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Investigations on the nitrogen storage property of $LaNi_5$ powder

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ABSTRACT

The nitrogen absorption and desorption property of $LaNi_5$ was investigated using NH_3 and N_2 as nitrogen sources. It was found that both as purchased and milling processed $LaNi_5$ powder can absorb and desorb nitrogen using NH_3 as the nitrogen source, while milled $LaNi_5$ powder can absorb and desorb more. XRD, cross sectional SEM and EPMA were performed to elucidate the nitrogen stored phases. When N_2 gas was used as the nitrogen source, it was found that the amount of absorbed nitrogen significantly decreased. By using high pressure for the absorption treatment or performing an activation treatment using hydrogen absorption/desorption before the nitrogen absorption treatment, milled $LaNi_5$ was found to absorb nitrogen of 0.1 mol/mol Finally, the mechanism of the nitrogen absorption was discussed from the EPMA and kinetic data of the nitrogen absorption, and it was suggested that the mechanism of the nitrogen absorption might be explained by a combined model of a diffusion controlled process and an interface controlled process.

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1. Introduction

Recently, nitrogen storage alloys have attracted attention as a new functional material [1–3]. They are the alloys that can absorb and desorb nitrogen reversibly, and thirteen examples have been reported so far [1–3], where the nitrogen is absorbed under an NH_3 or a N_2 atmosphere at high temperatures and desorbed under a H_2 atmosphere as NH_3. The nitrogen storage capacities per unit volume of these alloys are superior to those of conventional high pressure containers of nitrogen stored at 15 MPa.

The nitrogen storage alloys generally consist of both a metal having high affinity with nitrogen and another metal that can dissociate the nitrogen sources such as NH_3 and N_2. Rare earth metals are commonly used as the former metal and only iron was employed as the latter, though Ni, Co and Ru, etc. are also known to be able to dissociate NH_3 and N_2 [4].

Previously, we reported new nitrogen storage alloy candidates of Ca–Fe and Ca–Co alloy systems synthesized by Ball Milling method [5,6]. In this paper, we report the nitrogen storage property of $LaNi_5$, where Ni is employed as the metal to dissociate nitrogen sources, which may open a new research field of nitrogen storage alloy. The $LaNi_5$ has been actively studied for hydrogen storage alloy, and the acquisition of the compound is relatively easy. Also, the comparison of the gas absorption mechanism is not only practically important but also scientifically interesting. Thus, in this paper, an enhancement of the nitrogen storage property utilizing mechanical milling method using an agate-made mortar machine and the mechanism of the nitrogen absorption of the $LaNi_5$ alloy compound are investigated.

2. Experimental

The $LaNi_5$ powder (−100 mesh) of 99.9% purity was purchased from Nacalai Tesque. A nitrogen absorption treatment was performed on following samples; $LaNi_5$ as purchased, $LaNi_5$ milled for 21 h in toluene and Ni powder (grain size 63 μm) of 99.9% purity. An agate-made mortar machine was employed as the milling equipment, and the milling was done in air. For the nitrogen absorption treatment, 1 g of each sample was put in a quartz tube under a NH_3 or N_2 atmosphere at 270–600 °C for 15 min to 12 h, while the nitrogen desorption treatment was performed under a H_2 or vacuum atmosphere at 400 °C for 3 h. Above treatments were all performed under 1 atm. As for the nitrogen absorption treatment, a high pressure gas was also used; 1 g of each sample was put in a steel tube and the absorption treatment was carried out using N_2 of 1–40 atm at 350–450 °C for 3–12 h. Furthermore, for an activation treatment 10 cycle of hydrogen absorption (20 atm, 5 min, 120 °C) and desorption (vacuum, 5 min, 120 °C) was employed.

