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The effects of rapid quenching on the electrochemical characteristics and microstructures of AB_2 Laves phase electrode alloys

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Abstract

In order to improve the electrochemical characteristics of AB_2 Laves phase electrode alloys, the rapid quenching technology was used in the preparation of AB_2 type Ti- and Ti-Zr-based electrode alloys. The effects of the rapid quenching on the electrochemical characteristics and microstructures of AB_2 Laves phase electrode alloys were investigated comprehensively. The experimental results showed that the effects of the rapid quenching on the electrochemical properties and microstructures of AB_2 Laves phase electrode alloys were closely relevant with the compositions of the alloys. For Ti-based alloy, the capacity of the as-quenched alloy was enhanced obviously with the increase of the quenching rate, and a maximum capacity could be obtained at a certain quenching rate. The rapid quenching had little effect on the activation capability and improved the cycle stability slightly. For Ti-Zr-based alloy, the cycle stability was exalted significantly and the capacity and activation capability were reduced dramatically with the increase of the quenching rate. The main reason why the rapid quenching can modify the electrochemical performances of AB_2 Laves phase electrode alloys was that it has obviously changed the microstructures of the alloys.

Keywords: AB_2 Laves phase; Electrode alloy; Rapid quenching; Electrochemical characteristics; Microstructures

1. Introduction

Because AB_2 Laves phase electrode alloy have a high electrochemical capacity and long cycle life, the researchers in the world have been paying high attention to it for last twenty years. The research on AB_2 Laves phase electrode alloys has become a focus because its capacity and cycle stability are superior to those of AB_5 type rare-earth-based electrode alloy. Ovonic Company in USA, Panasonic Electrical Equipment Company in Japan, and Tokai University in Japan, etc. researched and developed this kind of alloy [1]. The structure of AB_2 Laves phase consists of hexagonal lattice (C14) and cubic lattice (C15). The capacity of the Zr-based Laves phase alloy is about 410 mAh/g [2], and its cycle life is more than 500, but its activation capability is very poor. The theoretical capacity of the Ti-based Laves phase alloy is about 540 mAh/g, but its capability of absorbing and releasing hydrogen reversibly and its cycle stability are very poor [3,4]. The literatures [5–7] reported that the capacity of AB_5 type electrode alloy and the activation capability of AB_2 Laves phase electrode alloy could be enhanced obviously by rapid quenching. In order to improve the cycle stability of Ti-based Laves phase alloy and the activation performance of Ti-Zr-based Laves phase alloy, the rapid quenching technologies were used in the preparation of AB_2 Laves phase electrode alloys.

The obtained results indicated that the effects of the rapid quenching on the electrochemical characteristics of the Ti- and Ti-Zr-based Laves phase alloys were different. So it could be concluded that the influences of the rapid quenching on the electrochemical properties of AB_2 Laves phase electrode alloys are closely relevant with the compositions of the alloys. The paper discussed the mechanism of the influences of the rapid quenching on the electrochemical performances of AB_2 Laves phase electrode alloys.

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2. Experimental details

2.1. Preparation of alloys

The Ti-based ($Ti_{0.8}Zr_{0.2}Mn_{0.5}V_{0.5}Ni_{1.0}$) and Ti-Zr-based ($Ti_{0.5}Zr_{0.5}Mn_{0.3}Cr_{0.5}V_{0.2}Ni_{1.0}$) alloys were prepared by vacuum induction melting in an argon atmosphere. The purity of all the component metals (Zr, Ti, Mn, V, Cr, Ni) is at least 99.5 wt.%. After induction melting, the melt was poured into a copper mould cooled by water, and a cast ingot was obtained. Part of the cast alloys was re-melted and quenched by melt-spinning with a rotating copper wheel, obtaining flakes of rapidly quenched alloy with the quenching rates of 2, 8, 14, 20, 26 and 32 m/s. The same rapid quenching technologies were used in the preparation of the Ti- and Ti-Zr-based alloys. The quenching rate was expressed by the linear velocity of the copper wheel used for the rapid quenching process.

