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Preparation and electrochemical properties of unidirectionally solidified $Ml(NiCoMnTi)_5$ alloys

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Abstract

Mischmetal based alloy $Ml(NiCoMnTi)_5$ (Ml: La-rich mischmetal) was prepared by unidirectional solidification process at an ultra-high temperature gradient (around 1300 °C cm^{-1}) and different growth rates (48~220 μm s^{-1}). The microstructures and electrochemical properties of these alloys have been investigated. It was shown that with increasing growth rate, the microstructure of unidirectional solidification alloy changed from cellular–columnar to columnar–dendritic structure and the primary columnar spacing λ_1 increased, reached a maximum value and then decreased. Electrochemical measurement indicated that unidirectional solidification alloy with the fine cellular–columnar structure prepared at growth rate R=48 μm s^{-1} has significantly improved discharge capacity, high-rate dischargeability and cycling stability of the alloy.

Keywords: Unidirectional solidification; Mischmetal based alloy; Microstructure; Electrochemical properties

1. Introduction

Recently extensive research has been carried out on utilizing mischmetal based alloys as a low cost electrode material for Ni/MH batteries. It was shown that with multicomponent substitutions [1], surface coating [2], optimization of rare earth composition in mischmetals [3], and by using non-stoichiometric AB_{5-x} compositions [4], the electrode properties could be significantly improved. It was also confirmed that the electrode performances greatly depended on the alloy composition, casting conditions and microstructures. The as-cast alloy with only the columnar structure had lower lattice strain, lower pulverizing rate and longer cycle life than those of the same alloy with the fine equiaxed structure. By rapid quenching, the Mn-free alloy with columnar structure could be obtained, while the Mn-containing alloy still had a fine equiaxed structure because manganese accelerated the nucleation of the alloy [5]. On the other hand, $LaNi_5$–Ni eutectic alloys with the columnar structure and improved resistance to pulverization have been obtained by using a conventional unidirectional solidification process at a rather low temperature gradient (40 °C cm^{-1}) and low growth rate (1.3~13 μm s^{-1}) [6]. However, there is no other report on the unidirectional solidification of multicomponent hydrogen storage alloys and their electrochemical properties. In the present work, the Mn-containing mischmetal based alloy $Ml(NiCoMnTi)_5$ was prepared by a rapid unidirectional solidification process at an ultra-high temperature gradient (around 1300 °C cm^{-1}) and different growth rate (48~220 μm s^{-1}), the microstructure and electrochemical properties of these alloys were examined and are reported here.

2. Experimental

A master alloy of composition $MlNi_{3.8}Co_{0.75}Mn_{0.40}Ti_{0.05}$ was prepared by induction melting the La-rich mischmetal Ml (wt.%: La 44.7; Ce 2.9; Nd 40.4; Pr 11.9) and commercial metals Co, Mn, Ni and Ti (purity 99%), and cast into a bar specimen of ϕ8 mm×120 mm, which was used for unidirectional solidification. The unidirectional solidification of the alloy specimen was carried out by using a rapid unidirectional solidification apparatus equipped with zone melting and liquid metal forced cooling system under argon atmosphere. The temperature gradient on the liquid–solid interface of the specimen was held at around 1300 °C cm^{-1}, the growth rate of the unidirectional solidified specimen was controlled at 48 μm s^{-1}, 97 μm s^{-1}, 150 μm s^{-1} and 220 μm s^{-1} respectively, corresponding cooling rate about 6~30 °C s^{-1}.

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The unidirectional solidified specimen was cut longitudinally into samples along the growth direction. Microstructure and composition distribution on both grain and grain boundary of the alloy were examined by optical microscope and the energy-dispersive X-ray analysis (EDAX), respectively.

Part of the alloy specimen was pulverized mechanically below 300 mesh, the alloy powder mixed with Cu powder in a weight ratio of 1:2 was pressed into a pellet electrode of ϕ8 mm. The electrochemical measurements were performed at 25 °C by the same procedure as reported previously [1]. The electrode activation and initial capacity (C_0) were measured at charge–discharge current 60 mA g^{-1} and discharge to −0.60 V (vs. Hg/HgO). The high-rate dischargeability (%), defined as $C_{350}\times100/(C_{350}+C_{35})$ was determined from the ratio of the discharge capacity measured at 350 mA g^{-1} (C_{350}) to the total capacity that was assumed to be the sum of C_{350} and C_{35} (the additional capacity measured at 35 mA g^{-1}). The cycling test was conducted at charge–discharge current 350 mA g^{-1} for 200 cycles, and the capacity degradation ratio S_{200} was defined as $S_{200}(\%)=C_{200}\times100/C_{max}$, where C_{200} was the discharge capacity at 200th cycle.