The content of nitrogen in the sample after the absorption and desorption treatment was determined using nitrogen/oxygen determinator (TC-336, LECO). The powder X-ray diffraction (XRD) with Cu-Kα radiation was performed to confirm the structural change of the samples utilizing RINT2000CMJ. The acceleration voltage and current was 40 kV and 30 mA, respectively, with the step width of 0.006° and time constant of 3 s. Texture observation was made using Scanning Electron Microscopy, SEM (JSM-5800 TYPE-C, JEOL).

3. Results

3.1. Nitrogen absorption and desorption properties using NH_3 as the nitrogen source

Table 1 shows the nitrogen contents of each sample where the nitrogen absorption treatment at 350 °C for 3 h under a NH_3

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Table 1
Nitrogen content after absorption with NH_3 and desorption with H_2 for $LaNi_5$, $LaNi_5$ (as milled), and Ni.

Sample	Cycle	Nitrogen content (mol/1 mol of alloys)		Desorbed nitrogen (mol/1 mol of alloys)
		After absorption	After desorption	
$LaNi_5$	1	0.3	0.1	0.2
$LaNi_5$ (as milled)	1	1.5	0.5	1.0
	3	1.3	0.5	0.8
Ni	1	0.0	0.0	0.0

Absorption was performed for 3 h at 350 °C with NH_3.
Desorption was performed for 3 h at 350 °C with H_2.

atmosphere and the desorption treatment at 400 °C for 3 h under a H_2 atmosphere were repeated for 1–3 times. The original $LaNi_5$ absorbs 0.3 mol of nitrogen per one mol $LaNi_5$ (mol/mol) and desorbs 0.2 mol/mol (From now on the unit “mol per one mol $LaNi_5$” will be expressed as “mol/mol” unless otherwise noted). On the other hand, the milled $LaNi_5$ absorbed 1.5 mol/mol of nitrogen and desorbed 1.0 mol/mol of nitrogen. In addition, the amount of absorbed and desorbed nitrogen decreases with the cycle number. The pure Ni neither absorbs nor desorbs nitrogen at all.

Fig. 1(a) and (b) shows the SEM images of $LaNi_5$ powder before/after the milling, respectively. These images indicate the grain size decreased from the initial size of 20–100 μm to below 20 μm by the milling, indicating the increased surface area. This increased surface area was attributed to the increased absorption of the milled $LaNi_5$ power, while improvement of nitrogen diffusion due to increased lattice imperfections can be also considered as other reasons for the increase of absorption.

Fig. 2 shows the typical X-ray diffraction patterns of $LaNi_5$, (a) as milled, (b) after the 1st absorption, (c) after the 1st desorption, (d) after the 3rd absorption and (e) after the 3rd desorption. $LaNi_5$ is known to have a hexagonal crystal structure with lattice constants of $a = 5.0125$ Å and $c = 3.9838$ Å, and this is consistent with the peaks in Fig. 2(a). Fig. 2(a) also confirms that there is no change in the crystal structure and composition in the $LaNi_5$ powder by the milling (data for the initial $LaNi_5$ powder before the milling not shown). New peaks were found after the absorption treatment (Fig. 2(b)), the Bragg reflections of which do not agree with any data of the JCPDS cards, coexisting with the initial hexagonal $LaNi_5$ and FCC Ni. The new peaks have a broadened shape, suggesting small grain sizes of the new phase compared with the initial $LaNi_5$ powder. These new peaks disappear after the desorption treatment, consistent with the nitrogen contents in Table 1. It should be noticed that similar trend was observed also for the case of the original $LaNi_5$ powder.

