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Crystal structure and protium absorption properties of La-rich La(Ni, M)$_x$ (x=3–4.7) (M=Al, Co, Mn, Si) melt-spun ribbons

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Abstract

The present study describes the rapid quenching effects on the solid-solution range of La(Ni, M)$_x$ (x=3–4.7) (M=Al, Co, Mn, Si) alloys prepared by melt-spinning and discusses their protium (hydrogen atom) absorption properties. It is found that the single phase with $CaCu_5$ crystal structure extends to $LaNi_{4.65}$ compositional alloys. When x in $LaNi_{5-x}$ becomes smaller, the alloy acquires better protium absorption properties including easier activation, better flatness of plateau region and a good hydrogen storage capacity comparable to those of $LaNi_5$ homogenized sample. On adopting a melt-spinning technique it is easy to form single phase of $CaCu_5$ type-structure for La-rich non-stoichiometric La–Ni–M alloys such as La(Ni, M)$_x$ (x=3–4.7) (M=Al, Mn, Si) alloys. The readiness of forming a single phase $CaCu_5$ type-structure in melt-spun La–Ni–M alloys is in order of Al≥Si>Mn>Co.The phases formed and protium absorption properties of La-rich $LaNi_{4.5}M_{0.2}$ melt-spun alloys are studied. It was found that $LaNi_{4.5}M_{0.2}$ alloys had better protium absorption properties such as easier activation than the $LaNi_{4.65}$ binary alloy and as good hydrogen storage capacity as that of homogenized $LaNi_5$.

Keywords: $LaNi_5$ melt-spun ribbons; Melt-quenching effects; La-rich $CaCu_5$-type phase; Limitation of solid solution of $CaCu_5$; Substitutional elements effects

1. Introduction

The $LaNi_5$ intermetallic compound exhibits excellent protium storage properties such as easy activation, low plateau pressure and high density of protium. Therefore, LaNi-based intermetallic compounds have been extensively studied for the negative electrodes of Ni–MH batteries. In today's practical use for the negative electrode of Ni–MH batteries, alloys must be of single phase. But it is well-known that it is difficult to make non-stoichiometric $LaNi_5$-based alloys with a single phase because of their limited solid-solution range [1]. Especially, $LaNi_x$ ($x<5$) alloys are hard to make a single phase, and a few studies on non-stoichiometric $LaNi_x$ ($x<5$) alloys have been reported [1]. On the other hand, $LaNi_x$ ($x>5$) alloys have good cycling properties although the amount of hydrogen absorbed is lower [2–6]. Rapid quenching techniques are applied to hydrogen absorbing alloys, to improve the hydrogen absorbing properties [7,8]. It is also reported that it is difficult to obtain amorphous phases in $LaNi_5$ alloys [9]. The amorphous $LaNi_5$ alloys prepared by sputtering have a low hydrogen absorbing capacity [10,11]. Since rapid quenching effects from molten metals such as those induced by melt-spinning technique, are arresting for segregation, forming of fine grains, increasing the homogeneity of the alloys and possibly forming of metastable phases [12,13]. Expansion of the solid solution range of intermetallic alloys has been observed at high cooling rate since the solidification rate of melt-spinning could be almost 1000 times higher, compared to the arc-melt process [8].

Quite a few studies of the effects of substitutional elements on the hydrogen absorbing properties for $LaNi_5$ alloys have been reported [5]. For Ni-rich La–Ni alloys, it is reported that the new metastable phase with $TbCu_7$-type structure was observed in $LaNi_x$ ($x>5$) melt-spun ribbons [14], and that Mn or Si addition stabilizes the $CaCu_5$ structure in the wider compositional range of $LaNi_{x-1}Mn$ (x=5–6.6), or $LaNi_{x-1}Si$ (x=5–8) melt-spun ribbons. Then it is also expected for La-rich La–Ni_x alloys ($x<5$) that the good effects of the substitutional elements will be obtained.

The purpose of the present study is to investigate rapid quenching effects on the solid-solution range and the protium absorption capacities of $LaNi_5$ type compounds with $CaCu_5$-type structure single phase alloy for the

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compositions of La(Ni, M)$_x$ (x=3–4.7) alloys prepared by melt-spinning with a single roller. The effects of partial substitutional elements such as Al, Co, Mn, Si etc. on the solid-solution range of LaNi$_5$ type compounds are also studied. Especially, the present study aims to clarify the effects of substitutional elements on the formations of CaCu$_5$-type structure for La-rich LaNi$_x$ (x<4.7) alloys, which are reported to be difficult to form as a single phase.

