Relationship between cooling rate and electrochemical performance of melt-spun AB₅ alloy[①]

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Abstract: The crystal structure and electrochemical properties of Ml(NiCoMnAl)₅ alloys prepared by both rapid solidification (melt-spinning) and conventional cast methods were systematically investigated. The results show that the charging/discharging cycle life of rapidly solidified alloy is greatly improved, and the mean capacity attenuation rate of the rapidly solidified alloy is 1−3 times lower than that of the as-cast alloy after 600 cycles. All of the melt-spun alloys have almost the same discharge capacity as the as-cast alloy except for the alloy with the cooling rate of 1.8×10^5 K/s, which has the largest discharge capacity of 310 mAh/g. The melt-spun alloys need longer activation process than the conventional cast alloy. High rate dischargeability becomes poorer as the cooling rate increases in solidification also. Obviously improved electrochemical properties of the melt-spun alloy are closely related to its fine grain, elimination of secondary phase AlNi₃ and uniform composition distribution.

Key words: hydrogen storage alloy; rapid solidification; electrochemical properties

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1 INTRODUCTION

Ni/MH secondary batteries have rapidly been developed and gradually substituted for Ni/Cd batteries in the recent decade due to its high specific energy density and having no poisonous element cadmium. The active material of negative electrode widely used in Ni/MH secondary batteries is AB₅-type hydrogen storage alloy nowadays. However, it is still needed to improve the comprehensive properties of AB₅-type hydrogen storage alloy for prolonging the service life of Ni/MH batteries. A normal method to improve the comprehensive properties of the alloy is by a process of post-annealing at high temperature for a long time[1−3]. Sakai and his co-workers firstly used different casting processes to prolong the cycle life and raise the comprehensive properties of the alloys by changing their microstructure[4, 5]. It was continuously reported that the rapid solidification techniques, such as melt-spinning and atomization, could greatly improve the properties of hydride electrode alloys, but there were great differences among different experiment results and their explanation[6−10]. For understanding the influence of the rapid solidification mode on the electrochemical properties of hydride electrode alloys, the widely used hydrogen storage alloy Ml(NiCoMnAl)₅ is chosen to comparatively investigate the phase composition, crystal structure, microstructure and electrochemical properties of both rapidly solidified and conventional cast alloys. The effect of cooling rate on the electrochemical properties of rapidly solidified alloy is further investigated in detail.

2 EXPERIMENTAL

2.1 Sample preparation and XRD analysis

The alloy with a composition of Ml(NiCoMnAl)₅ was prepared by induction melt under argon atmosphere in a levitation vacuum furnace with water cooled copper crucible. The cooling rate of the alloy in the copper crucible was about 10^2 K/s. The alloy prepared by the above process was called conventional cast alloy (or CC alloy). To ensure the uniformity of the alloy, it was turned over and re-melted 2 times. The composition of lanthanum rich mischmetal (Ml) was as follows: 42% La, 11% Ce, 13% Pr, and

34% Nd(mass fraction). The purity of the metals used in alloy melting was higher than 99.95%. Rapidly solidified alloy (or RS alloy) ribbons were prepared by melt-spinning technique, and the cooling rates were estimated by the following formula[11]:

$$v = A / d^2$$

where v is cooling rate, d stands for thickness of ribbon, A is a constant with a value of 4.8 × 10^{-3} m^{2}K/s according to experiment. More details are shown in Ref. [12].

The alloys prepared by the conventional cast and rapid solidification methods were mechanically ground into powders below 45 μm for preparing electrodes and samples in XRD experiment. The XRD data were tested in Riguku D/Max-3B diffractometer and the data analysis was performed in PC computer.

2.2   Electrochemical measurement

About 300 mg alloy powder was thoroughly mixed with 900 mg nickel powder and then pressed into pellet electrode. Electrochemical properties were tested in a standard trielectrode eletroanalysis cell open to the atmosphere. A Ni(OH)$_2$/NiOOH was used as the counter electrode and potentials were referred to an Hg/HgO/OH$^-$. Electrolyte was a 6 mol/L KOH solution. The electrodes were charged at 120 mA/g for 3.5 h, then discharged at the current of 60 mA/g. The discharge cut off potential was set at − 0.6 V. The testing temperature was 25 ℃.