2.2. Electrode preparation and electrochemical measurement

The fractions of the as-cast and quenched alloys, which were ground mechanically into power below 250 mesh, were used for the preparation of the electrodes. The electrode pellets with 15 mm in diameter were prepared by mixing 1 g alloy power with fine nickel power in a weight ratio of 1:1 together with a small amount of polyvinyl alcohol (PVA) solution as binder, and then compressed at a pressure of 3500 kg/cm^2. After drying for 4 h, the electrode pellets were immersed in 6 M KOH solution for at least 24 h in order to wet fully the electrodes before the electrochemical measurement.

The alloy electrodes were tested in a tri-electrode open cell using a 6 M KOH electrolyte, a Hg/HgO reference electrode, and a $Ni(OH)_2$/NiOOH counter electrode. The electrode activation, capacities and cycle life were tested by an automatic galvano-static charge–discharge unit (30 °C). Every cycle was overcharged to about 30% with constant current density of 100 mA/g, resting for 15 min, and then discharged with the same current density. The discharge cut-off potential was −0.5 V versus Hg/HgO reference electrode.

2.3. Phase and microstructure determination

The samples of the as-cast and quenched alloys were polished directly. The samples thus prepared were etched by 60% HF solution. The morphologies and microzone compositions of the alloys were observed and analyzed by scanning electron microscope (SEM). The phase structures of the alloys were identified by X-ray diffraction (XRD) using Cu Kα as source radiation, and the rays were filtered by graphite. The experimental parameters for determining the phase composition were: 160 mA, 40 kV and 10°/min. The alloy samples were crushed and pulverized into powder ($\leqslant$70 μm) by mechanical grinding. The obtained samples were dispersed in absolute alcohol for observing the grain morphology with transmission electron microscope (TEM), and for determining whether an amorphous phase existed in the samples with selected area electron diffraction (SAED).

3. Results and discussion

3.1. The effects of rapid quenching on the electrochemical characteristics

3.1.1. Discharge capacity

The discharge capacities of the as-cast and quenched Ti- and Ti-Zr-based alloys with different quenching rate were measured. The obtained relationship between quenching rate and discharge capacity was showed in Fig. 1. It can be seen from Fig. 1 that the effects of the rapid quenching on the capacities of the Ti- and Ti-Zr-based alloys were different. The capacity of the Ti-based alloy increased with increase of the quenching rate, and the maximum capacity (344 mAh/g) was obtained at the quenching rate of 14 m/s. The capacity began to decrease when quenching rate was more than 14 m/s. When the quenching rate reached 32 m/s, the capacity dropped to 320 mAh/g, which is still larger than that of the as-cast alloy (308 mAh/g). For Ti-Zr-based alloy, the results were on the contrary. The capacity of the Ti-Zr-based alloy decreased monotonically with the increase of the quenching rate. The maximum capacity of the as-cast alloy was 312 mAh/g, and the capacity of the as-quenched alloy with quenching rate of 32 m/s dropped to 193 mAh/g. The changes in capacities of the alloys with different compositions were very different although the same rapid quenching technology was used. It indicated that the influence of the rapid quenching on the capacity was related to the composition of the alloys.

3.1.2. Activation performance

Activation number, *n*, was characterized by the number of charge–discharge cycles required for attaining the great-

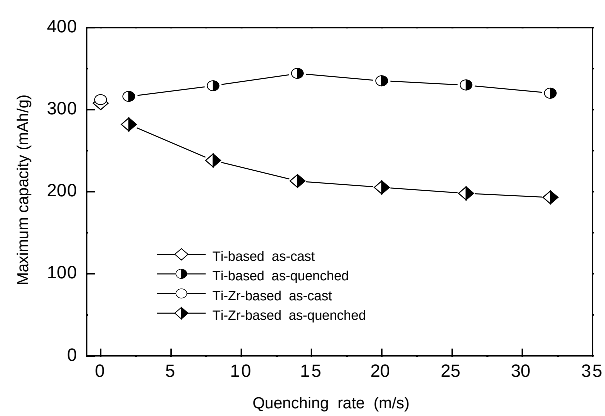

Fig. 1. The relationship between the quenching rate and the maximum discharge capacity.