2. Experimental procedures

All the La(Ni, M)$_x$ (x=3–4.7) alloys used in this study were prepared by arc-melting under purified argon atmosphere from industrial grade pure metals, with purities all better than 99 mass%. The alloy was melted into a button. The buttons were remelted several times for homogenization. Then, the ribbons were prepared by melt-spinning at the surface velocity of 60 m/s (approximately over 10^5 K/s) with a single roller under a purified argon atmosphere. The resulting grain size distribution depends on the composition of the alloys, varying typically from 0.1 to 1 μm. The phases existing in melt-spun ribbons were determined by X-ray diffractometer (XRD) with Cu K$_\alpha$ radiation. The pressure–composition isotherm (PCT) curves of the specimen were measured at 313 K by Sieverts-type apparatus.

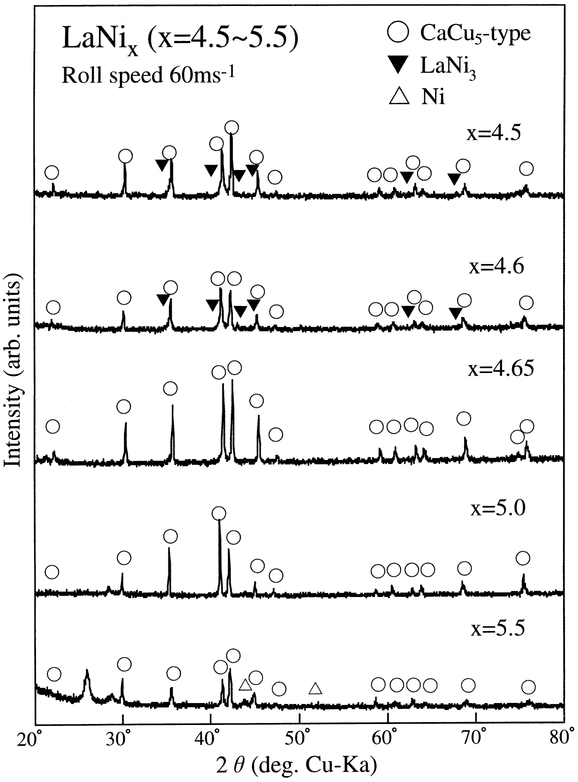

Fig. 1. X-ray diffraction patterns of LaNi$_x$ (x=4.5–5.5) melt-spun ribbons.

3. Results and discussions

3.1. LaNi$_x$ (x=4.5–5.5) melt-spun ribbons

The LaNi$_x$ (x=4.5–5.5) alloys were prepared by the melt-spun techniques, since it is important to know how the solid-solution range of LaNi$_5$ phase with CaCu$_5$-type structure will be expanded by the technique. Fig. 1 shows X-ray diffraction patterns of LaNi$_x$ (x=4.5–5.5) melt-spun ribbons. The LaNi$_{5.5}$ melt-spun ribbons contain Ni phase besides LaNi$_5$ phase, and LaNi$_x$ (x=4.5 or 4.6) ribbons consist of LaNi$_3$ and LaNi$_5$ phase, which are expected from the La–Ni binary phase diagram [1]. But the LaNi$_x$ (x=4.65–5) ribbons show CaCu$_5$-type structure, which indicates that the solid-solution range of the LaNi$_5$ phase is larger than the reported one (x=4.9) for the as-cast or homogenized alloys [1]. This result is consistent with the phase diagram reported by Itagaki [15]. It is found that the melt-spun technique has an effect for freezing the solid-solution range of LaNi$_5$ phase at high temperatures.

