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Author(s)	Yasuda, Naoto; Sasaki, Shino; Okinaka, Noriyuki; Akiyama, Tomohiro
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Self-Ignition Combustion Synthesis of LaNi₅

Utilizing Hydrogenation Heat of Metallic Calcium

Naoto Yasuda, Shino Sasaki, Noriyuki Okinaka, Tomohiro Akiyama*

Center for Advanced Research of Energy & Materials, Hokkaido University,

Kita 13 Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan

Phone: +81-11-706-6842

Fax: +81-11-726-0731

*Corresponding Author: takiyama@eng.hokudai.ac.jp

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Abstract (173 words)

This paper describes *self-ignition combustion synthesis (SICS)* of LaNi_5 in a pressurized hydrogen atmosphere using metallic calcium as both the reducing agent and the heat source. In this study, the effects of hydrogen on the ignition temperature and the hydrogenation properties of the products were mainly examined. In the experiments, La_2O_3 , Ni, and Ca were dry-mixed in the molar ratio of 1:10:6 and then heated up at a hydrogen pressure of 1.0 MPa until the ignition due to the hydrogenation of calcium. For the sake of comparison, the same experiments were performed in a normal argon atmosphere. The results showed that the ignition temperature was drastically lowered by hydrogen; it was only 600 K in the case of hydrogen as compared to 1100 K in the case of argon. The products also exhibited high initial activity and hydrogen storage capacity of 1.54 mass%. The proposed method offers many benefits for using cost-effective rare-earth oxide, saving productive time and energy, improving initial activity of the product and applying to any AB_5 -type hydrogen storage alloy.

Introduction

Nickel rare-earth metal compounds, so-called AB₅-type hydrogen storage alloys, have been extensively studied because of their good hydrogenation properties and potential applications such as hydrogen storage, chemical heat pumps, hydrogen purification and Ni-metal hydride batteries [1]. In general, hydrogen storage alloys are conventionally produced by using a *melting method* that requires several time- and energy-consuming processes such as heat treatment, pulverization, and activation treatment. In the heat treatment, the product is kept at high temperature for long time for homogenization. The following pulverization and activation treatment are a must for increasing the surface area of the product and improving the reactivity with hydrogen. In particular, the activation treatment needs a repeated procedure of hydrogenation and dehydrogenation by heating and vacuuming, which is the most energy consuming among the processes [2,3].

In 1997, one of the authors proposed the *hydriding combustion synthesis (HCS)* of the self-propagation mode as an innovative manufacturing process for a Mg-based hydrogen storage alloy [4,5]. The product, synthesized from a mixture of metallic powders in a hydrogen atmosphere, was pure hydride without any activation treatment. Most recently, Wakabayashi *et al.* [6-8] reported the use of *self-ignition combustion*

synthesis (SICS) to produce TiFe-based alloys; in this method, powders mixed in a desired molar ratio were uniformly heated up to the ignition point in pressurized hydrogen atmosphere. The product was also directly synthesized with the help of the exothermic reaction of titanium hydrogenation. The results showed that the SICS in pressurized hydrogen is considerably attractive as it has a relative short operating time, consumes relatively less energy because of the efficient utilization of the reaction heat and improves activation behavior of the products, in comparison to the conventional *melting method*. These results demonstrated the significant benefits of SICS on Mg-based and Ti-based alloys. However, no papers have reported the SICS of nickel rare-earth-based alloys, in spite of its engineering significance. In particular, LaNi₅ is one of the most commercially produced hydrogen storage alloys in addition to Mg₂Ni and TiFe.

According to literature research using a major database, for producing rare-earth-based materials *reduction-diffusion* (RD) process has been proposed based on the reduction of rare-earth oxide by calcium [9]. Itagaki *et al.* directly produced a nickel-mischmetal compound directly by using the RD process [10, 11], in which the raw materials were maintained at around 1273 K for as long as several hours because of the slow solid diffusion whereas a pulverization treatment is not required because

rare-earth oxide was directly reduced to powders by metallic calcium or calcium hydride. This paper elucidates a new production route of a rare-earth based alloy using the reduction of rare-earth oxide by calcium; however, the RD process is still time- and energy-consuming process. As far as we know, thus far, a combination of the SICS and the RD process has never been reported in spite of its engineering significance. Therefore, the purpose of this study is to synthesize LaNi_5 alloy by SICS using Ni and La_2O_3 powders as raw materials and calcium grains as both the reducing agent and the heat source; the SICS effectively utilizes the exothermic reaction due to the hydrogenation of calcium used as the heat source without a heat treatment for solid diffusion. In the experiments, the effect of atmosphere during the SICS on the properties of the products was mainly examined. The new findings lead to a new route for the nickel rare-earth-based alloy production that consumes less time and energy and has better activation than the existing methods.

Experiment

Figure 1 shows the schematic diagram of the experimental apparatus. A detailed explanation is given elsewhere [6], and hence, only the framework of the apparatus is described here. The chamber (size; $\phi 350 \times 350$ mm) with water cooling had a reactor and a graphite heater. The reactor had two R-type thermocouples for controlling the temperature inside the reactor and for measuring the sample temperature. We ensured that the graphite heater completely covered the sample in order to carry out the combustion synthesis of LaNi_5 on the self-ignition mode; the raw materials were uniformly heated up to 1773 K under a high pressure of up to 1.0 MPa in a hydrogen or an argon atmosphere. The pressure in the reactor was also maintained at constant value by using the on-off controller. A heating electric power of 7.5 kW was sufficiently large for the uniform heating of the sample to 1358 K.

Table 1 Heating conditions for self-ignition mode during combustion synthesis.

Run No.	Heating rate (kW)	Atmosphere	Pressure (MPa)
1	7.5	Argon	0.1
2	7.5	Hydrogen	1.0

La_2O_3 and Ni powders used had both 99.9 % in purity and were less than 45 μm

and 3-5 μm in size, respectively. Both of the powders were obtained from Kojundo Chemical Laboratory Company. Small chips of metallic calcium, purchased from Nirako Company, had 95 % in purity and were 1-3 mm in size. In the experiments, 40 g of the reagents was first mixed in the molar ratio of $\text{La}_2\text{O}_3:\text{Ni}:\text{Ca} = 1:10:6$, where the amount of Ca was twice as much as theoretical value, for accelerating the reduction of La_2O_3 . Then, when each sample was placed in a carbon crucible (dimensions: 45 mm \times 90 mm \times 35 mm), the crucible was carefully covered by a carbon sheet with thickness of 1.0 mm in order to prevent the sample from sticking between the crucible and the product. An R-type thermocouple placed inside a protective alumina tube with outer diameter of 6.0 mm was introduced into the center of the sample.