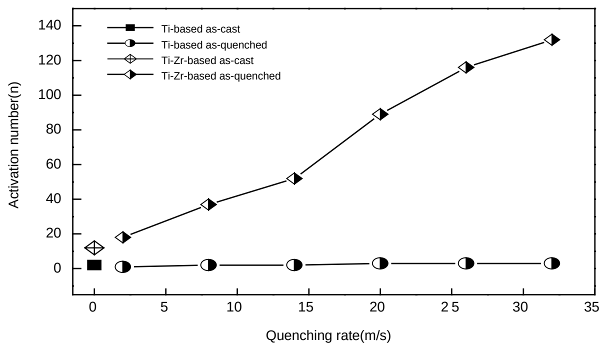

Fig. 2. The relationship between the quenching rate and the activation number.

est discharge capacity, through a charge–discharge cycle at the constant current density of 100 mA/g. The fewer the cycle number, the better the activation performance. Fig. 2 illustrated the quenching rate dependence of the activation number of the Ti- and Ti-Zr-based electrode alloys. Fig. 2 indicated that the rapid quenching had a very little influence on the activation performance of the Ti-based alloy, and both as-cast and quenched alloys could be activated fully through two to three cycles. But rapid quenching made the activation performance of Ti-Zr-based alloy decrease significantly, and the activation number was exalted dramatically with the increase of the quenching rate. The as-cast alloy could be activated completely through 12 cycles, and the activation number of the as-quenched alloy was increased from 18 to 132 when the quenching rate was increased from 2 to 32 m/s.

3.1.3. Cycle life

Cycle life, *N*, was characterized by the cycle number after which the discharge capacity of the alloy at the constant current charge–discharge rate of 100 mA/g was reduced to 60% of the maximum capacity. Fig. 3 showed the quenching rate dependence of the cycle life. The cycle lives of the as-cast Ti- and Ti-Zr-based alloys were 122 and 172, respectively; it indicated that Zr and Cr are beneficial to the cycle life of the AB_2 Laves phase alloys. It can be seen from Fig. 3 that the rapid quenching had a slight influence on the cycle life of the Ti-based alloy. Compared with Ti-based alloy, the influence on the cycle life of the Ti-Zr-based alloy was extremely significant. When the quenching rate was increased from 2 to 32 m/s, the cycle lives of the Ti- and the Ti-Zr-based alloys were enhanced from 131 to 193 and from 244 to 830, respectively. Obviously, it is related to the functions of Zr and Cr.

The above-mentioned results indicated that the influences of the rapid quenching on the electrochemical characteristics of the Ti- and Ti-Zr-based alloys are different. The main reason responsible for the difference is that the phase composition and the microstructure of the as-quenched alloys change dramatically with different compositions. So, only by means of the analysis and observation of the phase structures and morphologies, can the mechanism of the influence of the rapid quenching on the electrochemical performance of AB_2 Laves phase electrode alloy be understood and explained.

