Crystal Structure and Hydrogen Absorption Properties of $\text{La}(\text{Ni},\text{M})_x$ ($\text{M}=\text{Al}, \text{Co}, \text{Mn}, \text{Si}$, $x=3\sim 7$) Melt-Spun Ribbons.

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The present study describes the appeared phases and hydrogen absorbing properties of the non-stoichiometric LaNi_x and $\text{LaNi}_{x-1}\text{M}$ ($\text{M}=\text{Al}, \text{Co}, \text{Mn}, \text{Si}$) melt-spun ribbons. A new metastable phase with TbCu_7 -type structure is observed in LaNi_x ($x>5$) melt-spun ribbons. A high melt-spinning rate is able to form the single phase of the TbCu_7 structure. It is found that the Mn or Si addition stabilizes the CaCu_5 structure in wide compositional range of $\text{LaNi}_{x-1}\text{Mn}$ ($x=5\sim 6.5$), or $\text{LaNi}_{x-1}\text{Si}$ ($x=5\sim 8$) melt-spun ribbons. But the amount of absorbed hydrogen decreases with increasing Ni content.

Keywords: melt-spinning technique, LaNi_x melt-spun ribbons, metastable TbCu_7 phase, hydrogen absorbing properties.

I. Introduction

The LaNi_5 intermetallic compound exhibits excellent hydrogen storage properties such as easy activation, low plateau pressure and high hydrogen storage capacity. Therefore, LaNi_5 compound has been extensively studied for the negative electrode of Ni-MH batteries. In today's use for the negative electrode of Ni-MH batteries, alloys must be single phase. But it is well-known that it is difficult to make non-stoichiometric LaNi_5 alloys as single phase because of its limited solid-solution range⁽¹⁾. Therefore, only a few studies of non-stoichiometric LaNi_5 alloys have been reported^{(2) (3) (4)}.

Since rapid quenching effect from molten metals such as induced by melt-spinning technique, tends to exclude segregation of alloys, and this effect will sometime expand the solid-solution range of intermetallic alloys, and will possibly form alloys as single phase⁽⁵⁾.

The purpose of the present study is to investigate rapid quenching effects on the solid-solution range of $\text{La}(\text{Ni}, \text{M})_x$ alloys prepared by melt-spinning with a single roller in discussing their hydrogen absorption properties and the effect of partial substitutional elements such as Al, Co, Mn, and Si on the solid-solution range of LaNi_5 compound.

II. Experimental Procedures

All the AB_x alloys used in this study were prepared by arc-melting under purified argon atmosphere from starting metals, with a purity of better than 99mass%. The alloy was melted into a "button" form. The buttons were remelted several times in order to be homogeneous. Then, the ribbons were prepared by melt-spinning with a single roller under

a purified argon atmosphere.

The studied nominal compositions of the alloys are classified as follows.

- (i) LaNi_x ($x=3.0\sim 7.0$) alloys, melt-spun at roller surface velocity of 40m/s.
- (ii) LaNi_x ($x=6.5\sim 7.5$) alloys, melt-spun at roller surface velocity of 60m/s.
- (iii) $\text{La}(\text{Ni},\text{M})_x$ alloys, ($x=5.0\sim 8.0$, $\text{M}=1$) for $\text{M}=\text{Al}, \text{Co}, \text{Mn}$ or Si .

Melt-spun at roller surface velocity of 60m/s.

Appeared phases in melt-spun ribbons were determined by X-ray diffractometer (XRD) with $\text{Cu-K}\alpha$ radiation. The pressure-composition isotherm (PCT) curves of the specimen were measured at 313K by a Siverts-type apparatus.

III. Result and discussion

1. LaNi_x ($x=3\sim 7$) melt-spun ribbons

Figure 1 shows X-ray diffraction patterns of LaNi_x ($x=3\sim 7$) melt-spun ribbons at the surface velocity of 40m/s. The LaNi_3 and LaNi_4 melt-spun ribbons contain LaNi_2 , La_2Ni_7 phases besides the LaNi_5 phase which are expected from La-Ni binary phase diagram⁽¹⁾. But LaNi_6 and LaNi_7 melt-spun ribbons contain a metastable phase with the TbCu_7 -type crystal structure⁽⁶⁾ beside the LaNi_5 or Ni phases. In order to further study formation of the metastable TbCu_7 -type phase, LaNi_7 melt-spun ribbons are prepared with various surface velocity of the roller.