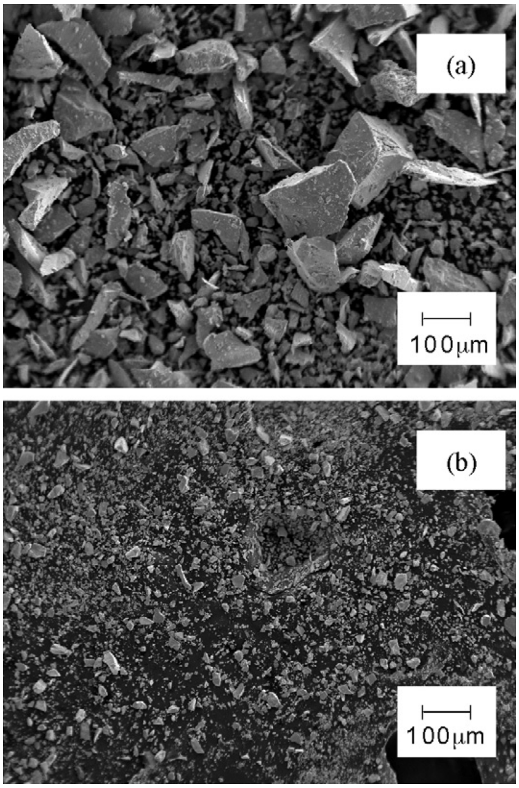

Fig. 1. (a and b) SEM image of $LaNi_5$ powder before and after the milling, respectively.

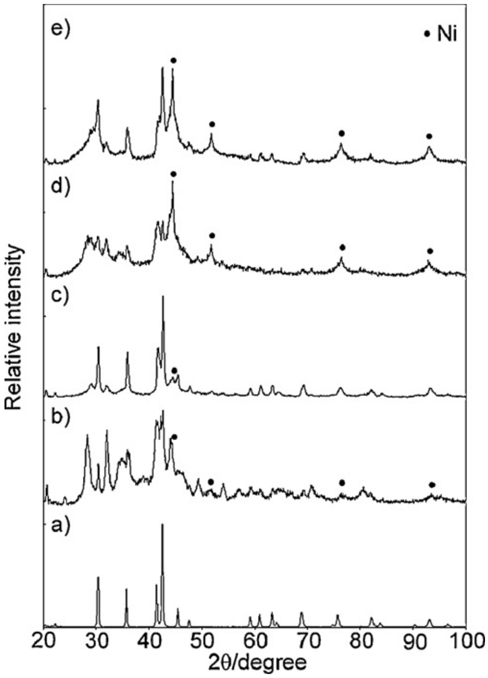

Fig. 2. XRD patterns of $LaNi_5$, (a) after the milling, (b) after the 1st absorption, (c) after the 1st desorption, (d) after the 3rd absorption, and (e) after the 3rd desorption.

The sharpness of the new peaks indicates that there are two phases. Under this assumption, a crystal structure was found to match with one of the new phases as shown in Fig. 3. Fig. 3(a) shows the simulated XRD pattern using a hexagonal crystal structure with lattice constants of $a = 4.96$ Å and $c = 3.72$ Å, and Fig. 3(b) shows the XRD pattern of a sample treated with NH_3 at 500 °C for 3 h.[1] It can be seen that the simulated pattern (Fig. 3(a)) matches with the peaks indicated with filled triangles in Fig. 3(b). Any of the other peaks

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[1] Higher temperature and longer treatment were used for this sample to obtain as large intensity of the new peaks as possible.

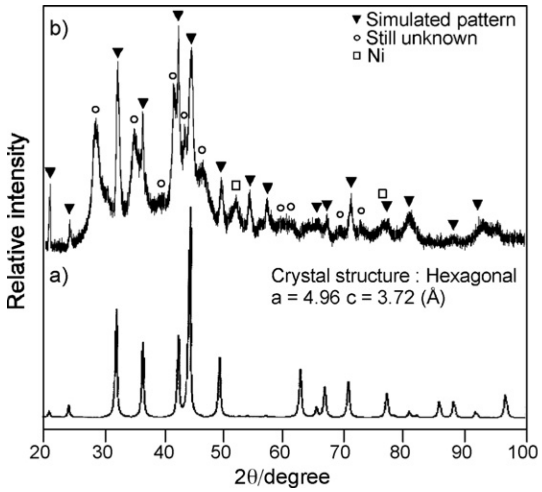

Fig. 3. XRD patterns of (a) simulated and (b) $LaNi_5$ after the absorption treatment at 500 °C for 3 h using NH_3