3.2. The effects of rapid quenching on phase structures and microstructures

3.2.1. Phase composition and structure

The phase composition and structure were determined by XDR. Fig. 4(a) illustrated the X-ray diffraction diagrams of the as-cast and quenched Ti-based alloys. Both the as-cast and quenched alloys consist of a large amount of hexagonal lattice C14 phase and a little TiNi phase. The Cubic lattice C14 phase was formed when quenching rate was more than 8 m/s. The hydrogen absorbing capabilities of C15 and C14 phases are much higher than that of TiNi phase. The X-ray diffraction peaks of (1 1 0), (2 0 0), and (2 1 1) crystal planes of TiNi phase can be seen from Fig. 4(a). The relative intensities of three diffraction peaks were compared, and the results were listed in Table 1. It was known from Table 1 that the relative intensities of the three diffraction peaks of the as-quenched alloy were lower than that of the as-cast alloy. It explained that the quantity of TiNi in the as-quenched alloy was smaller than that in the as-cast alloy. The main reason why the as-quenched Ti-based alloy had higher hydrogen absorbing capability was that a great deal of C14 and C15 phases existed in the as-quenched alloy. Table 1 showed that the amount of TiNi phase was not decreased monotonically with the increase of the quenching

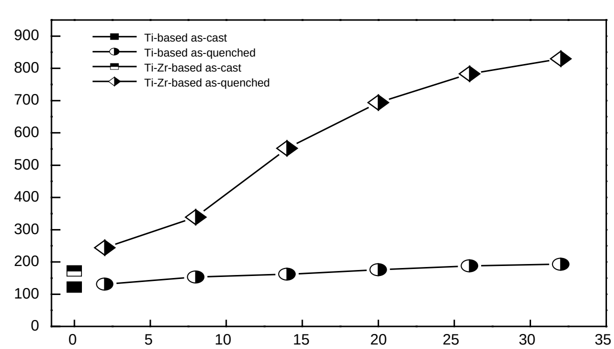

Fig. 3. The relationship between the quenching rate and the cycle life.

Table 1
The relative intensities of the diffraction peaks of TiNi phase in the as-cast and quenched Ti-based alloys

Quenched rate (m/s)	I_{hkl}/I_{max}		
	(1 1 0)	(2 0 0)	(2 1 1)
As-cast	65	14	28
2	55	11	22
8	27	–	26
14	18	9	8
20	13	–	15
26	17	–	–
32	19	–	–

