25 kg capacity vacuum induction melting furnace by melting pure metals (purity above 99%). The ingot was crushed into coarse particles, remelted and then rapidly solidified into thin ribbons in a 5T Advanced Melt Spinner (made by Marko Materials, Inc.). The ribbons were finally milled into powders below 200 mesh, named as QAB_2—4 in the text.

Co_3Mo powders and QAB_2—4 were mixed in the weight ratio of 1:9 and ball-milled in a planetary-type ball-miller under Ar atmosphere. The milling time was 0.5, 1, 2, 5 and 10 hours, respectively.

2.2. Measurement and analysis

XRD analysis was conducted in a Rigaku D/max-γ_A type X-ray diffractometer. SEM observation was performed with an S-360 type SEM made by Cambridge Instruments Ltd. TEM observation was made on a Philips EM420.

The discharge capacity was measured on a BT-2043 battery testing system made by Arbin Company, USA. The process of measurement was as follows:

1. Total weight of 3.00 g powders of hydrogen storage alloy and Ni were mixed in the ratio of 1:3;
2. The powders were cold-pressed into a 25 mm diameter electrode disc at a pressure of 624 MPa;
3. The disc was clamped between two $NiOOH/Ni(OH)_2$ electrodes with excessive capacity, and then put into a beaker with 6 M KOH solution;
4. The measurement was conducted at 298 ± 1 K;
5. The sample was charged at a current density of 60 mA/g for 8 hours, rested for 5 minutes, and then discharged at the same current density to a cut-off voltage of 1 V.

The cyclic voltammograms measurement was carried out by using a potentiostat/galvanostat (EG&G Princeton Applied Research M273). The sample was made by cold-pressing 0.50 g powders of hydrogen storage alloy and Ni (1:1 weight ratio) into a 10 mm diameter disc with a pressure of 624 MPa. The pressed disc was used for the cyclic voltammograms measurement in a three-electrode system after several cycles of activation. The potential scanning range was from -1.1 V to -0.4 V vs. HgO/Hg at a scanning rate of $5\ mV\ s^{-1}$

The electrochemical impedance measurement was made under open-circuit conditions by use of a M273 potentiostat/galvanostat and a 5208 two phase lock-in analyzer. The scanning frequencies were from 0.01 Hz to 10 kHz. The amplitude of perturbation was 5 mV in the high frequency region (10 kHz–6.3 Hz) and 10 mV in the low frequency region (6.3 Hz–0.01 Hz). The preparation of sample was the same as that for the cyclic voltammograms measurement.

3. Results and discussion

3.1. XRD analysis

XRD patterns of samples before and after mixing of QAB_2—4 and Co_3Mo, as well as the mixtures with different ball-milling time, are shown in Fig. 1. It can be seen from the figure that the diffraction peak becomes wider with increasing milling time and an obvious widening peak occurs when the milling time is over 10 hours.

3.2. SEM observation

Fig. 2 shows the SEM photographs of samples before and after mixing of QAB_2—4 and Co_3Mo, as well as the mixtures with different milling time. It can be seen from Fig. 2 that boundaries between QAB_2—4 and Co_3Mo powders can not be clearly identified after 2 hours milling, which indicates that contact between the two kinds of powders gets closer as the milling time increases.

3.3. TEM observation

Photographs of TEM observation and the selected area electron diffraction (SAED) are shown in Fig. 3 for those samples of QAB_2—4 and Co_3Mo mixed powders before milling, after 2 hours and 10 hours milling. It can be seen from the figure that the dominant phases are poly-crystalline for samples before milling and still poly-crystalline

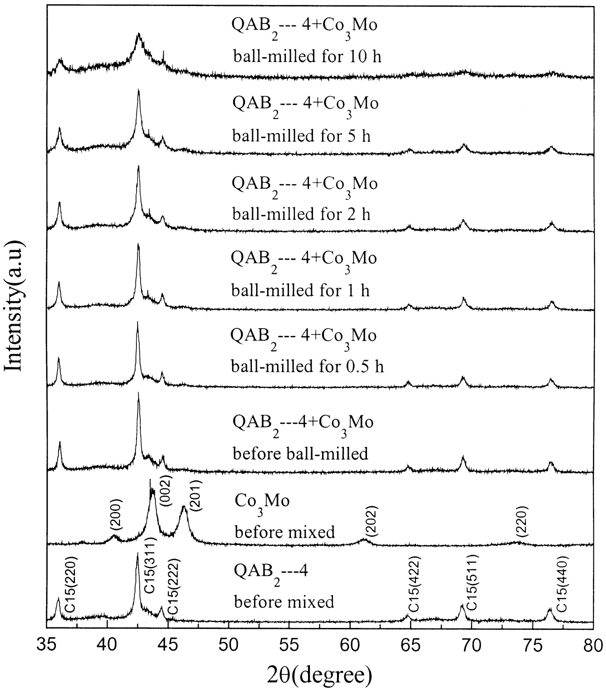

Fig. 1. XRD patterns of QAB_2—4 and Co_3Mo before and after mixing, and the mixture before milling and after milling for different times, respectively.