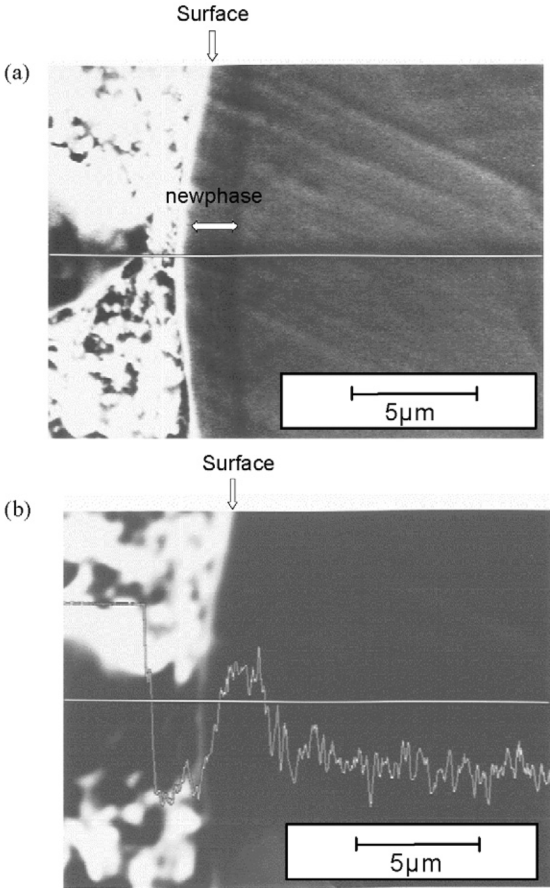

Fig. 4. (a) Cross sectional SEM image of the $LaNi_5$ powder (non-milled) after the absorption treatment. (b) Corresponding EPMA line profile of nitrogen in the $LaNi_5$ powder after the absorption.

indicated with open circles in Fig. 3(b), on the other hand, could not be assigned to any structures that can be generated by varying the lattice constants of cubic, tetragonal, and hexagonal structures, suggesting it has a complex structure.

The amount of the absorbed and desorbed nitrogen decreases with the increase of cycle number as shown in Table 1. Since the peaks of Ni shown in Fig. 2, are becoming stronger as the cycle increases, it is suggested that a part of $LaNi_5$ were decomposed after the absorption and desorption treatments, resulting in the decrease of nitrogen absorption. The decomposition might result from LaN and/or La_2O_3 formations, although they were not observed in the XRD patterns in Fig. 2.

EPMA was also performed on the sample powder (non-milled) after the absorption treatment at 350 °C for 3 h. Fig. 4(a) and (b) shows the SEM images and EPMA mapping of the sample after the absorption treatment, respectively. In Fig. 4(a), there is a region or layer formed on the $LaNi_5$ powder surface with 2 μm thickness where secondary electron absorbance differs from bulk powder (right side), and from Fig. 4(b) it can be seen that this contains higher nitrogen than inside, which means this is the new phase contributing to the nitrogen absorption.

Next, the temperature dependence of the absorption property was investigated, where the nitrogen absorption treatment was performed for 1 h under NH_3 atmosphere at several temperatures. Table 2 shows the nitrogen contents of milled $LaNi_5$ after the absorption and desorption treatments at each temperature. The desorption treatments at 400 °C for 3 h under H_2 atmosphere were performed only to the samples which had been nitrogenated above 500 °C. The XRD spectrums of these samples are shown in Fig. 5. It can be seen that the amount of the absorbed nitrogen is increased with temperature increased up to 500 °C, followed by a decrease to a constant value of 1.0 mol/mol at higher temperatures. The decrease and constant value of 1.0 mol/mol would be due to the formation of the LaN phase above 550 °C during the nitrogenation as confirmed from Fig. 5. Furthermore, it is also found that such LaN and Ni mixture does not desorb nitrogen by the desorption treatment, according to the X-ray analysis and nitrogen content. This would be due to the strong triplet bond between La and N in LaN.