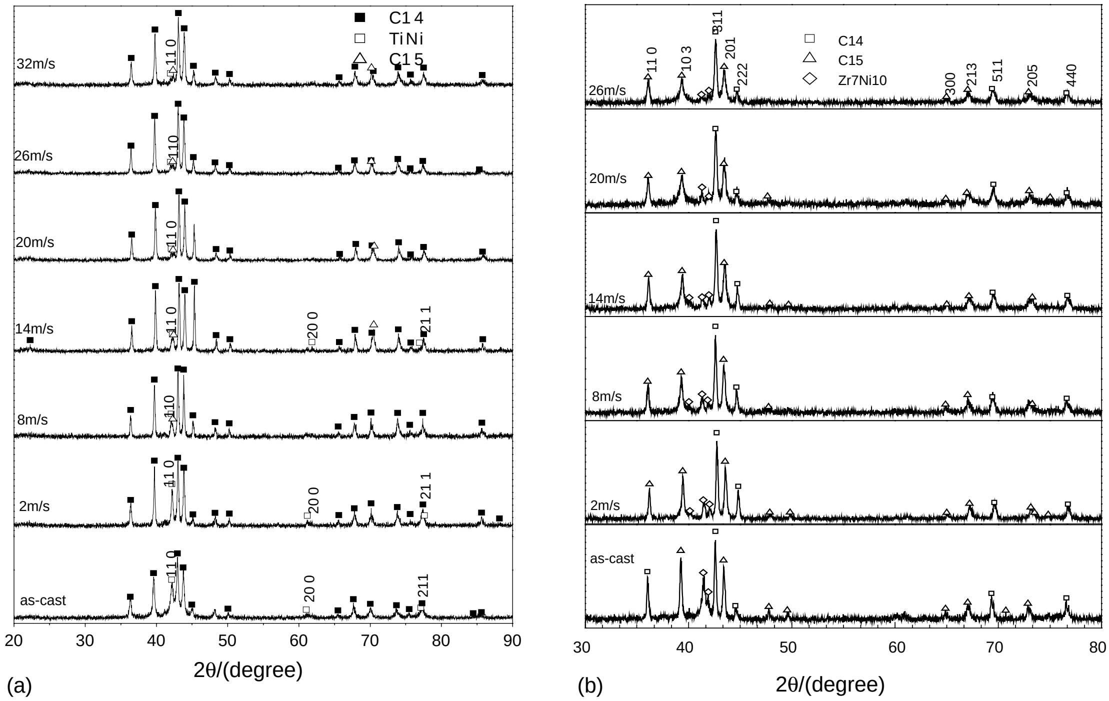

Fig. 4. X-ray diffraction diagrams of the as-cast and quenched alloys: (a) XRD diagrams of Ti-based alloy; (b) XRD diagrams of Ti-Zr-based alloy.

rate. The minimum relative intensity of (1 1 0) crystal plane corresponded to the quenching rate of 20 m/s, and that of (2 0 0), (2 2 0) crystal planes to 14 m/s. The reason why the Ti-based alloy obtained a maximum capacity at the quenching rate of 14 m/s probably was that a maximum amount of C14 and C15 phases existed in the alloy.

It can be known from Fig. 4(b) that the phase compositions of the as-cast and quenched Ti-Zr-based alloys consisted of main phase C15, and second phase C14 as well as a little Zr_7Ni_{10} phase, and the ratio of the three phases can be adjusted by using different quenching rate. The quenching rates resulted in the great change in phase composites and structures of Ti- and Ti-Zr-based alloys, but the change of their electrochemical characteristics were obviously different. It was difficult for researchers to explain the mechanism of the variations of the electrochemical performances by only using the change of the phase structure. It was necessary to observe and analyze morphologies and microstructure of the alloys further.

3.2.2. Microstructure and morphology

Mishima et al. [5] reported that the capacities of $LaNi_{4.6}Al_{0.4}$ and $LaNi_4Co_{0.6}Al_{0.4}$ alloys could be enhanced by rapid quenching. He considered that it was because the rapid quenching made the grain size of the alloy decreased, thus producing an additional amount of grain boundaries that provide good channels for the diffusion of hydrogen atoms. In addition, fine grain can improve the cycle life of the alloy on a certain degree. Lei et al. [7] reported that rapid quenching made the capacity of the $MI(NiCoMnTi)_5$ increased because the crystal state and compositions of the as-quenched alloy are more homogeneous. The experimental results indicated that the rapid quenching lead the grain fine (Fig. 5). Fig. 5 illustrated that the grain size of the alloy was reduced significantly with the increase of the quenching rate, and it is another important factor, which resulted in the capacity increase of the Ti-based alloy. It is certain for all alloys that rapid quenching makes grain fine and composition more homogeneous. So it is necessary to understand why rapid quenching has resulted in the sharp decrease in the capacity of the Ti-Zr-based alloy. Li and Cheng [8] investigated the hydrogen absorbing capability of La-Ni alloy amorphous film, and the results showed that the capacity of the amorphous film was half as large as that of the crystal alloy. So, it was concluded that the main reason of the rapid quenching leading to the capacity decrease of the Ti-Zr-based alloy probably was because of the amorphous phase formed. Thus, the crystalline state of the Ti- and Ti-Zr-based alloys was detected by TEM, and the results were illustrated in Figs. 6 and 7. It can be seen from Fig. 6 that the structure of the as-quenched Ti-based alloy with the quenching rate of 32 m/s consisted of main microcrystal and nanocrystal as well as a trace amount of amorphous phase. The crystal morphology, which appeared in bar and massive shapes, of the alloy was very complete and clear when quenching rates were 14 and 20 m/s, and the higher the quenching rate, the small the grain size. Fig. 7 showed that amorphous phase was formed in Ti-Zr-based alloy when quenching rate attained 5 m/s, and the amount of amorphous phase increased significantly with the increase of quenching rate. A quite amount of amorphous phase was formed in the Ti-Zr-based alloy when quenching