Table 1 shows the heating conditions for the self-ignition mode during combustion synthesis. The furnace was evacuated at a pressure of 20 Pa by rotary pump and was replaced by 99.999 % pure argon. After repeating four times this procedure of vacuuming and replacing to achieve substitution, we finally charged hydrogen or argon to a desired pressure. In the experiments, samples were uniformly heated by using the graphite heater at the rate of 7.5 kW, and temperature changes in the sample were monitored. As soon as an exothermic reaction was observed, the heating of the samples was immediately stopped and samples were naturally cooled in the same atmosphere of

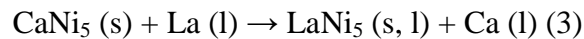
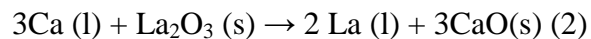
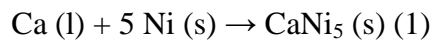
pressurized hydrogen or normal argon. Finally, the products were recovered from the furnace for the following analyses: phase identification by X-ray diffraction (XRD) and observation by scanning electron microscope (SEM). The products were polished in order to remove residue of carbon sheet from their surface and crushed using tungsten mortar. The product powders obtained were washed with an aqueous solution of 5 mass% acetic acid in order to remove the residue of calcium and byproduct of calcium oxide, and were kept in a desiccator in air at 353 K for 12 h.

Shortly after the washing treatment, the pressure-composition-isotherm (PCT) property of the products was evaluated using Sieverts' method by employing a commercially available reactor (Suzuki Shokan Co., Ltd.) after four cycles of hydrogenation/dehydrogenation. For measuring the initial hydrogenation kinetics, the reactor was first evacuated for at least 1 h at room temperature by using a turbo-molecular pump, and then was introduced by hydrogen with a pressure of 4.1 MPa at 298 K.

Results and discussions

Figure 2 shows the temperature changes in the sample with time during the SICS experiments in an argon atmosphere of 0.1 MPa (Run 1) and a hydrogen atmosphere of 1.0 MPa (Run 2). Note that the temperature changes in the sample strongly depended on the atmosphere because the thermal conductivity of hydrogen is one digit larger than that of argon.

In Run 1, the temperature of the sample increased at around 1100 K, close to the melting temperature of calcium (1115 K). Shortly after the exothermic reaction was observed, the electric heating was stopped, and then each sample was naturally cooled in the furnace. The melting of calcium increased contact area between calcium and the other raw materials, accelerating the following exothermic reactions:



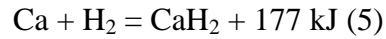
The reaction mechanism of SICS in argon atmosphere was similar to the RD process. Ohtsuka and Tanabe et al. [12,13] particularly reported that the formation mechanism of LaNi₅ in the RD process, CaNi₅ compound is generated as an intermediate product, and that the melting of calcium enhances the growth rate significantly. The overall reaction

in Run 1 can be expressed by the following equation;



Assuming that the ignition temperature was 1115 K, we estimated the adiabatic temperature of the reaction to be 1598 K; the value is melting point of LaNi_5 [14,15].

Meanwhile, the temperature of the sample in Run 2 increased sharply at around 600 K and jumped to 1238 K. As soon as the exothermic reaction occurred, the electric heating of the sample was turned off. Then, each sample was naturally cooled in the furnace. The ignition was triggered by the hydrogenation of calcium, accelerating the reduction of La_2O_3 by CaH_2 and the synthesis of LaNi_5 . The hydrogenation of calcium was accompanied by the considerable exothermic heat of formation.



In contrast, intermediate products of the SICS in the hydrogen atmosphere are not clear yet at this moment. When the amount of calcium was twice as the chemical equivalent value, the overall reaction in Run 2 could be expressed by the following equation:



Assuming that the ignition temperature was 600 K, we calculated the adiabatic temperature of the reaction to be as high as 1598 K. Under the assumption that the amount of calcium was equal to the chemical equivalent value, we calculated the

adiabatic temperature to be 1419 K. Excess calcium served as not only the reducing agent of La_2O_3 , but also the heat source due to hydrogenation.

It should be noted that the hydrogen atmosphere reduced the ignition temperature from 1100 to 600 K as compared to argon. This fact implies different trigger reactions—hydrogenation in the case of the hydrogen atmosphere and melting reactions of calcium in the case of argon atmosphere. The time taken for the ignition was 200 s, and the furnace temperature reached around 900 K at during this time. The results revealed that the SICS process is more attractive than the RD process, because the RD process requires heating at 1273 K for at least several hours.

Figure 3 shows the XRD patterns of the commercially available LaNi_5 reagent and the SICSed products after the washing treatment. The major peaks of the SICSed products were exactly indexed to the LaNi_5 phase, although, the peak, observed at 45° suggested the existence of un-reacted nickel. The ratio of un-reacted nickel will be zero when optimizing the experimental conditions such as the amount of reagents, heating rate and hydrogen pressure.

Figure 4 shows the SEM images of the products SICSed before and after the washing treatment. Calcium oxide and calcium on the grain surface of the alloy were removed by washing with 5 mass% acetic acid and distilled water in Runs 1 and 2.

During the washing treatment, calcium oxide and calcium reacted vigorously with acetic acid aqueous solution to be soluble in it, and then the product crumbled to less than 50 μm in size without pulverization.

Figure 5 shows the hydriding curves of the products obtained in different atmospheres, which were measured by using Sievert's method at temperature of 298K and initial hydrogen pressure of 4.1 MPa. We found that the products obtained in Run 2 had only one-third in full charge time, in comparison to the product obtained in Run 1. The initial activity was probably improved by hydrogen absorbed during the cooling period. In fact, many nanofissures were observed within the product due to the release of absorbed hydrogen [16] when the reactor was evacuated by a turbo-molecular pump or was heated up before the initial hydrogenation. As a result, the product had a large surface area of LaNi_5 phase, which was not poisoned by air. This was the reason why the hydrogenation proceeded very quickly. The product obtained in Run 2 showed 1.54 mass% in hydrogen storage capacity, as the same as the value of commercial-available LaNi_5 . Meanwhile, the product obtained in Run 1 stored hydrogen as much as 1.33 mass%; this value corresponds to 86% of the value commercial-available LaNi_5 . In conclusion, the high-pressure hydrogen atmosphere in SICS is considerably more attractive than the normal argon atmosphere because of the improvement in the kinetics

of the product due to large non-poisoned, fresh surface area caused by the nanofissures generated at initial stage.