Figure 2 shows the X-ray diffraction patterns of LaNi_7 melt-spun ribbons in comparison with that of homogenized ingots. The homogenized ingots annealed at 1473K for 50h consist of LaNi_5 and Ni phases but do not include metastable phase as are expected from the phase diagram.

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The metastable TbCu₇-type phase is observed near the surface of the ribbons at the roller-side after quenching at 60m/s. Increasing the roller velocity to 70m/s forms a single phase with the TbCu₇-type. This is the first observation that the TbCu₇-type phase is formed in binary La-Ni alloys.

Figure 3 shows the X-ray diffraction patterns of LaNi_x ($x=6.5\sim7.5$) melt-spun ribbons. The single phase is formed at $x=7$ but slight deviation of x from 7 forms like other phases such as Ni or LaNi₅.

Fig.1. XRD patterns of LaNi_x ($x=3\sim7$) melt-spun ribbons.

Fig.2. XRD patterns of LaNi₇ melt-spun ribbons.

Figure 4 shows the PCT curves of LaNi_x ($x=3\sim7$) melt-spun ribbons at the surface velocity of 40m/sec. The LaNi₅ alloys absorb the highest amount of hydrogen. With increasing the Ni content in the alloys, the absorbed amount of hydrogen decreases.

2. LaNi_{x-1}M (M=Al, Co, Mn and Si) melt spun-ribbons

LaNi_{x-1}M (M=Al, Co, Mn, and Si), ($x=5.0\sim8.0$, M=Al, Co, Mn or Si ($x=5.0\sim8.0$)) melt-spun ribbons are prepared at surface velocity of 60m/s.

Figures 5 and 6 show XRD patterns of LaNi_{x-1}Al, and LaNi_{x-1}Co melt-spun ribbons, respectively. Both of the alloy ribbons with the stoichiometry x larger than 5 are not a

Fig.3. XRD patterns of LaNi_x ($x=6.5\sim7.5$) melt-spun ribbons.

Fig. 4. PCT curves (of absorption) of LaNi_x ($x=3\sim7$) ribbons, melt-spun at 40m/s.

single phase structure and contain the TbCu_7 -type phase, which is similar to those observed in the LaNi_x melt-spun ribbons described above. Cooling rate of melt-spinning may be not fast enough to form the metastable single phase. The $\text{La}(\text{Ni}_4\text{Al})$ and $\text{La}(\text{Ni}_4\text{Co})$ alloys show the single phase of CaCu_5 structures.

Figures 7 and 8 show XRD patterns of $\text{LaNi}_{x-1}\text{Mn}$ and $\text{LaNi}_{x-1}\text{Si}$ melt-spun ribbons, respectively. In the $\text{LaNi}_{x-1}\text{Mn}$ and $\text{LaNi}_{x-1}\text{Si}$ ribbons, solid-solution range of the CaCu_5 structure is expanded. Especially, the solid-solution range of $\text{LaNi}_{x-1}\text{Si}$ melt-spun ribbons is from LaNi_4Si ($x=5$) to

LaNi_7Si ($x=8$). This could be a first observation that the addition of Si forms the CaCu_5 structure in wide compositional range by melt-spinning. The $\text{LaNi}_{x-1}\text{Mn}$ melt-spun ribbons have also the solid-solution range of the CaCu_5 structure from LaNi_4Mn ($x=5$) to $\text{LaNi}_{5.5}\text{Mn}$ ($x=6.5$).

Figure 9 shows lattice constants of $\text{LaNi}_{x-1}\text{Si}$ ($x=5\sim 8$) melt-spun ribbons. The lattice constants of all melt-spun ribbons with the CaCu_5 single phase structure change continuously, where a -axis decreases and c -axis increases with increasing x (Ni content). The variation of the lattice constants of $\text{LaNi}_{x-1}\text{Si}$ melt-spun ribbons is similar to that

Fig.5. XRD patterns of $\text{LaNi}_{x-1}\text{Al}$ melt-spun ribbons.

