

EXPERIMENTAL STUDY OF HYDROGEN ABSORPTION AND DESORPTION IN LaNi₅ ALLOYS WITH INDIUM ADDITION

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Abstract

The intermetallic phase LaNi₅ is known as a material for reversible hydrogen storage due to its suitable thermodynamic properties, and relatively fast kinetics of hydrogen absorption and desorption with the formation of LaNi₅H₆ hydride. This work focuses on the synthesis and characterization of a modified LaNi₅ phase with the addition of indium. The aim is to influence the microstructure and hydrogen storage properties of this material.

The samples were prepared by melting in an arc melting furnace under an inert atmosphere of pure argon and then annealed for a long time to establish a thermodynamic equilibrium state. Chemical composition and structural characterization were performed using X-ray diffraction (XRD) and electron microscopy (SEM) to identify present phases. Attention was paid to the effect of indium addition on the stability of the intermetallic structure and the stability of any secondary phases and subsequently produced hydrides. The thermodynamic hydrogenation properties of the prepared alloys were studied by measuring pressure-concentration isotherms (*p-c-T* curves) during hydrogen absorption and desorption cycles. The experiments made it possible to determine the maximum hydrogen storage capacity and enthalpy and entropy of the process. The results suggest that modifying the LaNi₅ alloy with indium can affect the thermodynamics and kinetics of hydrogen storage process, as well as the maximum hydrogen storage capacity.

Keywords: LaNi₅, hydrogen storage, stability, thermodynamics, SEM, XRD, *p-c-T* curves

1. INTRODUCTION

The binary phase LaNi₅ is known for its ability to form LaNi₅H₇ hydrides and is one of the materials suitable for hydrogen storage [1]. By adding a third element to the La-Ni binary system, it is possible to modify the thermodynamic properties of hydrogenation and dehydrogenation and thus optimize its applicability as a hydrogen storage material. In addition to LaNi₅ hydride, the literature also describes In₂La₁Ni₉H_{0.95} [2] and H₅In₁La₂Ni₂ [3] hydrides. The In-La-Ni system therefore appears to be an interesting material for studying phase equilibria, especially in the Ni-rich corner. In this work, we present isothermal sections of the ternary phase diagram at temperatures of 400 °C and 800 °C over the entire concentration range, with a special focus on areas where the LaNi₅ phase is also present in equilibrium.

2. STATE OF ART

Information on phase equilibria of the In-La-Ni ternary system is relatively scarce in the scientific literature. The only brief work was recently published in conference proceeding [4]. This paper presents a phase diagram at a temperature of 600 °C in the concentration range of 0-33.3 at% La, and at a temperature of 400 °C for concentrations higher than 33.33 at% La. Two binary phases, LaNi₅ and La₂In, showed solubility of the third element in significant amounts. Solubility of indium up to 8.5% was described in the structure of the binary

phase LaNi_5 at 600 °C. The binary phase La_2In contained 5% Ni in its structure at a temperature of 400 °C. A total of 14 ternary phases were described as stable. The crystallographic characteristics of these phases are summarized in **Table 1**. The work [4] are relatively brief and focused primarily on the structural analysis of individual phases. Apart from the design of the experimental phase diagram of In-La-Ni at combined temperatures of 400 and 600 °C, it does not provide further information on overall and phase chemical compositions of the individual samples. Therefore, the conclusions of the work cannot be validated.

The properties and stability of hydrides of ternary alloys of the In-La-Ni system have been studied primarily for the phases LaNi_2In , LaNiIn , and $\text{La}_2\text{Ni}_2\text{In}$. The ternary compound LaNi_2In can bind up to 3.5 hydrogen atoms in its structure [5, 6]. Hydrogenation of the ternary compound LaNiIn produces a hydride with the stoichiometry LaNiInH_2 . The hydride LaNiInH_2 decomposes in two steps, at temperatures of 267 °C and 357-405 °C. The melting point of pure LaNiIn was determined to be 784 °C [7]. Hydrogenation of the tetragonal phase $\text{La}_2\text{Ni}_2\text{In}$ causes a change in structure, and the resulting hydride $\text{La}_2\text{Ni}_2\text{InH}_5$ has a rhombohedral structure (space group Pbam). In this hydride, the volume of the crystal cell increases by 14.7% [3].