Fig. 2 shows the lattice constants of LaNi$_x$ (x=4.5–5.5) melt-spun ribbons as a function of composition x. The lattice constants monotonically increase with increasing La content. It was reported that the a-axes shrink, and c-axes expand with increasing the Ni content for the LaNi$_x$ (x>5) alloys [16]. For the La-rich LaNi$_x$ (x<5) alloys, it has been said that excess La atoms will randomly occupy the Ni sites in CaCu$_5$-type crystal structure, which expects that both a-axes and c-axes will expand with the increasing number of Ni atoms substituted by excess La atoms. The present study clarifies that the a-axes and c-axes expand for the La-rich LaNi$_x$ (4.65≤x≤5) alloys, since the

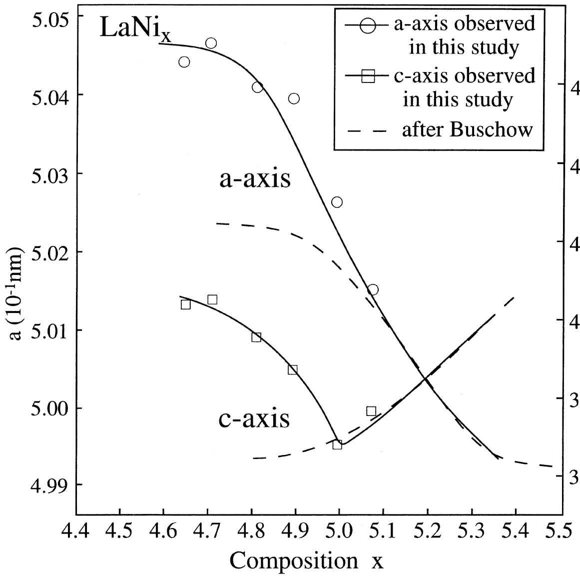

Fig. 2. The lattice constants of LaNi$_x$ (x=4.65–5.35) melt-spun ribbons as a function of composition x.

relatively large solid-solution range of $CaCu_5$-type crystal structure was obtained by melt-spinning in this study. This variation of lattice constants would be considered to be reasonable in assuming that larger size of La atoms will substitute the Ni atoms with increasing La content.

Fig. 3 shows the (a) PCT curves of 1st cycle for $LaNi_x$ (x=4.65, 4.8, 5) melt-spun ribbons without activation treatment and (b) PCT curves of 1st–50th cycles for $LaNi_{4.65}$ melt-spun ribbons. The 1st cycle curve in the figure corresponds to the activation treatments and shows that the pressure of the 1st cycle for absorbing protium turns out to be the lowest for La-rich $LaNi_{4.65}$ ribbons. This result suggests that the alloys with higher content of La may undergo easier activation treatments.

Fig. 3b indicates that protium content remains almost unchanged after the 50th cycle for the ribbons. No hydrogen-induced amorphization has been observed in La-rich ribbons. It was reported that the rare-earth rich Mm $(Ni, Al, Co, Mn)_{4.75}$ alloys prepared by rapid-quenching techniques show high capacity and long life cycling in secondary Ni–MH batteries [17,18]. It can be said that melt-spinning is an effective sample preparation technique for a higher protium content, less sloped plateau region and easier activation.

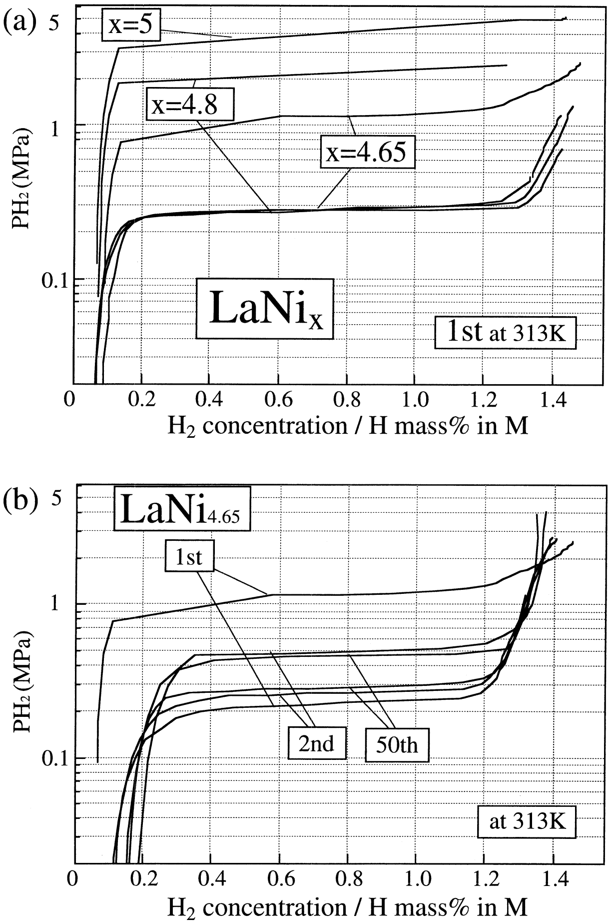

Fig. 3. (a) PCT curves of 1st cycle for $LaNi_x$ (x=4.65, 4.8, 5) melt-spun ribbons and (b) PCT curves of 1st to 50th cycles for $LaNi_{4.65}$ melt-spun ribbons.