3   RESULTS AND DISCUSSION

3.1   XRD analysis

Fig. 1 shows the XRD results of Ml (NiCo-MnAl)$_5$ prepared by the conventional cast and rapid solidification methods. It shows that there is a small amount of AlNi$_3$ precipitated in conventional cast alloy and no AlNi$_3$ appears in rapidly solidified alloys with the cooling rates of 10^5 ~ 10^6 K/s. This means that the rapid solidification process can effectively restrain the second phase (AlNi$_3$) to segregate during solidification and make the alloy form single phase of CaCu$_5$ structure.

The cell parameters of the main phase of the CC and RS Ml(NiCoMnAl)$_5$ alloys are listed in Table 1. The cell parameters and cell volumes of the RS alloys are contracted as compared with the CC alloy. As the cooling rate increases, the a-axis contracts, c-axis expands, and cell volume decreases gradually. The factors causing cell volume decrease in rapid solidified alloy are not clear. They may be related to change of the atom order and formation of defects, such as vacancies and dislocations, which are formed in melt-spinning process. They above results show that
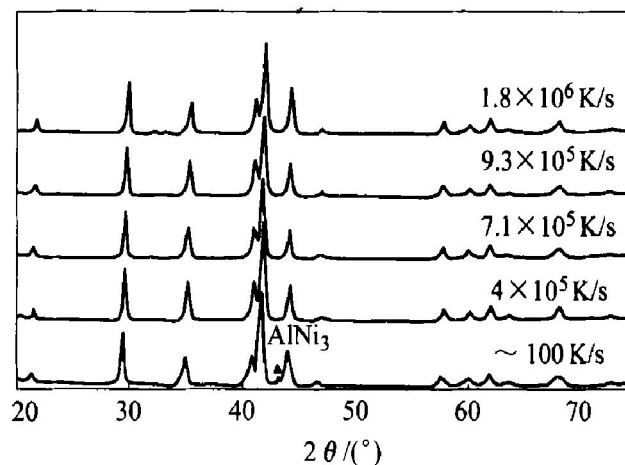
Fig. 1   XRD patterns of Ml(NiCoMnAl)$_5$ alloys prepared by conventional cast and rapid solidification methods

Table 1   Cell parameters and cell volumes (CaCu$_5$ structure) of Ml(NiCoMnAl)$_5$ alloys prepared by conventional cast and rapid solidification methods

| Alloy	Cooling rate/ (K·s^{-1})	a/ nm	c/ nm	V/ nm^3
Conventional cast	~ 100	0.502 7	0.404 3	0.088 48
Melt-spinning	4.0 × 10^5	0.502 4	0.404 7	0.088 46
	7.1 × 10^5	0.502 1	0.405 1	0.088 44
	9.3 × 10^5	0.501 9	0.405 3	0.088 42
	1.8 × 10^6	0.501 7	0.405 6	0.088 41

the microstructure of AB$_5$-type alloy changes in different rapidly solidified conditions.

### 3.2   Electrochemical properties

The activation curves of Ml(NiCoMnAl)$_5$ alloys prepared by rapid solidification and conventional cast methods are shown in Fig. 2. It indicates that after 3 charging-discharging cycles the CC alloy reaches the largest discharge capacity, 300 mAh/g, while the RS alloys need more than 5 cycles to be completely activated and the activation cycles increase from 5 to 10 cycles as the cooling rate increases from 4 × 10^5 to 1.8 × 10^6 K/s. All the RS alloys have almost the same discharge capacity as CC alloy except for the RS alloy with cooling rate of about 4 × 10^5 K/s, whose discharge capacity is 310 mAh/g.