Figure 6 shows three PCT curves of a reagent of LaNi_5 with 99.9% in purity and two products obtained at 298K; these curves were measured by Sievert's method. The equilibrium pressure of the products was the same as that of the reagent. The peak positions in XRD patterns of the products were also exactly the same as those of the reagent. The product obtained in Run 2 was larger in effective hydrogen storage capacity than the reagent. This was probably caused by higher crystallinity of the product.

Figure 7 shows the temperature dependences of the PCT curves. From the PCT curves, we could draw the van't Hoff plot on the temperature dependences of the hydrogenation and dehydrogenation plateau pressures of the products at the half of the hydrogen storage capacities. Data plotted at both pressures showed good linearity with good correlation coefficients according to least mean square approximation (see Fig.7)

Table 2 Reaction heat ΔH of a reagent and products of LaNi_5 .

Sample Name	Reaction Heat	
	[kJ/mol- H_2]	
	Absorption	Desorption
Reagent	-31.9	32.5
Run 1	-32.4	32.0
Run 2	-32.1	31.9

Table 2 shows the reaction heat ΔH of a reagent and products of LaNi_5 . They were calculated from the equation: $\ln P = \Delta H/(RT) - \Delta S/R$. The value of ΔH of the product obtained by SICS agreed well with that of a reagent of LaNi_5 .

Conclusion

The *self-ignition combustion synthesis* (SICS) of LaNi₅ hydrogen storage alloys in high-pressure hydrogen and normal argon atmospheres from La₂O₃, Ni, and Ca was comparatively studied and the following conclusions were derived.

1. In both atmospheres, SICS could produce LaNi₅ successfully, whereas the ignition temperature was quite different; only 600 K caused by $\text{Ca} + \text{H}_2 \rightarrow \text{CaH}_2$ in the case of the hydrogen atmosphere as compared to 1100 K caused by melting reaction of calcium in argon atmosphere. During the SICS in the hydrogen atmosphere, excess calcium worked as not only the reducing agent of La₂O₃, but also the heat source due to the hydrogenation of calcium.
2. The hydrogenation time of the product obtained in hydrogen atmosphere was only one-third in comparison to the product obtained in argon atmosphere. This demonstrated that the products were well-activated in hydrogen atmosphere.
3. The product obtained in hydrogen showed 1.54 mass% in hydrogen storage capacity and 0.17 MPa in equilibrium dissociation pressure; they were as the same property as commercial-available product.

The results also demonstrated that the SICS in hydrogen atmosphere offers many benefits for using cost-effective rare-earth oxide instead of metal, lowering ignition

temperature, minimizing operation time and energy, improving initial activity of the product and applying to mass production of any AB₅-type hydrogen storage alloy.

Acknowledgments

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References

- [1] H.H. Van Mal, K.H.J. Buschow, A.R. Miedema, Hydrogen Absorption in LaNi₅ and Related Compounds: Experimental Observation and Their Explanation, *J. Less-Common Met.* 35 (1974) 65–76.
- [2] L. Belkbir, N. Gérarda, A. Percheron-Guégan, J.C. Achard, Kinetics of hydrogen absorption and desorption by ternary LaNi₅-type intermetallic compounds, *Int. J. Hydrogen Energy.* 6 (1979) 541–557.
- [3] G.D. Sandrock, P.D. Goodell, Surface poisoning of LaNi₅, FeTi and (Fe, Mn)Ti by O₂, CO and H₂O, *J. Less-Common Met.* 73 (1980) 161–168.
- [4] T. Akiyama, H. Isogai, J. Yagi, Hydriding combustion synthesis for the production of hydrogen storage alloy. *J. Alloys Compd.* 252 (1997) 1–4.
- [5] I. Saita, L. Li, K. Saito, T. Akiyama, Pressure–composition–temperature properties of hydriding combustion synthesized Mg₂NiH₄, *Mater Trans.* 43 (2002) 1100–1104.
- [6] R. Wakabayashi, S. Sasaki, I. Saita, M. Sato, H. Uesugi, T. Akiyama, Self-ignition combustion synthesis of TiFe in hydrogen atmosphere, *J. Alloys Compd.* 480 (2009) 592–595.
- [7] R. Wakabayashi, S. Sasaki, T. Akiyama, Self-ignition combustion synthesis of oxygen-doped TiFe, *Int. J. Hydrogen Energy.* 34 (2009) 5710–5715.

- [8] N. Yasuda, R. Wakabayashi, S. Sasaki, N. Okinaka, T. Akiyama, Self-ignition combustion synthesis of $\text{TiFe}_{1-x}\text{Mn}_x$ hydrogen storage alloy, *Int. J. Hydrogen Energy*. 34 (2009) 9112–9117.
- [9] C. Song, O. Ogawa, Diffusion coefficients of samarium in intermetallic compounds samarium cobalt (SmCo_5 and $\text{Sm}_2\text{Co}_{17}$), *Shigen to Sozai*. 106(12) (1990) 761-767.
- [10] Z. Li, K. Yasuda, K. Itagaki, Calciothermic reduction of mischmetal oxide and formation of RmNi_5 , *J. Alloys Compd.* 193 (1993) 26–28.
- [11] T. Takeya, Y. Tsugita, Y. Okajima, T. Sakai, H. Miyamura, N. Kuriyama, I. Ishikawa, I. Uehara, Hydrogen storage alloy powders produced by a reduction-diffusion process and their electrode properties, *J. Alloys Compd.* 192 (1993) 167-169.
- [12] M. Ohtsuka, D.Y. Kim, K. Itagaki, Formation of RE_xNi_y (RE = La, Ce, Pr or Nd) compound by calciothermic reduction of La_2O_3 , CeO_2 , Pr_6O_{11} and Nd_2O_3 , *J. Alloys Compd.* 230 (1995) 46-52.
- [13] T. Tanabe, Z. Asaki, Formation Mechanism of LaNi_5 in the Reduction-Reduction process, *Metallurgical and Materials Transactions B*. 29B (1998) 331-338.
- [14] N.P. Gorbachuk, V.B. Muratov, Heat capacity and enthalpy of LaNi_5 in the temperature range 57-1542 K, *Powder Metallurgy and Metal Ceramics*. 44(9-10) (2005) 467-471.