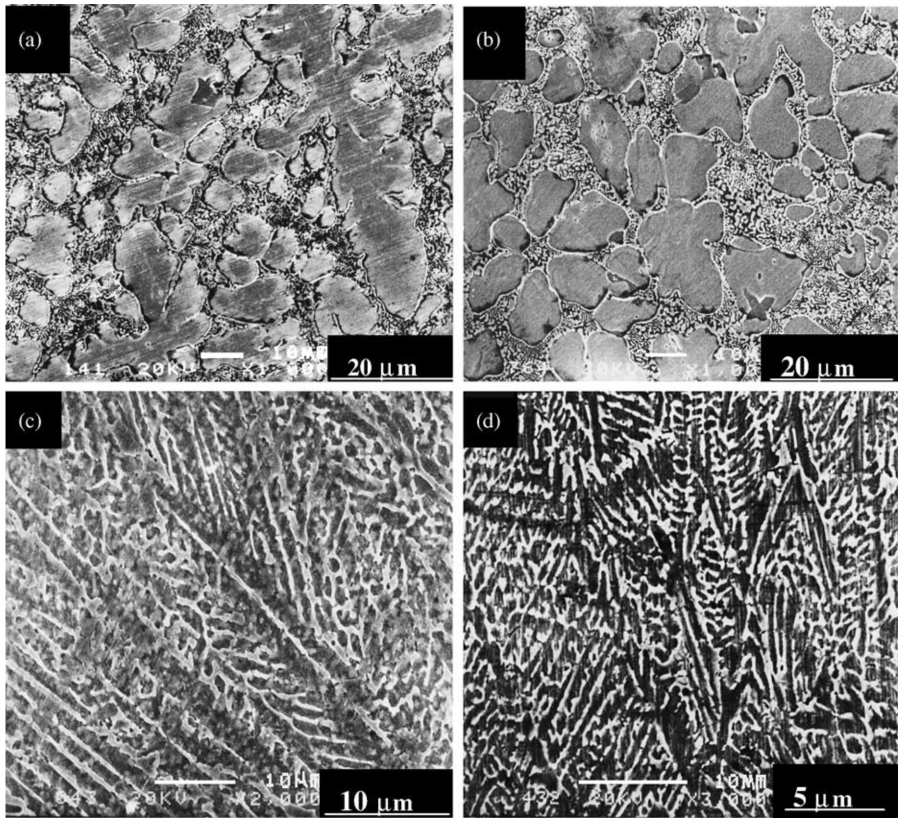

Fig. 5. The morphologies of the as-cast and quenched Ti-based alloys taken by SEM: (a) and (b) cross-section and longitudinal section of as-cast alloy; (c) and (d) cross-sections of the as-quenched alloys with quenching rate of 2 and 8 m/s.

rate reached 26 m/s. So, it could be confirmed that the difference in the electrochemical performances was resulted from the different quantities of amorphous phase formed in Ti- and Ti-Zr-based alloys after rapid quenching. The effects of rapid quenching on the capacity were complicated: both the increase in the amount of hydrogen absorbing phase and the decrease in grain size as a result of rapid quenching were favorable for the capacity, on the one hand, and formation of the amorphous phase was unfavorable on the other. Therefore, whether rapid quenching would increase or decrease the capacity of the alloy depended on the predominant one of the above. Author considered that the effect of amorphous was much stronger. The favorable influence would be covered fully when a proper amorphous phase was formed in the as-quenched alloy, but the general effect of amorphous phase was disadvantageous to the capacity. The cycle stability was exalted significantly and the activation capability was reduced sharply when a certain amount of amorphous phase existed in the alloy [9].