Fig. 3 shows the cycle lives of Ml(NiCo-MnAl)$_5$ prepared by the rapid solidification and conventional cast methods. It is shown that the RS alloys have much longer cycle life than that of the CC alloy and the cycle life of RS alloys is further improved with the increase of cooling rate. By comparing the cycle life with the mean capacity attenuation rate, dC/dN, one can know that the CC alloy has the largest $dC/$
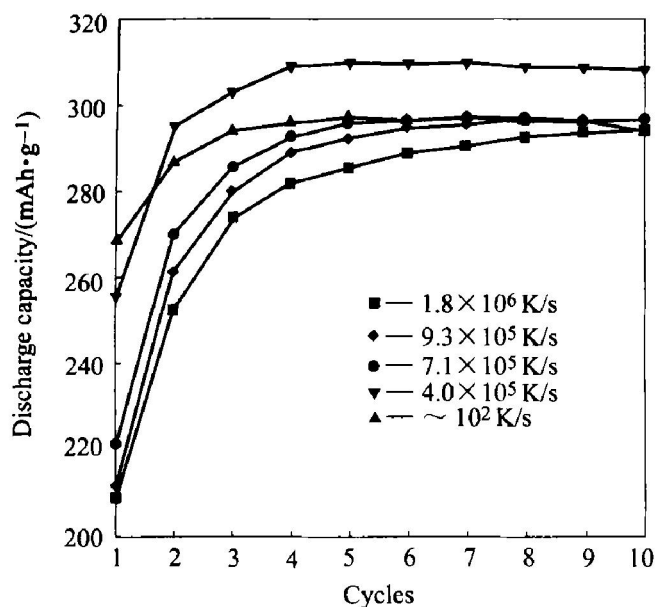
Fig. 2   Activation curves of CC and RS alloys
with different cooling rates(25 ℃)
(Charging for 4 h at 100 mAh/g and
then discharging at 50 mAh/g)
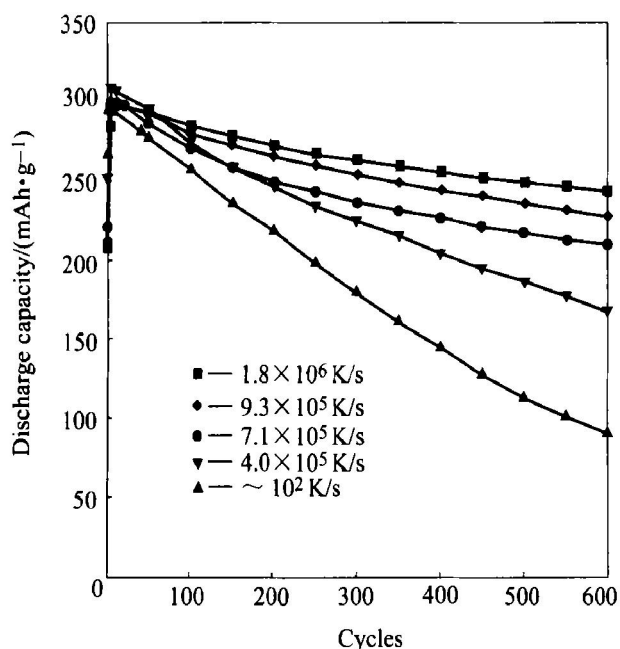
Fig. 3   Cycle life of Ml(NiCoMnAl)$_5$ alloys
prepared by conventional cast and rapid
solidification methods(25 ℃)
(Charging for 4 h at 100 mAh/g and
then discharging at 50 mAh/g)

dN value, 0. 344 mAh/ (g•cycle). As for the RS al-
loys, the dC/dN values decrease from 0. 273 mAh/
(g•cycle) to 0. 085 mAh/(g •cycle) as the cooling
rate of RS alloys increases from 4 × 10^5 K/s to
1. 8 × 10^6 K/s, which are only a quater to half of that
of CC alloy.

The microstructure of the CC alloy is dendrite
with serious composition segregation and a small
amount of AlNi$_3$ segregation,   so it is easy to be

cracked and pulverized in absorbing hydrogen. The
microstructure of the RS alloy is fine columnar struc-
ture with homogeneous distribution of composition
and the AlNi$_3$ forming is restrained in the solidifica-
tion process. This is also verified in another experi-
ment[13]. The fine columnar structure and homoge-
neous composition are beneficial to restraining the al-
loy from pulverization, elements dissolution and cor-
rosion in the charging-discharging process. It is the
main reason to prolong the cycle life of RS alloys but
make the RS alloys more difficult to activate at same
time. The quicker the cooling rate, the finer the
grain size and the more even the composition distribu-
tion of the RS alloy, the longer the cycle life.