Finally, the effects of different gas atmospheres on the desorption property were investigated. Table 3 shows the nitrogen content of the samples on which desorption treatments were made under

Table 2
Nitrogen content absorbed at different temperature with NH_3 for $LaNi_5$ (as milled).

Temperature (°C)	Nitrogen content (mol/1 mol of alloys)		Desorbed nitrogen (mol/1 mol of alloys)
	After absorption	After desorption	
230	0.1	N/A	N/A
260	0.3	N/A	N/A
290	0.4	N/A	N/A
320	0.5	N/A	N/A
350	1.1	N/A	N/A
400	1.4	N/A	N/A
500	1.5	0.5	1.0
550	1.0	1.0	0.0
600	1.0	1.0	0.0

Absorption was performed at each temperature for 1 h with NH_3.
Desorption was performed at 400 °C (mol/1 mol of alloys) for 3 h with H_2.
N/A stands for not available.

Table 3
Desorption properties for $LaNi_5$ (as milled).

Conditions	Nitrogen content (mol/1 mol of alloys)		Desorbed nitrogen (mol/1 mol of alloys)
	After absorption	After desorption	
H_2, 400 °C	1.5	0.5	1.0
Under vacuum, 400 °C	1.5	1.3	0.2

Absorption was performed at 350 °C for 3 h with NH_3.
Desorption was performed for 3 h.

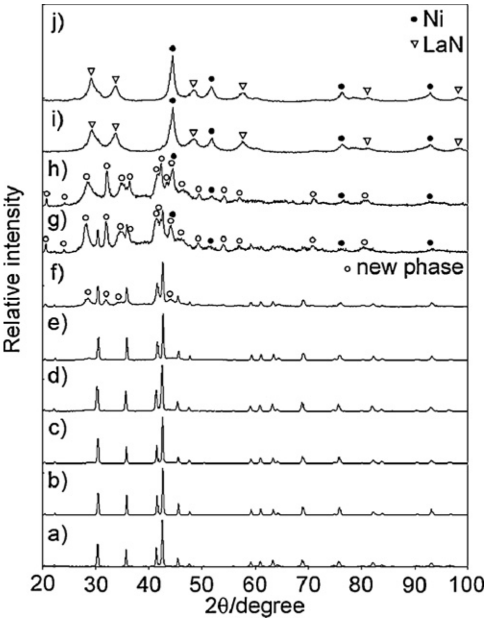

Fig. 5. XRD patterns of $LaNi_5$ (a) after the milling, and after the absorption treatment at (b) 230 °C, (c) 260 °C, (d) 290 °C, (e) 320 °C, (f) 350 °C, (g) 400 °C, (h) 500 °C, (i) 550 °C, and (j) 600 °C

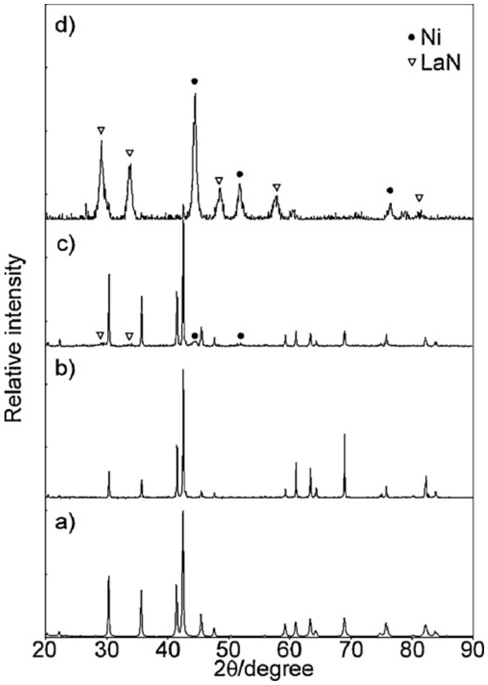

Fig. 6. XRD patterns of $LaNi_5$ (a) after the milling, and after the absorption treatment using N_2 at (b) 500 °C, (c) 550 °C, and (d) 600 °C.