3. Results and discussion

Fig. 1A shows the microscopic longitudinal section (along the growth direction) of the unidirectionally solidified alloy at different growth rate R. The microstructures of the alloy were characterized by the parallel arrangement of the columnar grain structure. However, when the growth rate increased from $R=48$ μm s^{-1} to 97 μm s^{-1}, the microstructure changed from a fine cellular–columnar structure to a rather coarse columnar–dendritic structure. With increasing growth rate R, the columnar–dendritic structure remained, but the columnar grain size became finer. Fig. 2 also shows that with increasing growth rate from $R=48$ μm s^{-1} to $R=97$ μm s^{-1}, the primary columnar spacing increased from $\lambda_1\approx40$ μm to a maximum value of $\lambda_1\approx100$ μm, then the λ_1 values decreased with increasing of growth rate again. The results revealed that Mn-containing mischmetal based alloy with the columnar structure could be obtained by the unidirectional solidification process over a wide range of growth rate, and there is a critical range of growth rate for the cellular–dendritic transition and grain size variation. Therefore it is possible to obtain a favorable grain structure by controlling the suitable solidification condition.

Fig. 1B shows the distribution of composition elements by at.% on columnar grain and grain boundaries of the unidirectionally solidified alloy prepared at growth rate $R=150$ μm s^{-1}. It was found that elements La and Mn caused positive segregation and Ni and Co caused negative segregation on grain boundaries, respectively, while Ti

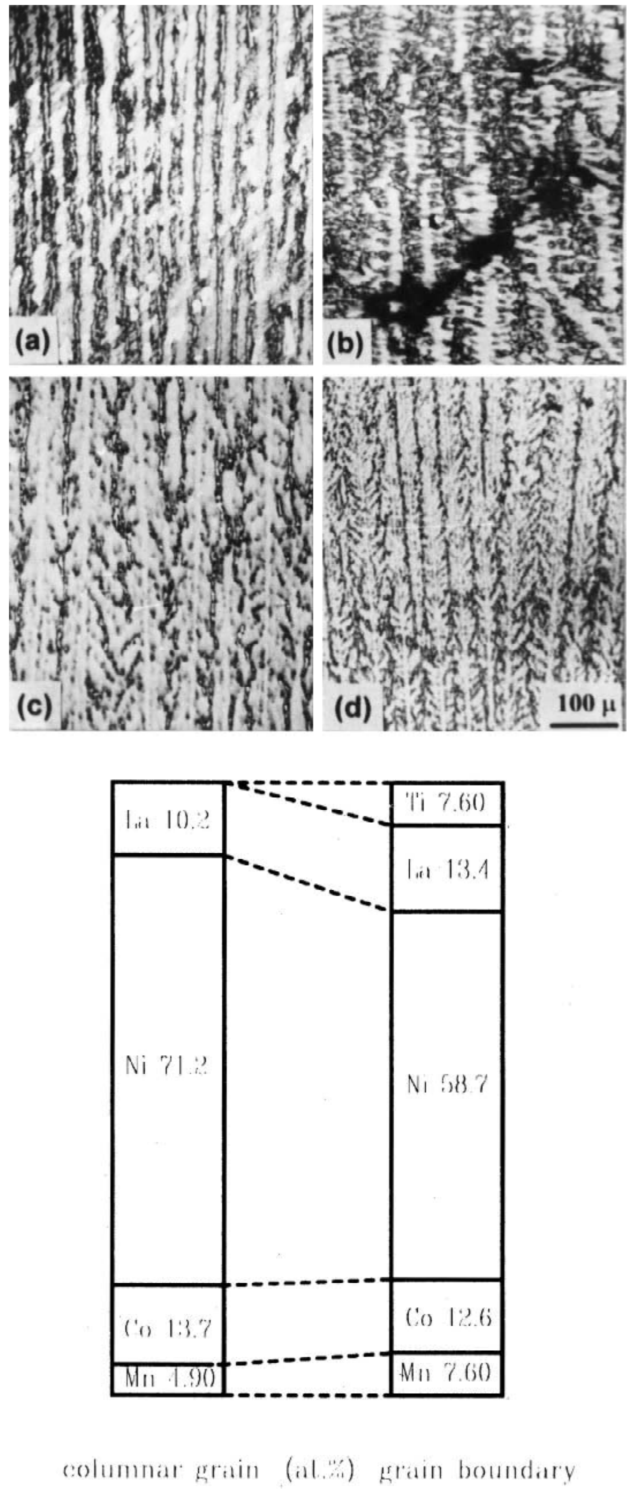

Fig. 1. (A) Microstructures of the unidirectionally solidified alloy at different growth rate (longitudinal cross-section along the growth direction). (a)$R=48$ μm s^{-1}; (b) $R=97$ μm s^{-1}; (c) $R=150$ μm s^{-1}; (d) $R=220$ μm s^{-1}. (B) Element distribution on columnar grains and on grain boundaries for the unidirectionally solidified $Ml(NiCoMnTi)_5$ alloy ($R=150$ μm s^{-1}).