The high rate dischargeability of the RS alloys is
not as better as that of CC alloy as indicated in Fig. 4.
The high rate dischargeability of the RS alloys is also
decreased with the cooling rate increasing. Just the
same reason, the rapid solidification processing makes
the pulverization rate of Ml(NiCo-MnAl)$_5$ alloy de-
crease, and thus decreases the specific surface of alloy
and finally leads to lower high rate dischargeability of
the RS alloys. AlNi$_3$ segregation in the CC alloy in
solidification will be beneficial to its high rate dis-
chargeability.
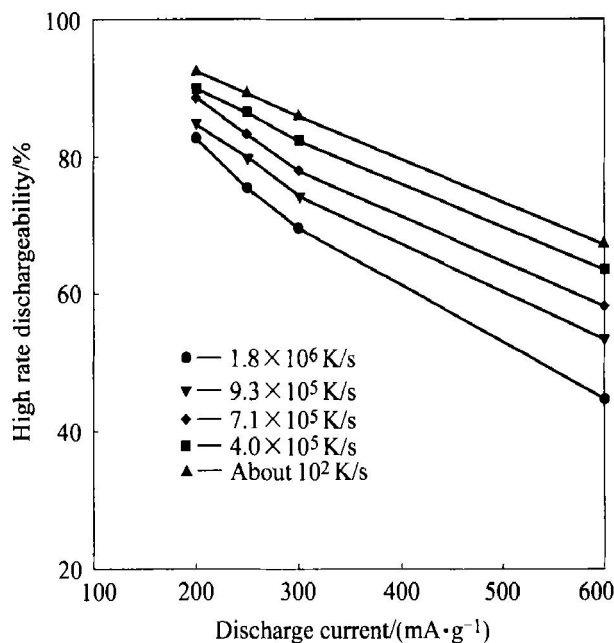
Fig. 4   High rate dischargeability of
Ml(NiCoMnAl)$_5$ alloys prepared by
conventional cast and rapid solidification
methods after 50 cycles (25 ℃)

Fig. 5 shows the discharge potential curves of Ml
(NiCoMnAl)$_5$ alloys prepared by the conventional
cast and rapid solidification (7. 1 × 10^5 K/s) methods
after 25 cycles. It shows that the discharge potential
plateau of the RS alloy is higher and flatter than that
of the CC alloy. Rapid solidification process makes
the alloy composition distribute more homogeneously
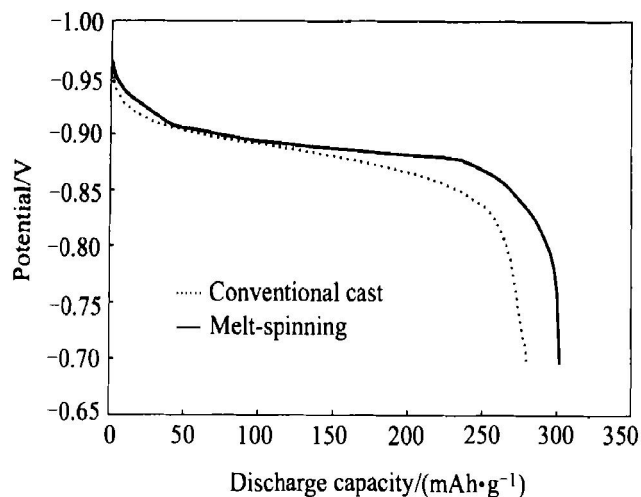
Fig. 5 Potential plateaus of Ml(NiCoMnAl)$_5$ alloys prepared by conventional cast and rapid solidification methods at 25th cycle (25 ℃)

and restrains the secondary phase AlNi$_3$ segregating, which decreases the over potential, increases the discharge potential and flattens the potential plateau.

4 CONCLUSIONS

1) The electrochemical properties of the rapidly solidified (RS) alloys are greatly improved as compared with the conventional cast (CC) alloy. With the same discharge capacity as the CC alloy, the RS alloys have much longer cycle life, but need more charging/ discharging cycles to activate. The quicker the cooling rate, the more activation cycles the RS alloys need.

2) The high rate dischargeability of the RS alloy is slightly poorer than that of the CC alloy, however the RS alloy has higher and flatter plateau potential than the CC alloy. The reasons for the electrochemical properties changes of RS alloys are due to fine grains, having no second phase and homogeneous composition distribution.

3) The fine grains of RS alloys greatly raise the pulverization-resistant ability, and the homogeneous composition and disappearance of component segregation will slow the element dissolution and corrosion rate, which makes a great contribution to the longer cycle life of RS alloys.

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