either the H_2 or vacuum atmosphere, following the absorption treatment under a NH_3 atmosphere for 3 h at 350 °C. It was found that the H_2 atmosphere promotes the desorption compared to the vacuum atmosphere. According to Koeninger's report, the desorption treatment under an Ar atmosphere is less effective than that under the H_2 atmosphere for Sm_2Fe_{17} [7], and they proposed that lattice expansions due to the hydrogen diffusion into/in Sm_2Fe_{17} make it easier for the nitrogen atom to diffuse. This explanation can be reasonable for this case, while it can be additionally suggested that the hydrogen atoms assists the detachment of the nitrogen atom from the surface by reacting with the nitrogen to form NH_3, and the reaction on the surface was reported in the former paper [1].

3.2. *Nitrogen absorption properties using N_2 as nitrogen source*

When actual applications are considered, the development of a nitrogen storage alloy that can efficiently absorb and desorb nitrogen using N_2 as a nitrogen source is desirable because of the convenience and harmlessness of N_2. Motivated with such requirement, we investigated the nitrogen storage property of $LaNi_5$ using N_2 as a nitrogen source under both 1 atm and higher pressure. Table 4 shows the nitrogen contents of samples after the nitrogen absorption treatments at 500–600 °C for 3 h using N_2 under 1 atm. It turned out that absorption does not occur below 500 °C and furthermore, above 550 °C, $LaNi_5$ absorbs nitrogen in the form of LaN as shown in Fig. 6(c) and (d). LaN was formed even after the absorption treatment using NH_3 above 550 °C, and it did not desorb nitrogen for the both cases. Such no or slower absorption from N_2, compared to NH_3, was also reported in previous studies [2,3], suggesting the difficulty in dissociating the strong triple bond in the molecular nitrogen.

From the above findings and former reports, it can be reasonably inferred that the rate determining step of absorption using N_2 is to dissociate a molecular nitrogen into atomic nitrogen. Since

Table 4
Nitrogen content after absorption with N_2 and desorption with H_2 for $LaNi_5$ (as milled).

Temperature (°C)	Nitrogen content (mol/1 mol of alloys)		Desorbed nitrogen (mol/1 mol of alloys)
	After absorption	After desorption	
500	0.0	N/A	N/A
550	0.2	N/A	N/A
600	0.8	0.8	0.0

Absorption was performed at each temperature for 1 h with N_2.
Desorption was performed at 400 °C for 3 h with H_2.

Table 5
Absorption properties with N_2 under different pressure for $LaNi_5$ (as milled).

Temperature (°C)	Pressure (MPa)	Time (h)	Nitrogen content (mol/1 mol of alloys) After absorption
450	0.10	3	0.0
	1.01	3	0.0
	4.04	3	0.0
		12	0.1
350	4.04	12	0.0
	4.04	24	0.0
With activation			
450	4.04	3	0.1

a high pressure absorption treatment is expected to enhance the absorption, we also employed the absorption using high pressure (10–40 atm) N_2. The nitrogen contents after the absorption treatment with various N_2 pressures are summarized in Table 5. The nitrogen absorption was only detected when the absorption treatment was performed under 40 atm at 450 °C for 12 h, suggesting that a high pressure e.g. 40 atm could have an effect on the nitrogen storage ability.