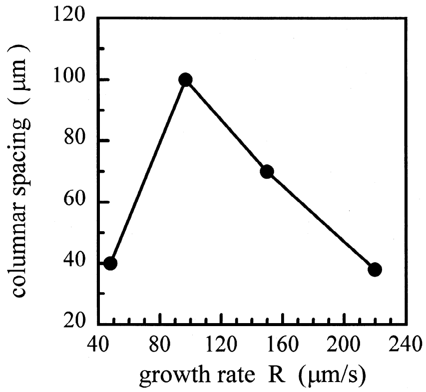

Fig. 2. Effect of growth rate R on the primary columnar spacing λ_1.

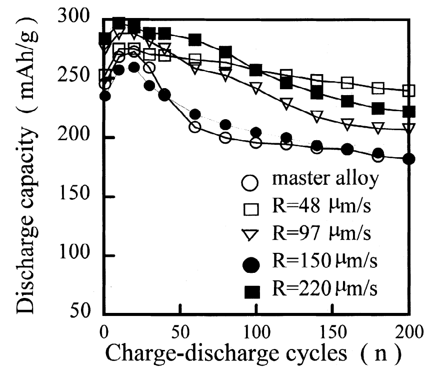

Fig. 3. Influence of solidification condition on the cycling stability of the $Ml(NiCoMnTi)_5$ alloy.

precipitated almost totally on grain boundaries. The behavior of element segregation during alloy solidification has been related to the difference of atomic radius of constituent elements [7]. Generally the larger atoms tend to precipitate preferentially on the grain boundaries.

The electrochemical properties of the alloy prepared at different solidification conditions are shown in Table 1 and Fig. 3. It was found that unidirectional solidification seemed to have no effect on the activation of electrode, but could improve the discharge capacity, high-rate dischargeability and cycling stability of the alloy significantly. For the unidirectionally solidified alloy, generally the discharge capacity and high-rate dischargeablity increased with increase of growth rate. However the effect of growth rate on the cycling stability of the alloy showed an irregular pattern. After 200 cycles, the alloy with a fine cellular–columnar structure ($\lambda_1=40$ μm) prepared at growth rate $R=48$ μm s^{-1} showed a rather low rate of capacity decay of 12.0% compared with 30.0% for the corresponding master alloy. Unidirectional solidification improved the discharge capacity and high-rate dischargeability of the alloy. This might be attributed to the fact that, the unidirectionally solidified alloy had a better homogeneity and crystallinity, and the preferential precipitation of Ti, Ni and Co on the grain boundaries, which could improve the electrocatalytic activity of the alloy surface. The reason the alloy with columnar structure showed high endurance has been ascribed to the observation that columnar grains grow preferentially in the perpendicular direction to the c-axis of the hexagonal $CaCu_5$-type structure, leading to the low lattice strain and high resistance to pulverization of the alloy [5]. However the detailed mechanism remains to be further clarified.

4. Conclusion

Unidirectionally solidified mischmetal based $Ml(NiCoMnTi)_5$ alloy with the columnar structure has been successfully prepared. It is found that there is a critical growth rate (R) for the cellular–dendritic structure transition and the primary columnar spacing (λ_1) variation of the alloy. The unidirectionally solidified alloy with a fine cellular–columnar structure prepared at growth rate of $R=48$ μm s^{-1} significantly improves the discharge capacity, high-rate dischargeability and cycling stability of the alloy.

Table 1
Electrochemical properties of the $Ml(NiCoMnTi)_5$ alloy prepared at different solidification conditions

Solidification condition	Discharge capacity (mAh g^{-1})		Activation number	High-rate dischargeability (%) (at 150th cycle)	Rate of capacity decay after 200 cycles S_{200} (%)
	C_0^b	C_{max}			
Master alloy	158	270	2	88.8	30
US-alloy[a]					
48 μm s^{-1}	198	303	2	92.2	12
97 μm s^{-1}	226	312	2	91.0	25
150 μm s^{-1}	183	281	2	93.6	21
220 μm s^{-1}	252	321	2	93.6	23

[a] Unidirectionally solidified alloy.
[b] Discharge capacity at the first cycle.

References

[1] Y.Q. Lei, Z.P. Li, C.P. Chen, J. Wu and Q.D. Wang, *J. Less-Common Met*., 172–174 (1991) 1265.
[2] T. Sakai, H. Yoshinaga, K. Ogaro, C. Iwakura and H. Yoneyama, *J. Electrochem. Soc*., 134 (1987) 558.
[3] Y.Q. Lei, J.J. Jiang, D.L. Sun, J. Wu and Q.D. Wang, *J. Alloys Comp*., 231 (1995) 611–615.
[4] M. Negami, M. Tadokoro, M. Kimoto, Y. Chikano, T. Ise and N. Furukawa, *Denki Kagaku*, 9 (1993) 1088.
[5] T. Sakai, H. Miyamara, N. Kuriyama, H. Ishikawa and I. Uehara, *Z. fur Phys. Chem*., 183 (1994) 333.
[6] T. Ogawa, K. Ohnishi and T. Misawa, *J. Less-Common Met*., 138 (1988) 143.
[7] T. Sakai, H. Yoshinaga, H. Miyamura, N. Kuriyama and H. Ishikawa, *J. Less-Common Met*., 180 (1992) 37.