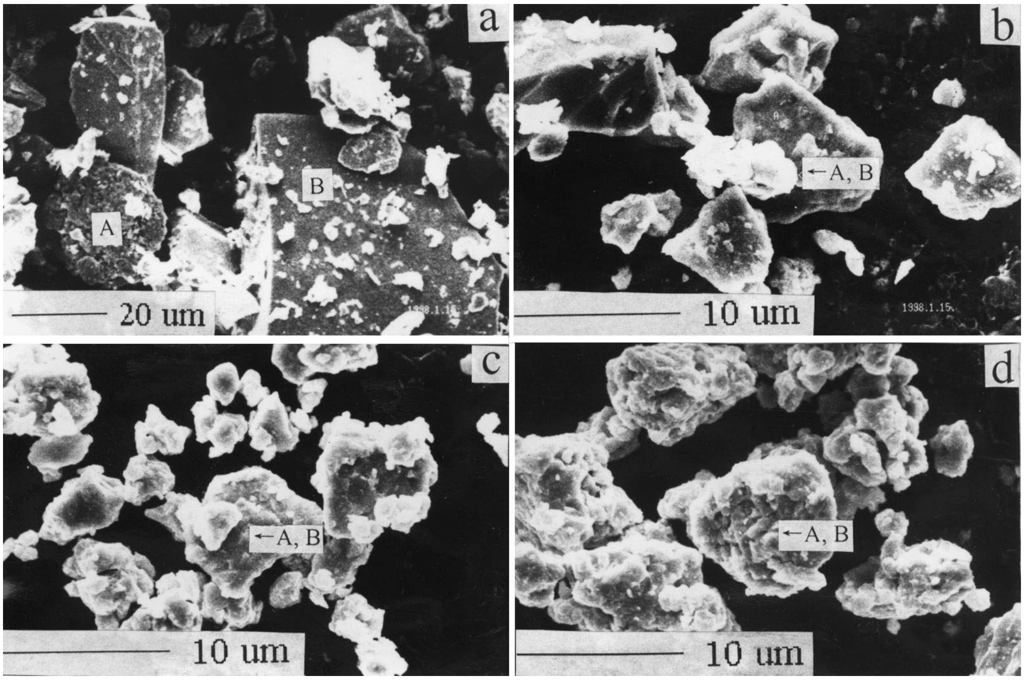

Fig. 2. SEM images of the mixture of QAB_2—4 and Co_3Mo before milling and after milling for different time. a) before milling; b) milling for 0.5 h; c) milling for 2 h; d) milling for 10 h. The signs 'A' and 'B' represent Co_3Mo and QAB_2—4, respectively.

with some amorphous phases after 2 hours milling. However it is difficult to find crystalline powders after 10 hours milling and the SAED pattern becomes a typical amorphous ring, which indicates that most of the mixed powders have transformed into the amorphous.

3.4. Discharge capacity

Curves of discharge capacity vs. cycle number for samples of QAB_2—4 and Co_3Mo mixed powders before milling and after different milling times are shown in Fig. 4. It can be concluded from the figure that the activity of the electrode alloy is improved by addition of Co_3Mo; the activity is further improved by milling; 2 hours milling reaches the highest activity; and the activity becomes decreasing with longer milling time. The main reason for the above results can be attributed to the strong electrocatalytic activity of Co_3Mo that plays a well catalytic role in the processes of anodic oxidation and cathodic reduction of hydrogen. The electrochemical activity was obviously enhanced even though QAB_2—4 and Co_3Mo were simply mixed. After milling, the contact of two kinds of alloys gets much closer and the reaction resistance becomes much less, which results in a more effective discharging. However too long a milling time increases the amorphous formation. As shown in Figs. 1 and 3, most of the mixed powders became amorphous after 10 hours milling, then the capacity for both hydrogen accommodation and hydrogen diffusion were decreased, which had a bad influence on both the hydrogen storage capacity and the kinetic property.