3.2. $LaNi_{x-0.5}M_{0.5}$ (x=3–4.5), $LaNi_{x-0.2}M_{0.2}$ (x=4–4.5) (M=Al, Co, Mn, Si) melt-spun ribbons

$LaNi_{x-0.5,0.2}M_{0.5,0.2}$ (M=Al, Co, Mn, Si) (x=3–4.5) melt-spun ribbons were prepared in order to pursue the possibility to obtain the La-rich $CaCu_5$-type crystal structure by substitutional elements. Fig. 4 shows the XRD patterns of $LaNi_{x-0.5}M_{0.5}$ (x=3–4.5) melt-spun ribbons. The Al substitution tends to form the wide compositional range of $CaCu_5$-type crystal structure. Table 1 summarizes the phases in the $LaNi_{x-0.5}M_{0.5}$ (x=3–4.5) and $LaNi_{x-0.2}M_{0.2}$ (x=4–4.5) (M=Al, Co, Mn, Si) melt-spun ribbons. The Al and Si substitutions form the widest range of $CaCu_5$-type crystal structure. The readiness of forming of $CaCu_5$-type phase in La–Ni–M system will be in orders of Al≥Si>Mn>Co. However, the protium absorbing properties of these ribbons turn out to be not better than those of binary alloys.

3.3. $LaNi_{4.5}M_{0.2}$ melt-spun ribbons

The effects of the substitutional elements on the hydrogen absorbing properties of $LaNi_5$ and $MmNi_5$ alloys have been extensively studied [5], but few works on non-

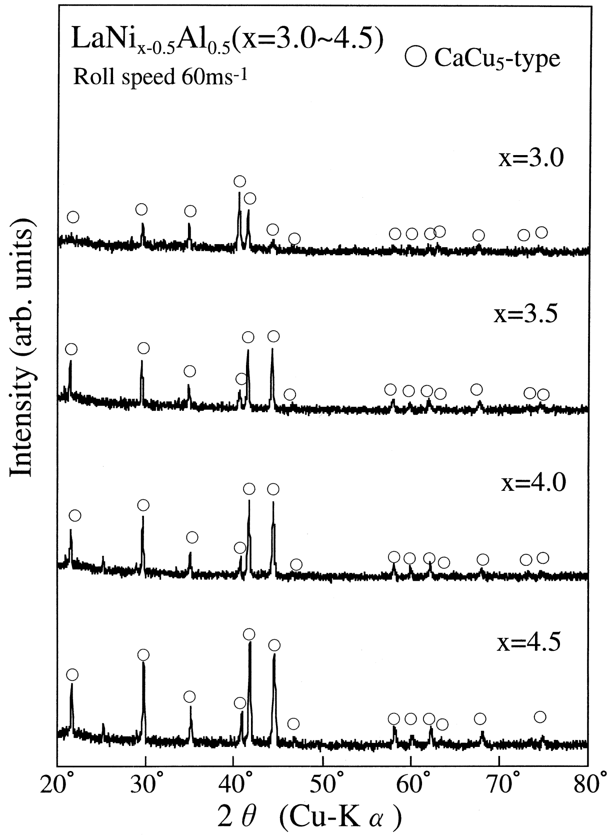

Fig. 4. XRD patterns of $LaNi_{x-0.5}Al_{0.5}$ (x=3–4.5) melt-spun ribbons.