[15] S. Watanabe, O.J. Kleppa, A thermochemical study of liquid and solid alloys $\{(1-x)\text{lanthanum} + x(\text{nickel})\}$ at 1376 K, J. Chemical Thermodynamics. 15(7) (1983) 633-644.

[16] T. Akiyama, K. Saito, I. Saita, Kinetic Improvement of Hydrogen Storage Alloy by Generating Nanofissures, J. Electrochemical Society. 150(9) (2003) 450-454.

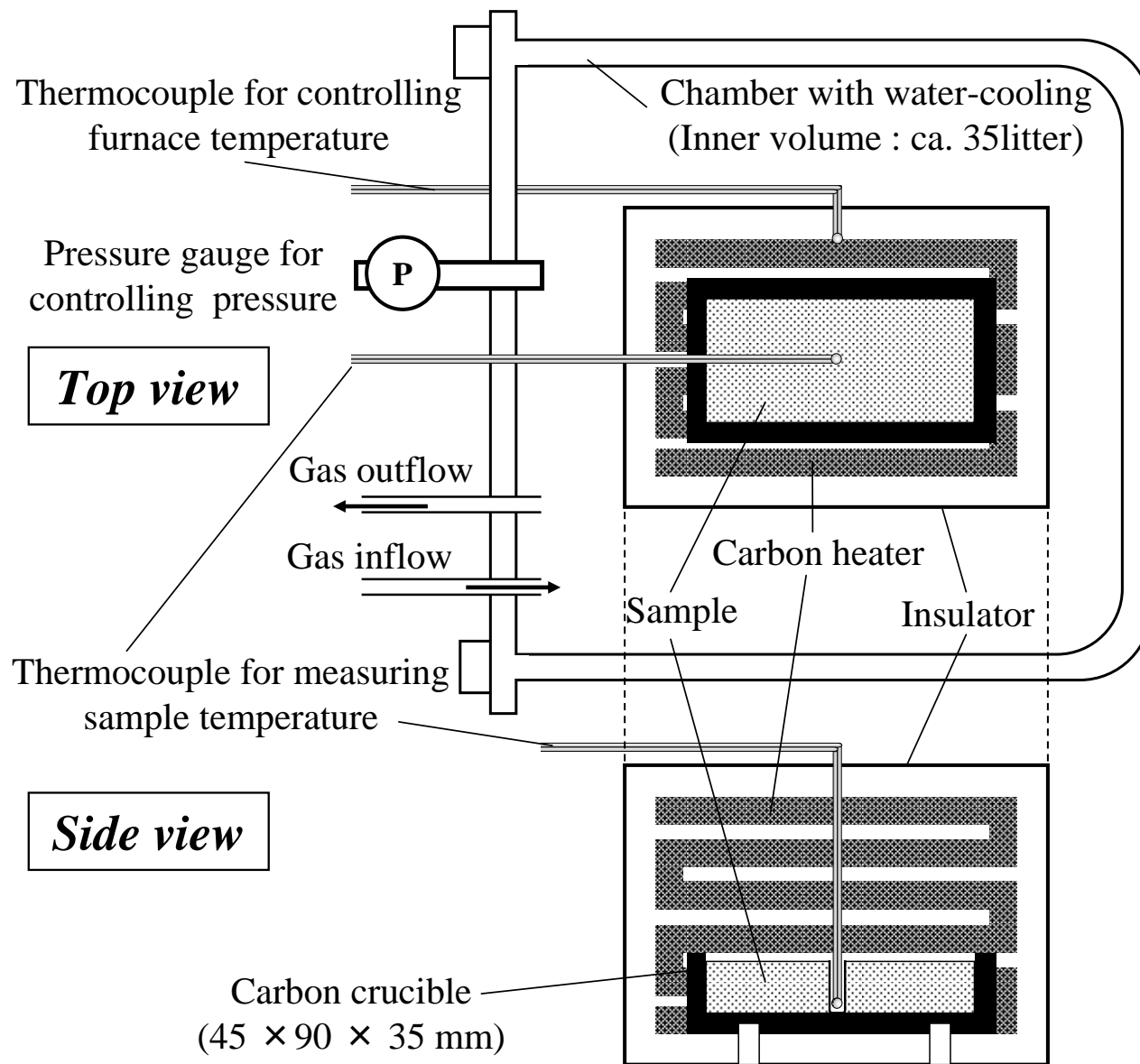


Fig. 1 Schematic diagram of *self-ignition combustion synthesis* (SICS) reactor, in which well-mixed powders of La_2O_3 , Ni, and Ca were uniformly heated by a graphite heater in argon or hydrogen atmosphere.