3.5. Measurement of cyclic voltammograms and impedance

Cyclic voltammograms measurement curves are shown in Fig. 5 for samples of QAB_2—4 and Co_3Mo powders before mixing, after mixing, after 2 hours and 10 hours milling. The height of the oxidation/reduction peak shown in the figure (represented by current) reflects the kinetic property of electrode and the peak area indicates the capacity of hydrogen absorption and desorption. From Fig. 5 it can be clearly seen that either the height or area of the peaks in the range of -700 and -600 mV is well consistent with the variation of electrode activity as well as discharging capacity mentioned above, i.e., 2 hours milling of QAB_2—4 and Co_3Mo powders reaches the highest activity and the longer milling time results in a decrease of the activity.

Impedance spectra are shown in Fig. 6 for those samples of QAB_2—4 and Co_3Mo powders before mixing, after mixing, after 2 hours and 10 hours milling. The Cole–Cole plots are composed of two semicircles, of which the smaller semicircle in the high frequency region is mainly related to the resistance and capacitance between the current collector and the pellet powder, which is almost unchanged, while the larger semicircle in the low frequency region is attributed to electrode reactions and double-layer capacitance on the alloy powders [10]. From Fig. 6 it can be seen that the surface electrochemical reaction resistance is very large for QAB_2—4 that was not treated. After mixing with Co_3Mo, the surface electrochemical activity of the electrode was enhanced and the