3. EXPERIMENTAL PROCEDURE

Sample compositions were selected to characterize the stability of the LaNi_5 binary phase within the In-La-Ni ternary system and to map the phase equilibria in which it participates. These samples underwent p-c-T analysis to evaluate their hydrogenation and dehydrogenation behavior and reaction kinetics. Long-term annealed samples were then characterized using a combination of scanning electron microscopy (SEM-EDX) by TESCAN LYRA 3 XMU and X-ray diffraction (XRD) techniques by diffractometer PanAnalytical Empyrean. In-La-Ni alloy samples were prepared from bulk materials. Samples were synthesized directly from pure elemental starting materials (5N purity) using an arc melting furnace (Edmund Bühler MAM-1). Each sample had a total mass of 1200 mg and was melted under an inert 6N Ar atmosphere. A titanium getter was employed to further purify the atmosphere and suppress oxygen contamination, due to the strong affinity of lanthanum for oxygen.

All prepared alloys were sealed in evacuated quartz glass ampoules. Prior to sealing, each ampoule was flushed three times with pure argon to minimize residual oxygen. The encapsulated samples were then subjected to long-term annealing at 400 °C. Annealing was carried out in a forced-air circulation furnace to ensure uniform temperature distribution throughout the chamber. Quenching was performed by submerging the ampoules in liquid nitrogen and breaking them beneath its surface, thereby limiting oxidation exposure. The quenched samples were immediately transferred to a drying oven preheated to 50 °C to prevent moisture condensation. Metallographic preparation for SEM analysis was carried out using isopropyl alcohol as the

cutting and polishing medium, replacing the conventional water-based coolant to avoid surface oxidation.

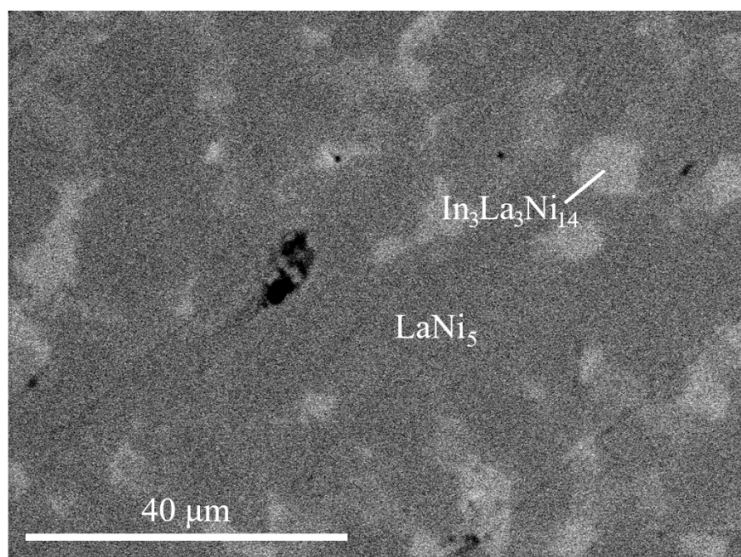


Figure 1 SEM micrograph in BSE mode of the sample 400_26 consists of LaNi_5 and $\text{In}_3\text{La}_3\text{Ni}_{14}$ phases

A micrograph of sample 400_b is shown in **Figure 1**. This image was acquired using an SEM in BSE mode. The sample contains two phases: a major binary phase of LaNi_5 (dark matrix) and a minor ternary phase $\text{In}_3\text{La}_3\text{Ni}_{14}$ (bright grains).

The overall chemical composition of the samples and the chemical compositions of the individual phases are listed in **Table 1**.

Table 1 The overall and phase chemical composition of the studied samples

Sample (T_No.)	Overall composition (at%)			Phase	Phase composition (at%)		
	Ni	In	La		Ni	In	La
400_25	81.1	2.6	16.3	LaNi_5	82.0	0.6	17.5
				In_2LaNi_9	75.8	14.7	9.4
400_26	77.6	5.5	16.9	LaNi_5	82.0	0.6	17.4
				$\text{In}_3\text{La}_3\text{Ni}_{14}$	70.0	15.0	15.0
400_27	77.5	11.7	10.7	LaNi_5	81.3	1.0	17.8
				$\text{In}_3\text{La}_3\text{Ni}_{14}$	68.7	16.5	14.8
				In_2LaNi_9	74.7	16.3	9.0

Hydrogen absorption under pressure up to $p = 2.5$ MPa and desorption into a fixed volume with the hydrogen pressure below the equilibrium pressure $p_{\text{eq}}(T)$ was carried out using Sieverts-type gas sorption analyzer *PCT-Pro Setaram Instrumentation* at temperatures T lying between 35-60 °C. Prior to the measurements, the as-cast and annealed material was crushed into a powder using a laboratory mortar and subsequently sieved through a 0.100 mm mesh. This powdering procedure was chosen to preserve the original microstructure formed during annealing. The mass of the sample used for sorption measurements was approximately 0.3 g. Before the sorption measurements, the materials were activated at 50 °C by four absorption–desorption cycles.