Table 1
The phases in the $LaNi_{x-0.5}M_{0.5}$ (x=3–4.5) and $LaNi_{x-0.2}M_{0.2}$ (x=4–4.5) (M=Al, Co, Mn, Si) melt-spun ribbons

La:Ni:M	Al	Co	Mn	Si
1:2.5:0.5	○[a]	1–5 + unknown	○	○
1:3.0:0.5	○	○	○	○
1:3.5:0.5	○	○	○	○
1:4.0:0.5	○	○	○	○
1:3.8:0.2	○	1–3 + 1–5	1–3 + 1–5	○
1:4.3:0.2	○	1–3 + 1–5	1–3 + 1–5	○

[a] ○, $CaCu_5$-type single phase.

stoichiometric $LaNi_{4.7}$ alloys have been reported. The effects of a small amount (x=0.2) of additional element on the forming of $CaCu_5$-type crystal structure for $LaNi_{4.7}$ were also studied here since $LaNi_{4.7}$ melt-spun ribbons are all of single $CaCu_5$-type phase. Fig. 5 shows the XRD patterns of $LaNi_{4.5}M_{0.2}$ (M=Al, B, Co, Cr, Cu, Fe, Ge, Mn, Si, Sn, Ti, V) melt-spun ribbons. All of the ribbons with substitutional elements contain the single phase with $CaCu_5$-type crystal structure. Fig. 6 shows the PCT curves of (a) 1st cycle (absorbing process) and (b) 50th cycle (desorption process) for $LaNi_{4.5}M_{0.2}$ melt-spinning ribbons in comparison with those of $LaNi_{4.65}$ melt-spinning ribbons without activation treatment. The pressure of the 1st cycle for absorbing protium turns out to be higher for B and Sn substitutional ribbons than that of $LaNi_{4.65}$ ribbons. The Fe, Ge, Si, V, Cr substitutions all lower the pressure for activation. After 50 cycles, most of the ribbons except the ribbons with B and V show almost the same protium absorbing capacity, and lower plateau pressures as shown in Fig. 6b. The Al, Cr, Ge, Si, and Sn substitutions all make the hysteresis for the absorption–desorption process smaller. In conclusion, it can be said that a small amount of element substitutions improves the initial activations while the protium capacity remains the same as that of $LaNi_{4.65}$ ribbons.

Acknowledgements

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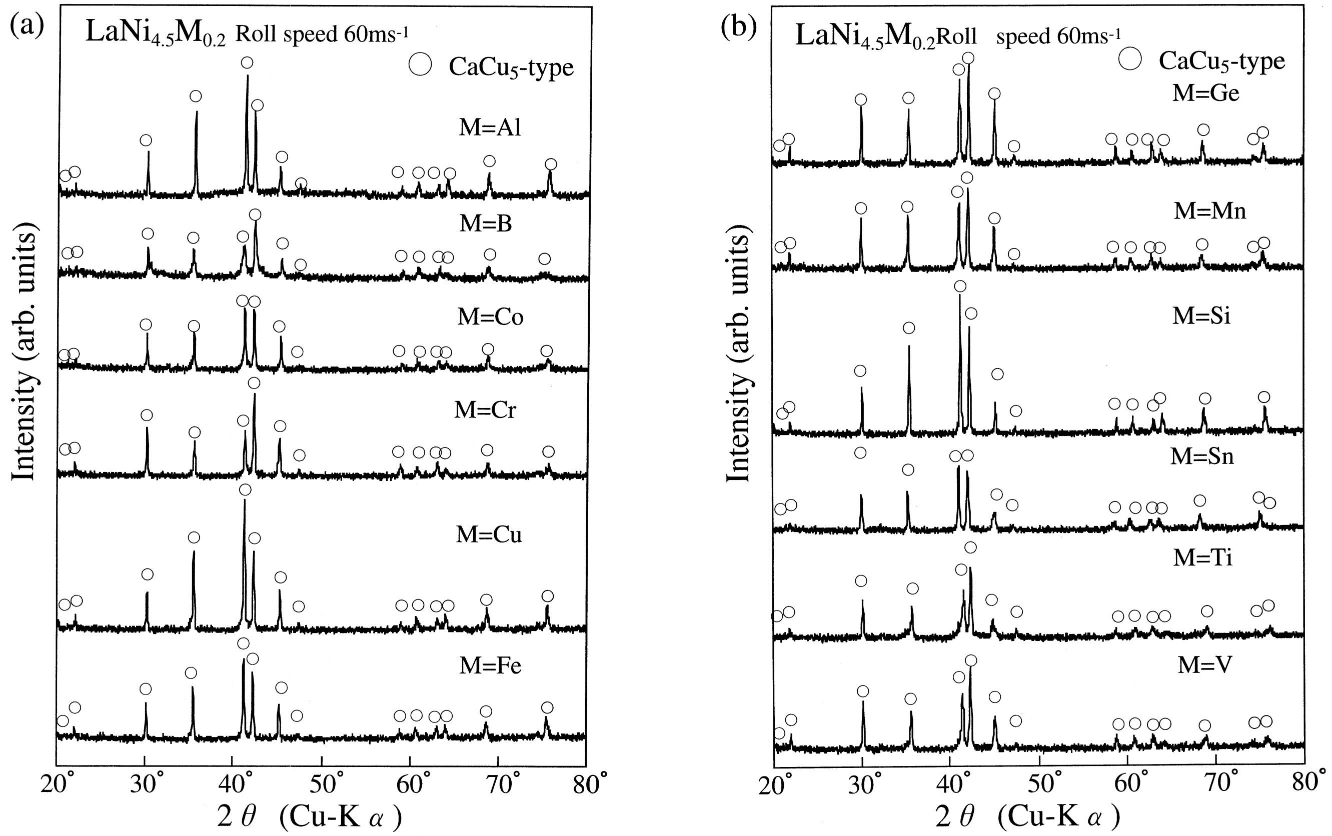