Fig.6. XRD patterns of $\text{LaNi}_{x-1}\text{Co}$ melt-spun ribbons.

Fig.7. XRD patterns of $\text{LaNi}_{x-1}\text{Mn}$ melt-spun ribbons.

Fig.8. XRD patterns of $\text{LaNi}_{x-1}\text{Si}$ melt-spun ribbons.

of LaNi_x ($x=5.0\sim 5.4$) alloys reported by Buschow⁽⁷⁾. This variation was explained by random substitution of a pair of Ni atoms for some of the La atoms. The crystal structures of $\text{LaNi}_{x-1}\text{Si}$ ($x=5\sim 8$) melt-spun ribbons are regarded as a modified CaCu_5 -type, where they change from the CaCu_5 -type to the TbCu_7 -type continuously in randomly substituting the pair of Ni atoms for some of the La atoms in the CaCu_5 structures. The $\text{LaNi}_{x-1}\text{Mn}$ ($x>6.5$) ribbons include the nickel beside CaCu_5 -type phase. Then it can be said that the effect of silicon addition for forming the single phase with the CaCu_5 structure is stronger than that of manganese addition.

Figure 10 shows the PCT curves of absorption of LaNi_4M ($\text{M}=\text{Al}, \text{Co}, \text{Mn}$ and Si) melt-spun ribbons. The LaNi_4Co melt-spun ribbon has a plateau pressure as was reported⁽⁸⁾. But others have almost no plateau pressure. Similar tendency of hydrogen absorption property of $\text{LaNi}_{4.55}\text{Al}_{0.45}$ melt-spun ribbon was reported⁽⁹⁾.

Fig. 9. Lattice constants of $\text{LaNi}_{x-1}\text{Si}$ melt-spun ribbons as a function of composition x .

Fig. 10. PCT curves of LaNi_4M ($\text{M}=\text{Al}, \text{Co}, \text{Mn}$ and Si) ribbons, melt-spun at 60m/s.

Figure 11 shows PCT curves of $\text{LaNi}_{x-1}\text{Si}$ ($x=6\sim 8$) melt-spun ribbons and indicates that there are no plateau pressure, and that absorbed amount of hydrogen decreases with increasing of Ni content. Same tendency was reported in $\text{LaNi}_{x-1}\text{Cu}$ system ($x=5\sim 6$)⁽¹⁰⁾.

It has been regarded that the solid solution range of the CaCu_5 -type structure of La-Ni-M systems was very narrow, and that the formation of non-stoichiometric CaCu_5 -type alloys with a single phase structure is difficult by traditional

Fig. 11. PCT curves of absorption of $\text{LaNi}_{x-1}\text{Si}$ ($x=6\sim 8$) ribbons, melt-spun at 60m/s.

melting and casting technique. But present study adopting a melt-spun technique shows that it is possible to form a single phase structure with non-stoichiometric compositions in La-Ni-M alloy systems.

IV. Conclusion

(1) A metastable TbCu_7 -type phase exists in the La-Ni and La-Ni-M ($\text{M}=\text{Al}, \text{Co}$) systems which is only stabilized by melt-spun technique. The single TbCu_7 -type single phase structure is formed after melt-spinning at the surface velocity of over 70m/s.

(2) There exist wide solid solution ranges of the CaCu_5 -type structure in $\text{LaNi}_{x-1}\text{M}$ ($\text{M}=\text{Mn}, \text{Si}$) melt-spun ribbons and relation between composition of ribbons and solid-solution ranges of single-phase structure are as follows.

- ① $\text{LaNi}_{x-1}\text{Mn}$ melt-spun ribbons: $x=5\sim 6.5$.
- ② $\text{LaNi}_{x-1}\text{Si}$ melt-spun ribbons: $x=5\sim 8$.

However, the Ni-rich single phase absorbs less amount of hydrogen than that of stoichiometric LaNi_x alloys.

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