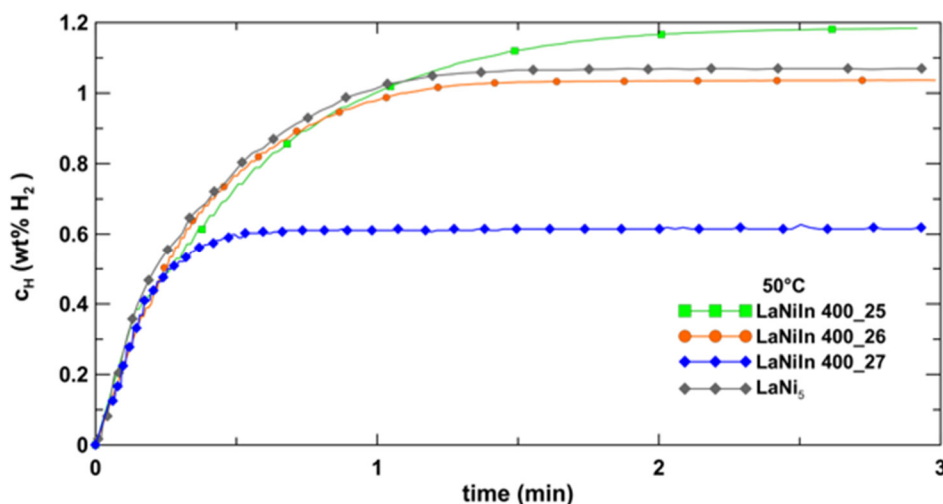


Figure 2 Kinetic curve of experimental samples

Increasing indium content does not significantly influence the kinetics of hydrogen absorption and desorption. As shown in **Figure 2**, the hydrogen absorption curves exhibit very similar absorption rates compared to the other experimental alloys as well as to LaNi_5 [8]. The primary effect of increasing indium content is observed in the thermodynamic properties of hydrogen absorption and desorption, as well as in the maximum hydrogen storage capacity. The maximum hydrogen capacity of the experimental alloys continuously decreases with increasing indium content. This decrease is attributed to the reduced fraction of the LaNi_5 phase, which forms

the reversible hydride LaNi_5H_6 , and to the increasing presence of the LaNi_9In_2 phase, which forms the hydride $\text{LaNi}_9\text{In}_2\text{H}_{0.95}$ that is stable at the measured temperatures.

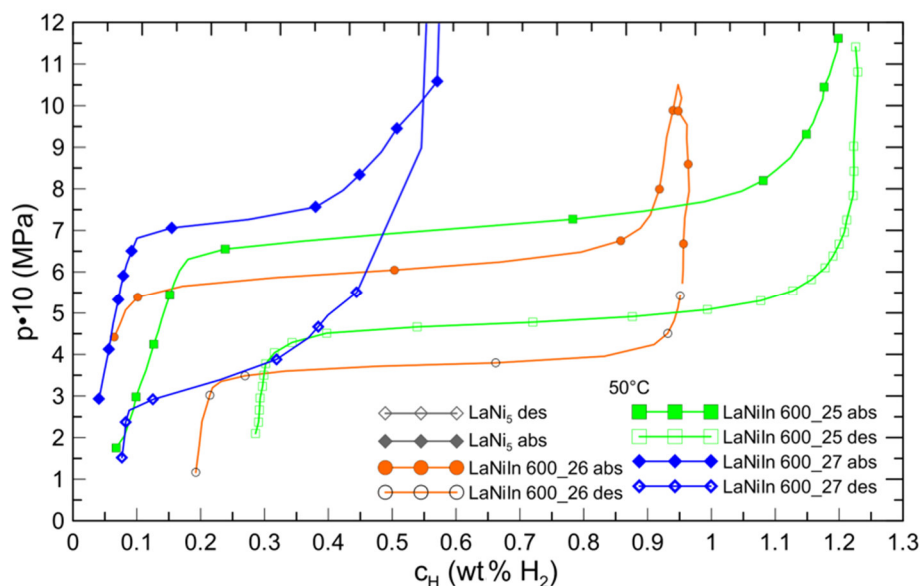


Figure 3 PCT curves of experimental samples

A particularly interesting effect is the synergy between these hydrides and its influence on the equilibrium pressures of absorption and desorption. Experimentally measured p - c - T curves are shown in **Figure 3**. At low contents of the LaNi_9In_2 / $\text{LaNi}_9\text{In}_2\text{H}_{0.95}$ phase, the absorption and desorption pressures decrease or remain close to the equilibrium pressure of LaNi_5H_6 . However, due to increasing internal stress caused by the formation of two different hydride phases and the higher indium content, the hysteresis becomes more pronounced. At higher contents of the LaNi_9In_2 / $\text{LaNi}_9\text{In}_2\text{H}_{0.95}$ phase, the absorption pressure increases. Nevertheless, the thermodynamic stability of LaNi_5H_6 remains very similar to that of LaNi_5 . The formation/decomposition enthalpy changes (absorption/desorption) were determined to be $-29.7 \pm 0.7/31.4 \pm 0.9$, $-29.9 \pm 0.7/32.6 \pm 1.1$, and $-27.0 \pm 2.9/32.2 \pm 2.6$ $\text{kJ mol}^{-1} \text{H}_2$ for samples LaNiIn a, b, and c, respectively. The evaluation of ΔH is described in literature [9,10].