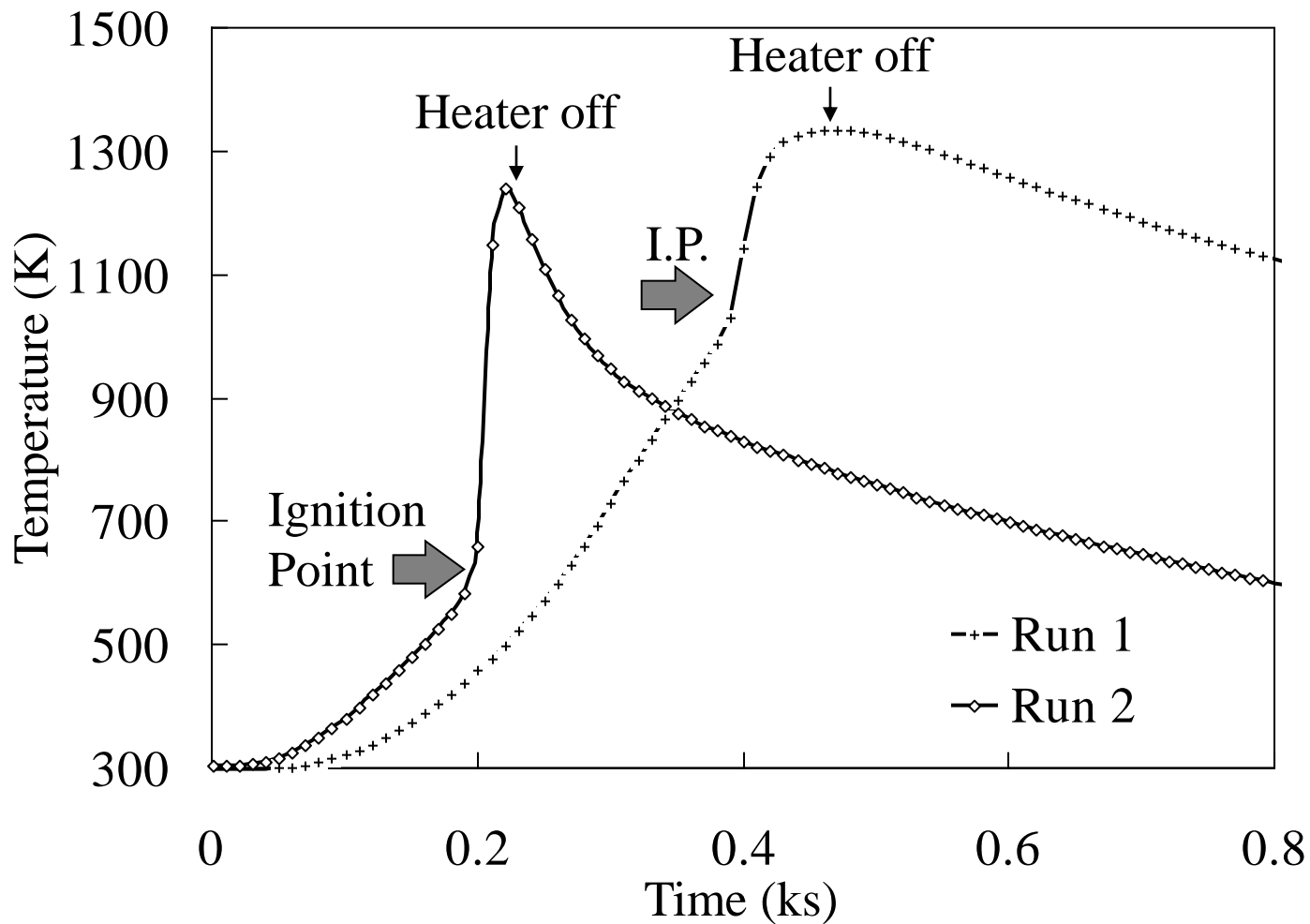


Fig. 2 Changes in sample temperature with time during SICS experiments in hydrogen atmosphere of 1.0 MPa (Run 1) and in argon atmosphere of 0.1 MPa (Run 2). Note that thermal conductivity of hydrogen is larger than that of argon and major ignition point in Run 2 was much lower than that in Run 1, implying different trigger reactions.

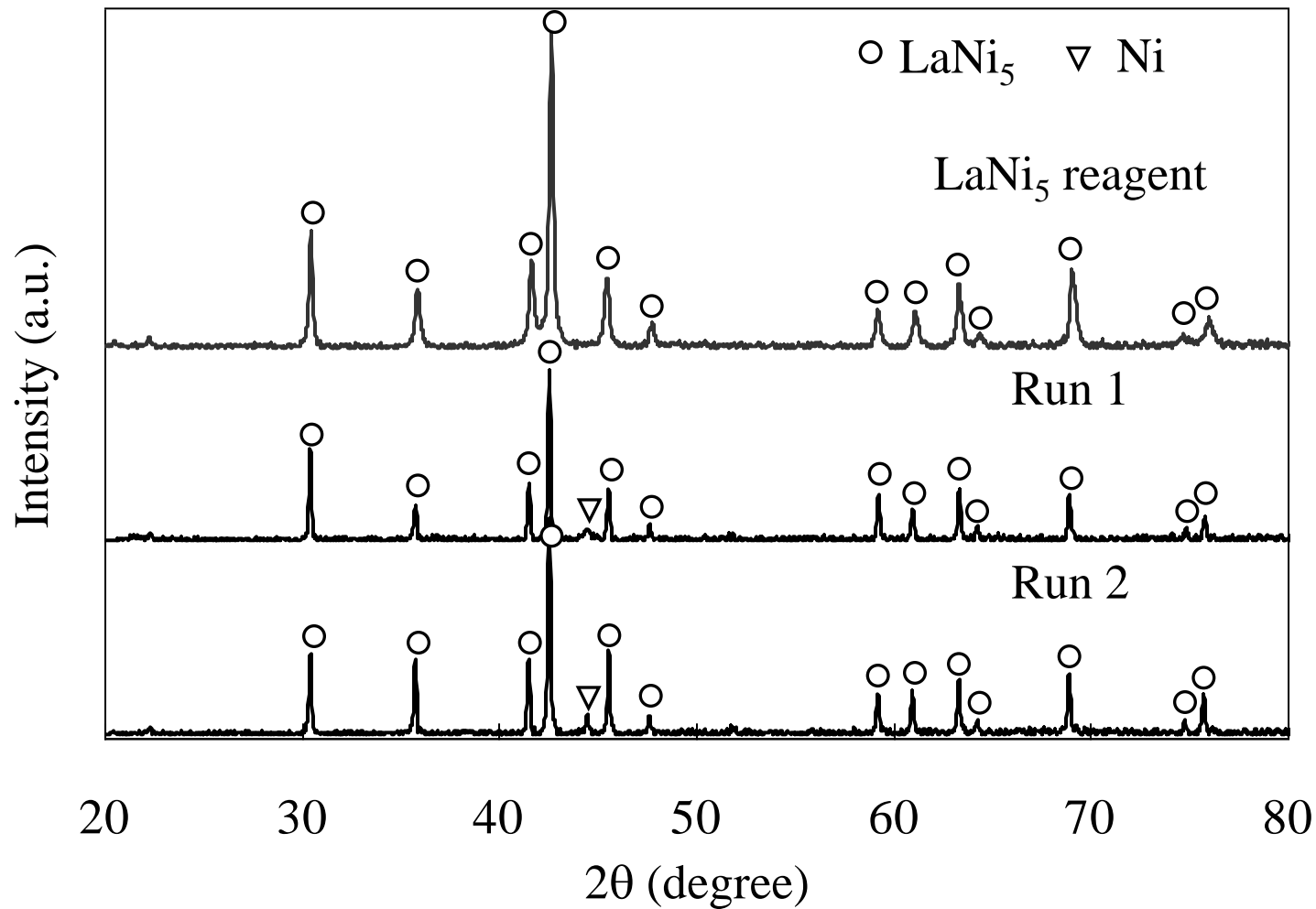


Fig. 3 XRD patterns of the commercially available LaNi₅ reagent and the SICSed products after the washing treatment, showing successful syntheses of LaNi₅ phase through SICS process in Run1 and Run 2.