An activation treatment was also examined to promote the absorption, where 10 times of H_2 absorption and desorption treatments were performed prior to the N_2 absorption. The "activation" process is often employed for a hydrogen storage study, where a pre-heating process under a hydrogen atmosphere or vacuum prior to the hydrogen absorption treatment was performed on hydrogen storage alloys, which do not absorb hydrogen effectively at an early stage of absorption because of the formation of oxides on the surface or the adsorption of other gases. The activation thus promotes the removal of the oxides barriers or impurity gases [8]. Additionally the $LaNi_5$ is known to crack after several hydrogen absorption and desorption treatments due to the lattice expansions, which should lead to the increased surface area and exposure of new surfaces with higher catalytic activity. The hydrogen absorption treatment was at 120 °C for 5 min under H_2 gas at 20 atm and the desorption treatment at 120 °C for 5 min under vacuum, and the following nitrogen absorption treatment was at 450 °C for 3 h under N_2 at 40 atm. The nitrogen content before and after the above treatment is shown also in Table 5. Although the pulverization and cracking of the $LaNi_5$ sample was confirmed with SEM after the activation treatment, the increase in the absorbed nitrogen is rather small (0.1 mol/mol).

It should be noticed that these findings do not confirm that nitrogen is an absorption in an atomic nitrogen invaded into $LaNi_5$, because there is a possibility that a molecule nitrogen is adsorbed only on the surface due to the activation treatment. The surface is supposed to be relatively free of impurity gases and has many sites for physisorption, and the XRD pattern after the absorption process shows no change, suggesting no structural change due to the absorption.

4. Discussion

The rate determining step of nitrogen absorption is discussed here. When the mechanism of nitrogen absorption is assumed to be similar to hydrogen absorption by $LaNi_5$, the rate determining step can be one of following steps (i) NH_3 dissociates at the powder surface and diffuses into $LaNi_5$, (ii) nitrogen diffuses into the center of the particles and (iii) nitrogen solid solution or nitride phase is formed and the grain grows [9]. The possible nitrogen distributions, when each step is the rate determining step, were proposed by Koyama, as shown in Fig. 7. Fig. 7(a) corresponds to the case where the step (i) is the rate determining step, (b) to the case where the step (ii) is the rate determining step, and (c) to the case where the step (iii) is the rate determining step. By comparing these profiles with the observed profile shown in Fig. 3, it can be found that the step (i) the dissociation of NH_3 and invasion of nitrogen is not the rate determining step for the nitrogen absorption of $LaNi_5$.

The mechanism was further investigated from the time dependence of nitrogen concentration, as shown in Fig. 8, where the observed nitrogen concentration (rectangular) together with the calculated nitrogen concentration when the rate determining step is assumed to be (A) the diffusion of nitrogen (diffusion controlled, bar) or (B) the formation of nitrogen absorbing phase (interface controlled, circle), respectively, are plotted as a function of nitrogen absorption treatment time. For the case (A), the total nitrogen concentration (mol/mol) in the powders at any time t, $x(t)$, can be estimated by the following equation [9],

$$x(t) = \int_0^{Rs} \frac{4\pi(Rs - r)^2 c(r, t)dr}{(4/3)\pi Rs^3}$$

x: total amount of the nitrogen in the powder (mol/mol), Rs: the radius when the particle is assumed to be spherical, r: distance from

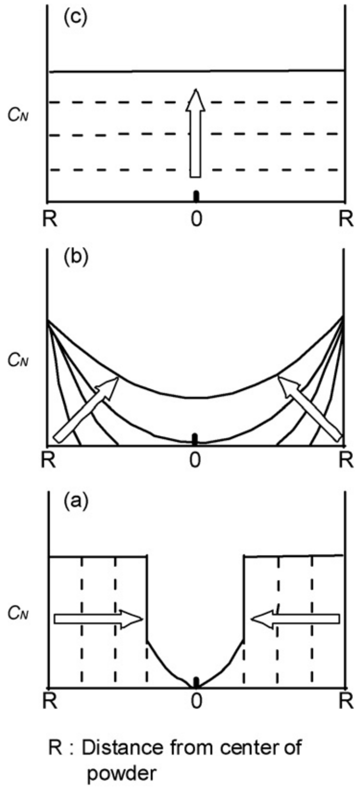

Fig. 7. Nitrogen distribution profiles for three reaction controlling processes: (a) nitrogen dissociation/invasion controlling process, (b) nitrogen diffusion controlling process, and (c) reaction controlling process.