The reason that rapid quenching lead to the increase of the capacity of the Ti-based alloy was that it made the total quantity of C14 and C15 phases increased and the grain fined. The capacity of the Ti-based alloy began to decay when quenching rate was more than 14 m/s. It probably was that some amorphous phase was formed at 14 m/s. A certain amount of amorphous phase could be observed clearly when quenching rate reached 32 m/s, but the capacity of the as-quenched Ti-based alloy was still higher than that of the as-cast alloy. Maybe it was because advantageous factor was still predominant. The effect of rapid quenching on the activation performance of the Ti-based alloy was not obvious, and it was relevant with a trace amount of amorphous existed in the as-quenched Ti-based alloy. Although the formation of amorphous phase was unfavorable for the activation capability, it was well offset by the beneficial factor produced by the fined grain. The fined grain was helpful for the cycle life on a certain degree. The cycle life of the Ti-based alloy increased significantly when quenching rate was larger than 20 m/s. It was closely related to the contribution of amorphous phase to the cycle life.

Different from Ti-based alloy, the amorphous phase could be formed easily in the as-quenched Ti-Zr-based alloy. A quite amount of amorphous phase existed in the Ti-Zr-based alloy when quenching rate reached 5 m/s. The capacity of the Ti-Zr-based alloy lowered monotonically with the increase of the quenching rate. It indicated that the disadvantageous effect of amorphous phase on the capacity far exceeded the beneficial function produced by the grain fined. Also the poor activation capability of the as-quenched Ti-Zr-based alloy was because of the amorphous phase existing. The excellent cycle stability of the as-quenched Ti-Zr-based alloy was attributed to amorphous phase and grain fined.