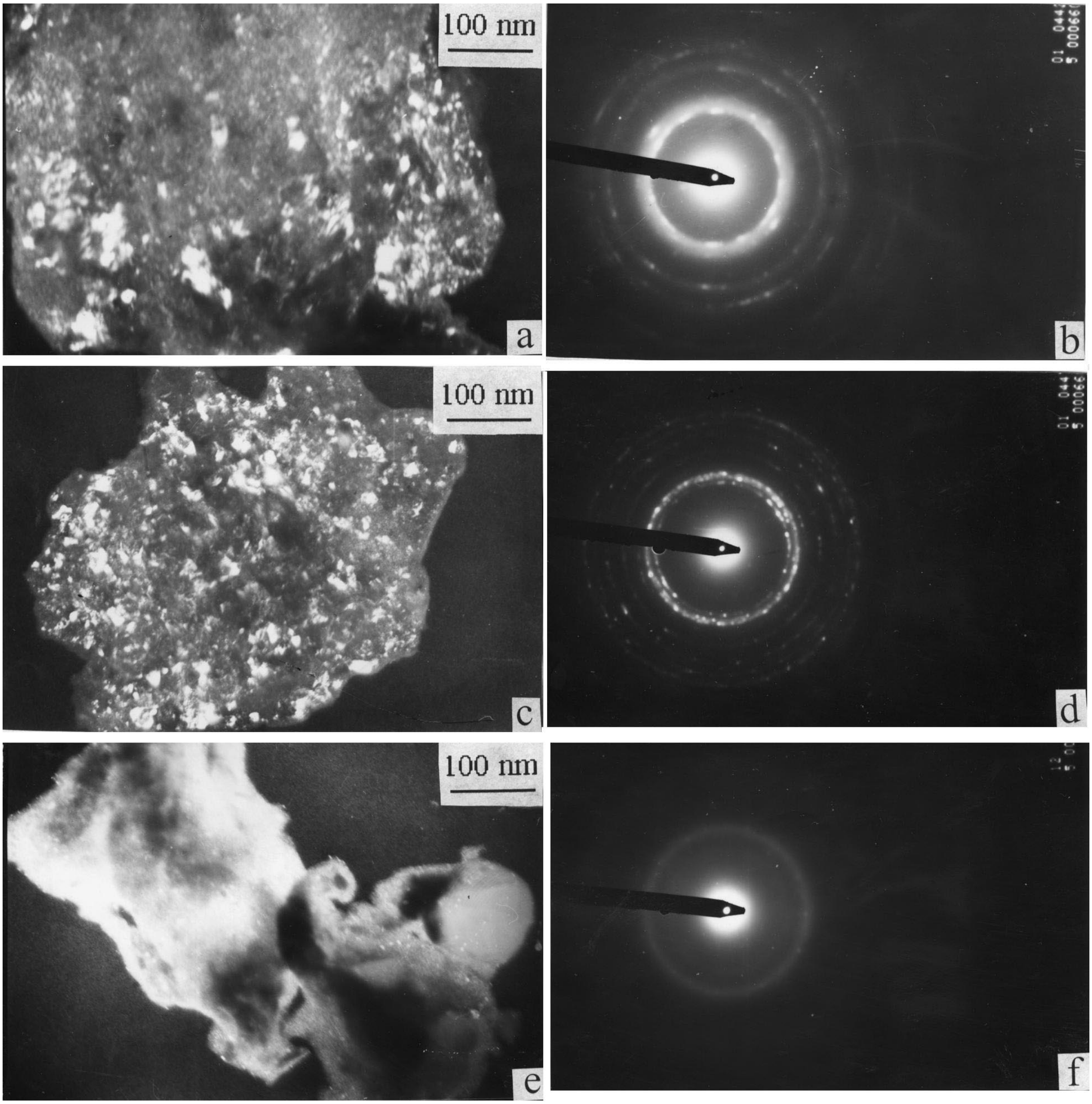

Fig. 3. Dark-field TEM images and relevant SAED patterns of the mixture of QAB_2—4 and Co_3Mo before milling and after milling for different times. a, b) before milling; c, d) milling for 2 h; e, f) milling for 10 h.

reaction resistance was reduced. The activity of the ball-milled electrode was further improved and the reaction resistance was largely decreased. However, longer milling time results in an increase of surface reaction resistance, which is probably due to the change of surface state of Co_3Mo, lowering the electrocatalytic activity after a long time milling.

4. Conclusion

The kinetic property of a rapidly solidified AB_2 type hydrogen storage alloy is greatly improved by ball-milling with Co_3Mo, an electrocatalytic material. The activity of the electrode increases with increasing milling time in a certain time range. Too long milling produces a bad influence on both the hydrogen storage capacity and kinetic property due to the transformation of most milled powders into amorphous state.

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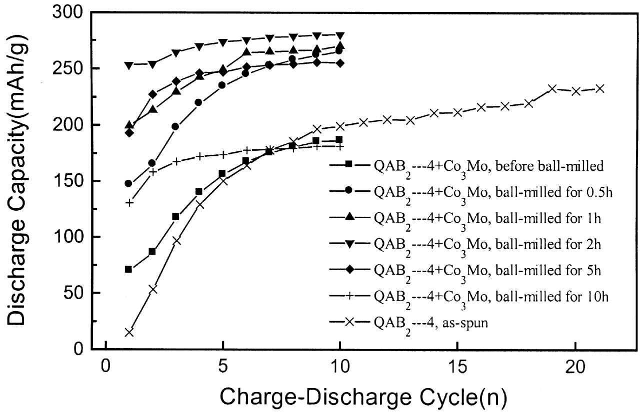

Fig. 4. Activation of QAB_2—4 and Co_3Mo before and after mixing, and the mixture before milling and after milling for different times, respectively.

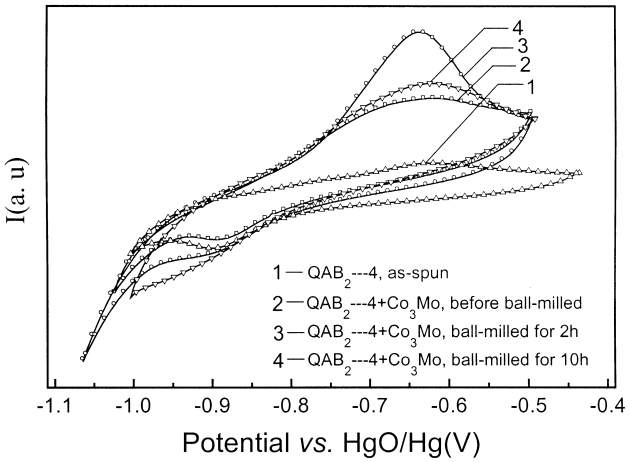

Fig. 5. Cyclic voltammograms of QAB_2—4 electrode before and after milling modification.

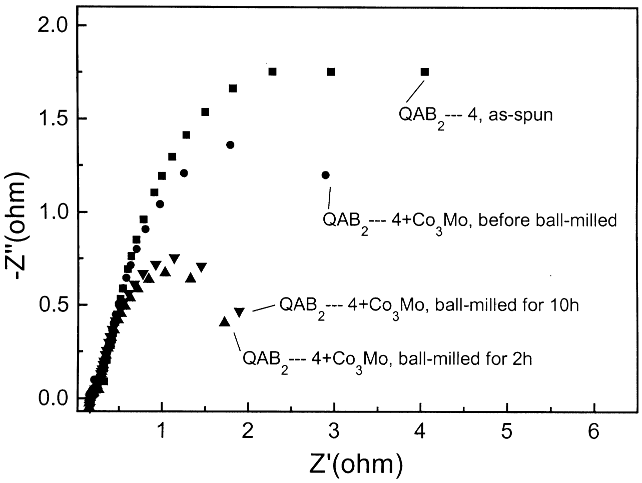

Fig. 6. Impedance spectra of QAB_2—4 electrode before and after milling modification.

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