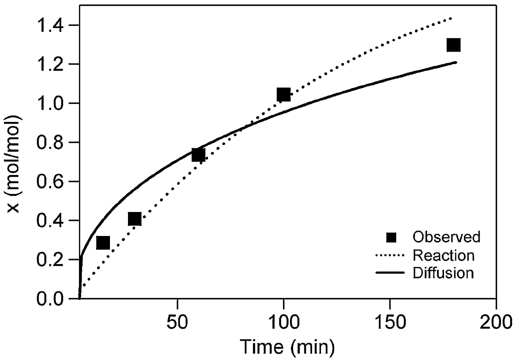

Fig. 8. Nitrogen content versus absorption treatment time: observed value (rectangular) and calculated values for diffusion control (black bar) and reaction control (circle).

the powder surface, and t: nitrogen absorption treatment time.

$c(r,t)$ is given by

$$c(r,t) = C_0 \mathrm{erfc}\left(\frac{r}{2\sqrt{Dt}}\right)$$

C_0: the nitrogen concentration at $r = 0$, e.g. at the surface, D: diffusion coefficient, and erfc: the complimentary error function.

And for the case (B), the nitrogen concentration should be given by the following equation:

$$x(t) = C_0 \frac{(4/3)\pi Rs^3 - (4/3)\pi (Rs - Vgt)^3}{(4/3)\pi Rs^3}$$

C_0: the nitrogen concentration of the nitrogen absorbed phase and Vg: the growth rate of the nitrogen absorbing phase.

The estimated radius of 4.5 μm obtained using the image analysis software was used for the Rs value, and Vg was estimated from Fig. 4 to be 2.24/180 = 0.0124 μm/min, and C_0 (and also D for the case (A)) were adjusted to give the best fitting to the observed date. Finally, in diffusion case C_0 is determined as 4.0 mol/mol and D as 2.7×10^{-17} m^2/s, and for case (B) C_0 as 1.65 mol/mol, respectively.

Both simulations do not completely fit with the observed values exactly, and it is likely that the combination of these two cases can give more consistent result with the observed values. Indeed, it was also observed by Koyama that the time dependence of the nitrogen absorption of Sm_2Fe_{17} can be explained using a mixture model of the diffusion activated step and the interface activated step [9]. Thus, we suggest the following absorption mechanism as our hypothesis. In the initial stage, the diffusion control reaction takes place, then it is superseded with the reaction control. Further investigations are, however, required to elucidate the mechanism of the nitrogen absorption in $LaNi_5$.

5. Conclusion

The nitrogen absorption and desorption property of $LaNi_5$ was investigated for the first time. Original $LaNi_5$ powder was found to absorb 0.3 mol of nitrogen per one mol $LaNi_5$ (mol/mol) and desorb 0.2 mol/mol, while milled $LaNi_5$ was found to absorb nitrogen of 1.5 mol/mol and desorb 1.0 mol/mol with NH_3 as the nitrogen source. XRD studies revealed formation of new phases, and a crystal structure was proposed to explain one of the phases. Formation of a new phase was also confirmed by cross sectional SEM and EPMA analysis. When nitrogen gas was used as the nitrogen source, it was found that high pressure absorption treatments or an activation treatment were necessary for milled $LaNi_5$ powder to absorb nitrogen. Finally, the mechanism of the nitrogen absorption was discussed from the EPMA and kinetic data of the nitrogen absorption, and it was suggested that the mechanism of the nitrogen absorption might be explained by a combined model of a diffusion controlled process and an interface controlled process.

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