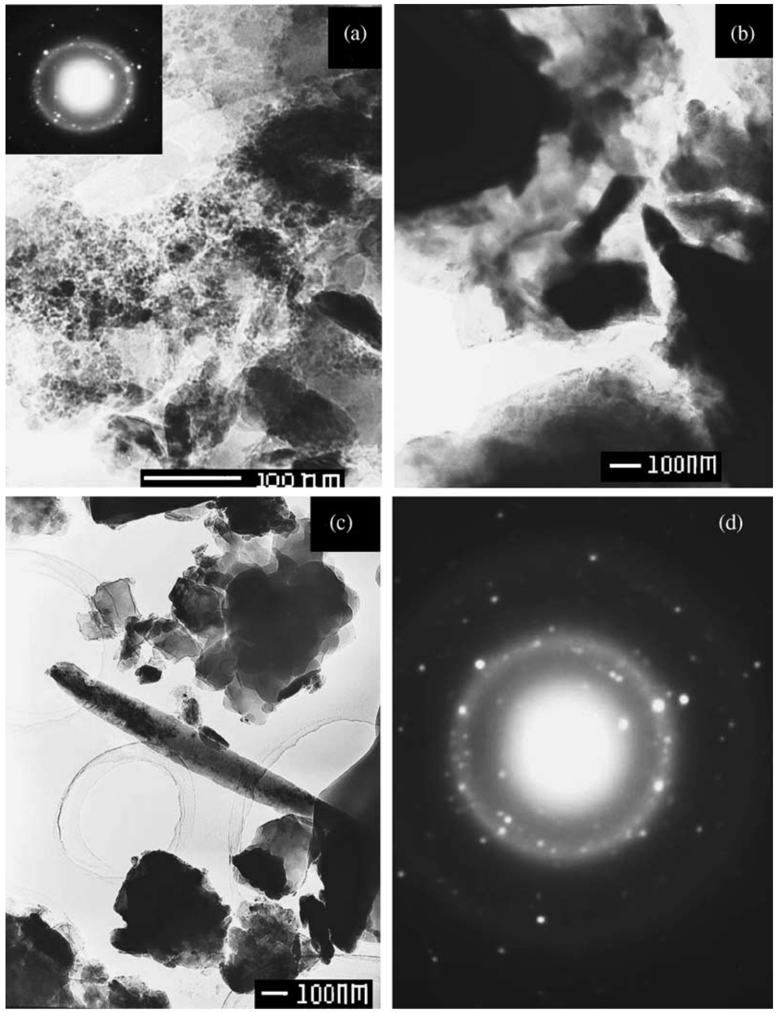

Fig. 6. The morphologies of the as-quenched Ti-based alloy taken by TEM: (a) and (d) 32 m/s; (b) 20 m/s; (c) 14 m/s.

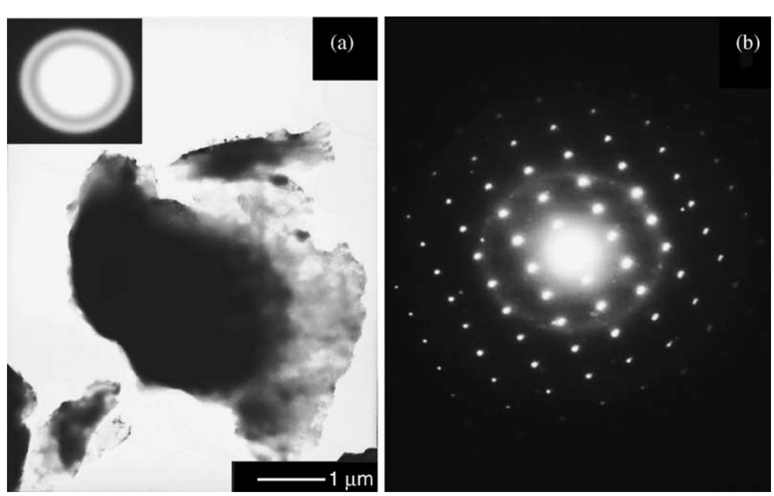

Fig. 7. The morphologies of the as-quenched Ti-Zr-based alloy (5 m/s) taken by TEM: (a) amorphous morphology and SAED; (b) diffraction pattern of single crystal.

According to the above-mentioned experimental results, it could be concluded that element Zr is beneficial to the formation of amorphous phase. So it is very possible to prepare AB_2 Laves phase electrode alloy with good synthetically electrochemical characteristics through adjusting Zr content and using suitable rapid quenching technology, for which the researching work is being carried out deeply and comprehensively.

4. Conclusions

1. Rapid quenching produced significant influences on the electrochemical characteristics of AB_2 Laves phase electrode alloys, and it made the capacity of the Ti-based alloy increased, and had a little influences on the cycle stability and activation performances. Rapid quenching made the capacity and activation capability of the Ti-Zr-based alloy decrease sharply, and cycle stability exalted dramatically. The effects of rapid quenching on the electrochemical characteristics of AB_2 Laves phase electrode alloys were closely relevant with their compositions.
2. The decrease of the grain size produced by rapid quenching was advantageous to the capacity and cycle stability of AB_2 Laves phase electrode alloy, and it had a little influence on the activation performance. The amorphous phase made the capacity and activation capability decrease obviously and the cycle life increased dramatically.
3. The phase structure and composition of AB_2 Laves phase electrode alloys can be controlled through adjusting chemical compositions and quenching rate. It was difficult to obtain amorphous phase in the Ti-based alloy through rapid quenching, but it was very easy in Ti-Zr-based alloy.
4. Rapid quenching produced advantageous and disadvantageous influences on the capacity of AB_2 Laves phase electrode alloys. So the relationship between the quenching rate and the capacity was non-linear. The synthetically electrochemical properties of AB_2 Laves phase electrode alloys can be adjusted elastically by rapid quenching, it is very possible to prepare AB_2 Laves phase electrode alloy with excellent synthetically electrochemical characteristics through scientific design of the chemical compositions and suitable selection of rapid quenching technology.

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