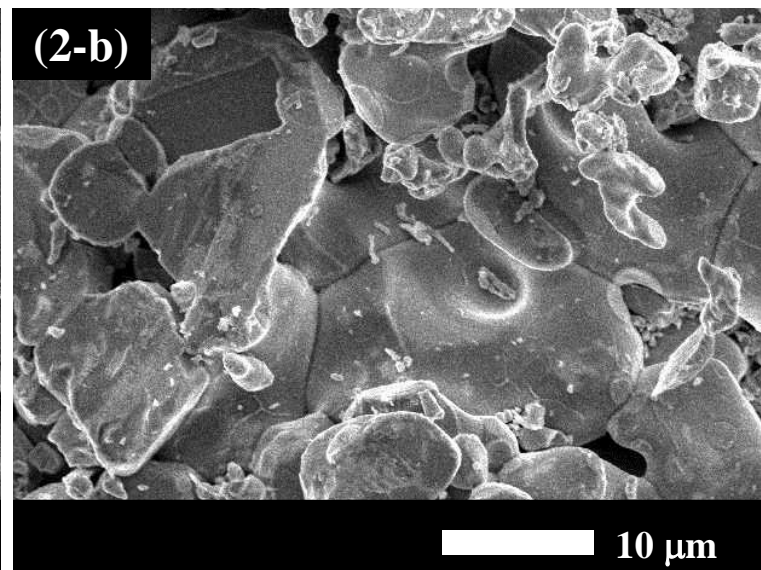
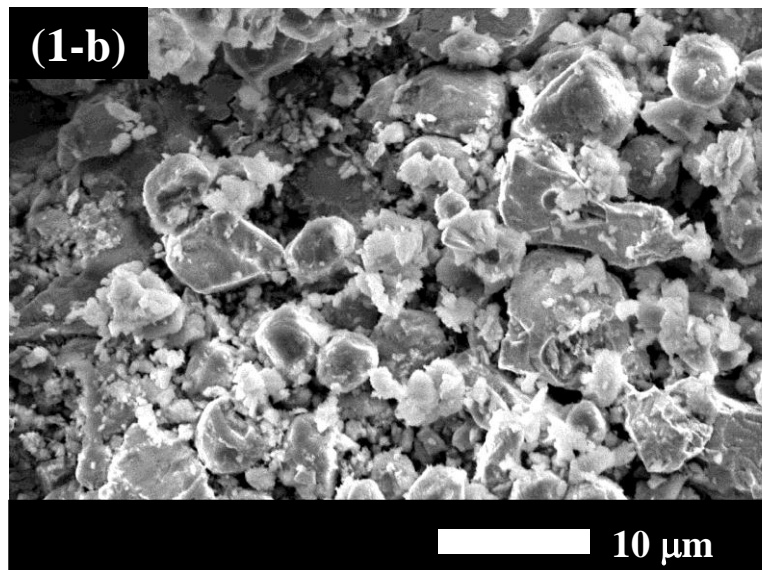
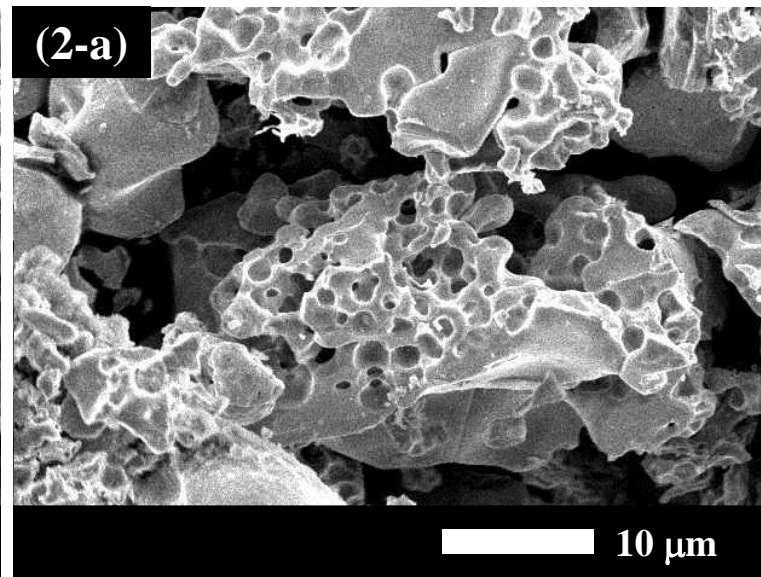
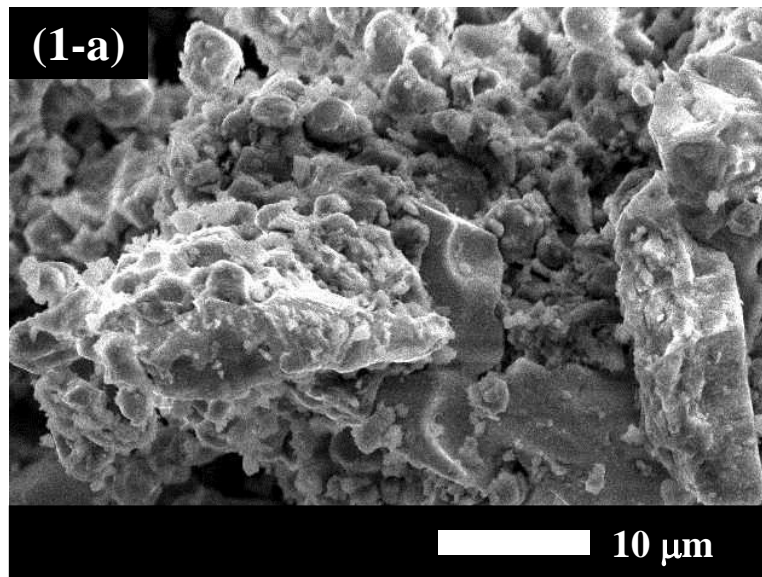


Fig. 4 SEM images of the SICSeD products in:
(1-a) Run 1 before washing; (1-b) Run 1 after washing;
(2-a) Run 2 before washing; (2-b) Run 2 after washing.
CaO and Ca on the grain surface were removed by washing the sample with distilled water of 5 mass% acetic acid in Runs 1 and 2.