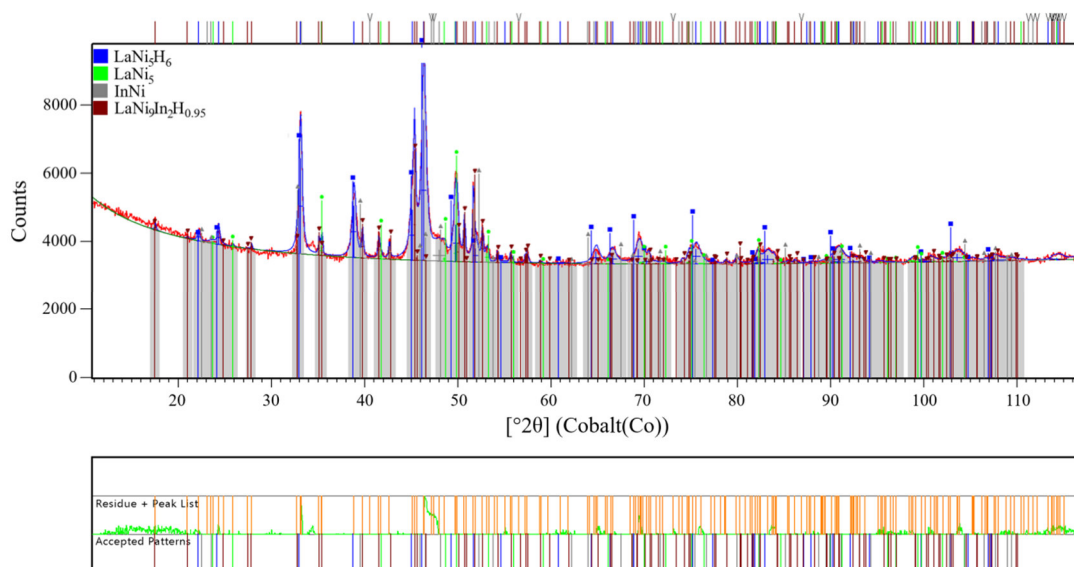


Figure 4 Evaluated XRD pattern of sample 400_25 after hydrogenation. Two types of hydrides- LaNi_5H_6 and ternary hydride $\text{LaNi}_9\text{In}_2\text{H}_{0.95}$ were found

Crystallographic structure of present phases was measured by XRD. **Figure 4** shows the evaluated XRD diffractogram of the sample 400_25 after hydrogenation. Two types of hydrides were found. The majority of hydrogen was stored in the structure of the binary phase LaNi_5 and the hydride LaNi_5H_6 was found to be stable. Another hydride was the ternary compound $\text{LaNi}_9\text{In}_2\text{H}_{0.95}$.

4. CONCLUSION

This study investigated the effect of indium on the phase stability, microstructure, and hydrogen storage properties of LaNi_5 -based alloys in the In–La–Ni ternary system. The experimental results confirmed that partial substitution with indium leads to the formation of secondary ternary phases, notably LaNi_9In_2 and $\text{In}_3\text{La}_3\text{Ni}_{14}$, alongside the primary LaNi_5 phase. Measurements of hydrogen absorption and desorption demonstrated that increasing indium content has no significant effect on the kinetics of hydrogen absorption and desorption. However, a significant effect on thermodynamic behavior was observed. Specifically, the maximum hydrogen storage capacity decreases with increasing indium concentration, which is directly related to the reduced proportion of the hydrogen-active LaNi_5 phase and the increasing presence of less active ternary phases. The simultaneous presence of multiple hydride-forming phases leads to changes in equilibrium pressures and increased hysteresis during the hydrogen cycle. Despite these changes, the thermodynamic stability of the LaNi_5H_6 hydride remains comparable to that of the undoped LaNi_5 system. Overall, it can be said that the addition of indium provides a viable approach to modifying the thermodynamic properties of LaNi_5 -based hydrogen storage materials, albeit at the cost of reduced storage capacity. These findings contribute to a deeper understanding of phase equilibria and hydrogenation behavior in the In–La–Ni system and may support the targeted design of advanced hydrogen storage alloys.

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SUPPLEMENTARY DATA

Supplementary data to this article can be found online at DOI: 10.5281/zenodo.20029603

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