Fig. 5. XRD patterns of $LaNi_{4.5}M_{0.2}$ melt-spun ribbons.

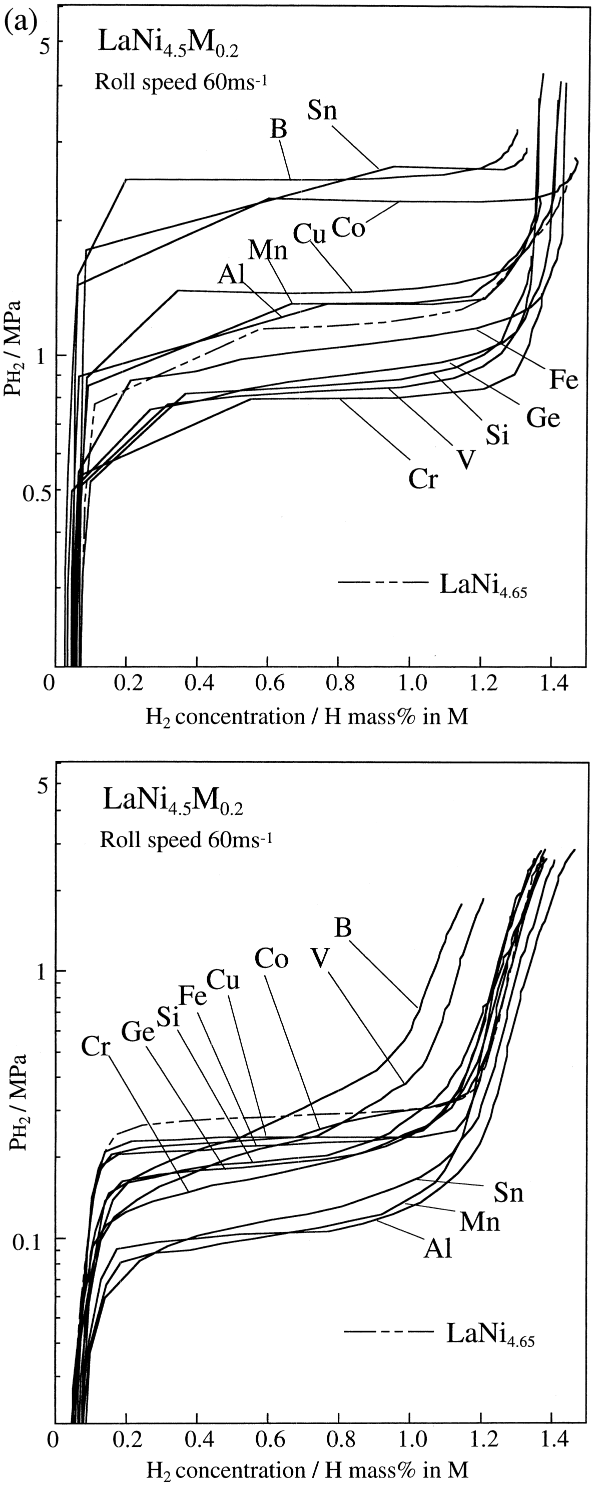

Fig. 6. PCT curves of (a) 1st cycle (absorbing process) and (b) 50th cycle (desorption process) for $LaNi_{4.5}M_{0.2}$ melt-spun ribbons.

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