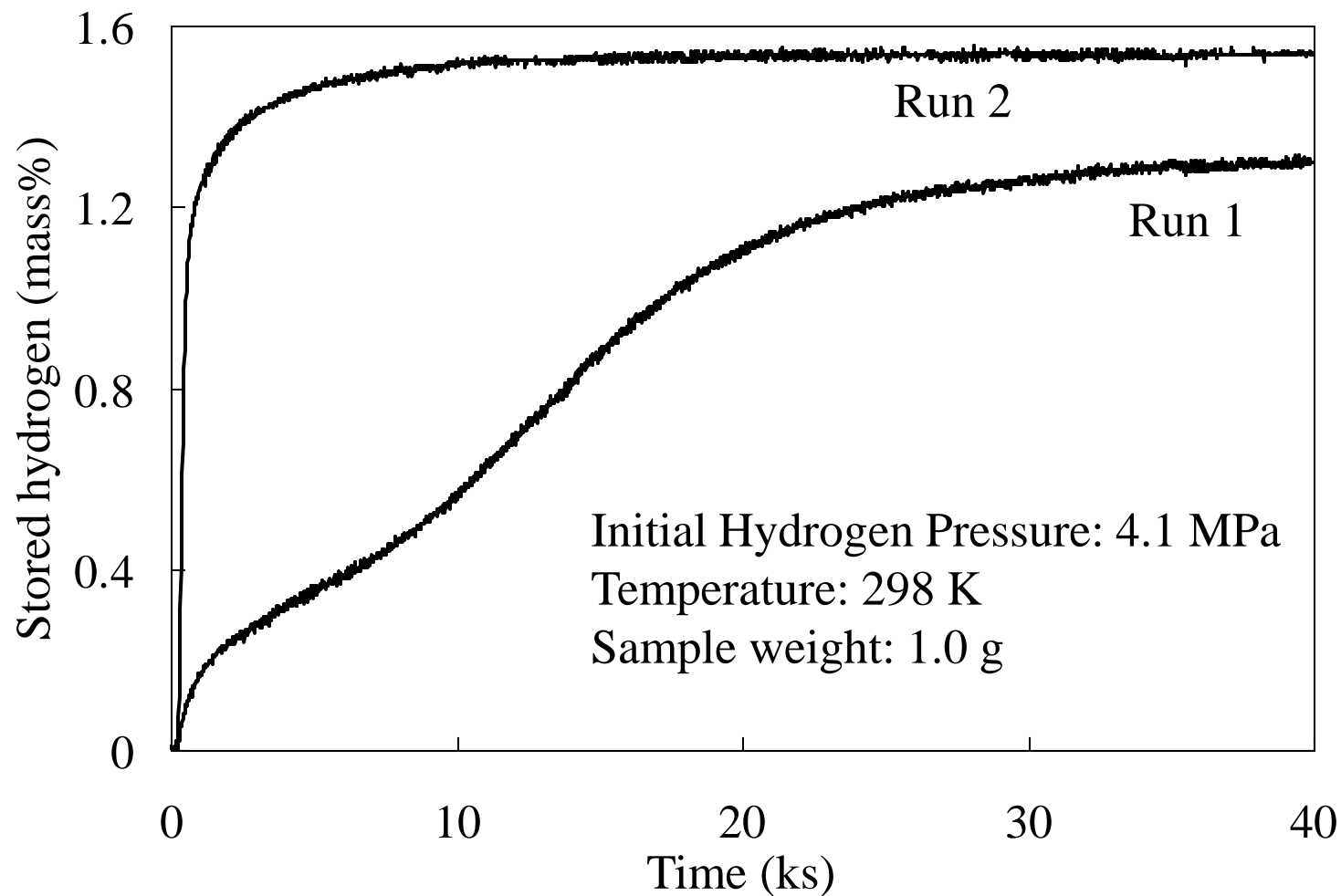


Fig. 5 Hydriding curves of SICSeD LaNi₅ in different atmospheres, measured by using Sievert's method at temperature of 298 K and initial hydrogen pressure of 4.1 MPa. Here, the products SICSeD in Run 2 had only one-third in full charge time, in comparison to the product SICSeD in Run 1, showing 1.54 mass% in hydrogen storage capacity, as the same as the value of commercial-available LaNi₅.

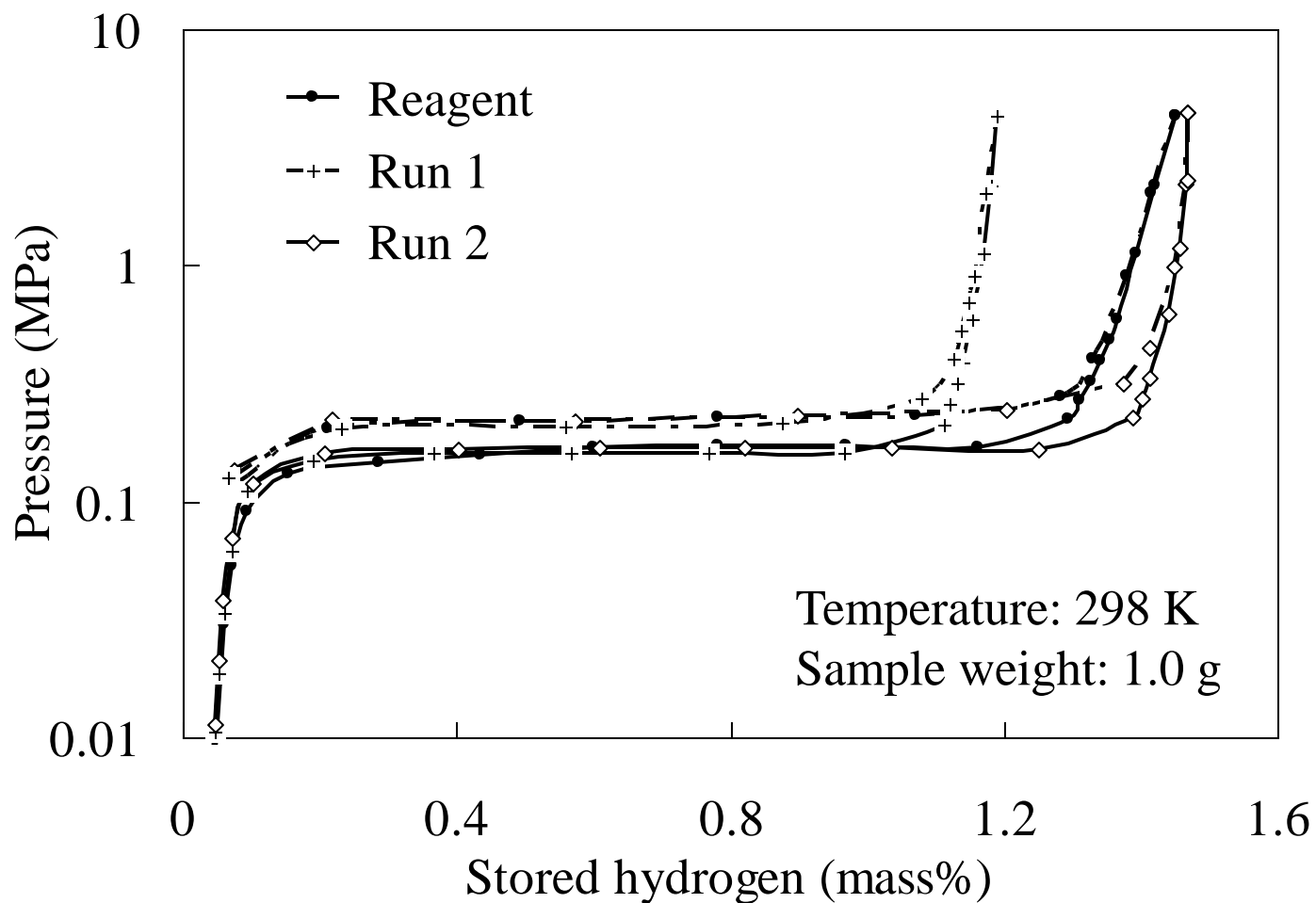


Fig. 6 Three PCT curves of a reagent of LaNi_5 with 99.9% in purity and two products of SICSeD LaNi_5 at 298K, measured by using Sievert's method, in which the equilibrium pressure of the SICSeD products were the same as that of the reagent.

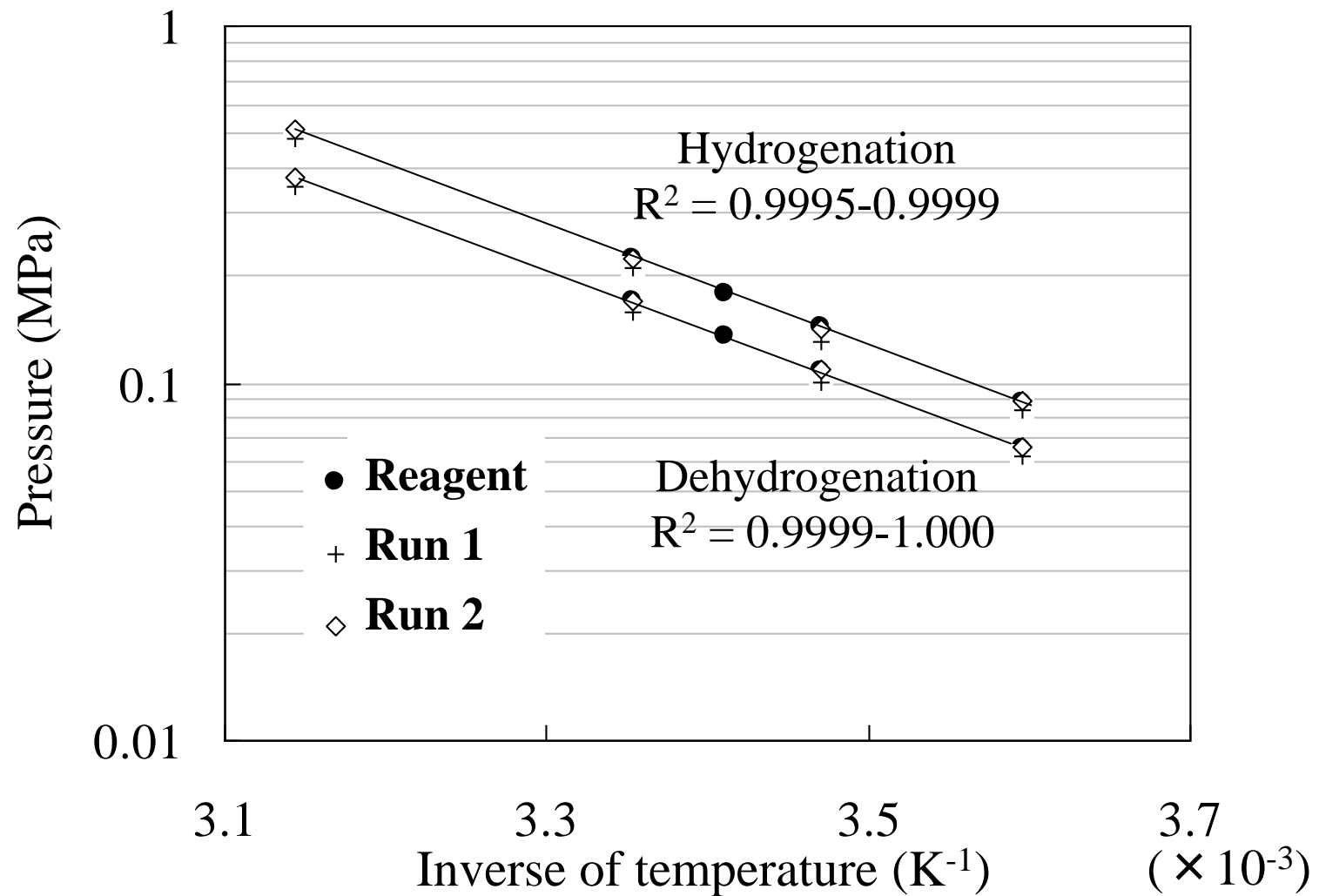


Fig. 7 Van't Hoff plots for a reagent and products of SICSeD LaNi₅, here we can calculate the reaction heat ΔH and entropy ΔS easily using the following equation:
 $\ln P = \Delta H / (RT) - \Delta S / R$.