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The Use of Lanthanum as a Crucial Alloying Element in Alloys for the Development of Sustainable Energy

F. Radkovský *, B. Smetana, M. Kawuloková
VSB - Technical University of Ostrava, Czech Republic
* Corresponding author: E-mail address: filip.radkovsky@vsb.cz

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Abstract

The melting of lanthanum, a rare metal, requires a temperature of around 920 °C, which is relatively low compared to the melting points of other rare earth metals. Lanthanum is a soft, silvery-white metal that has wide industrial applications, particularly in the production of hydrogen fuel cells and other technologies. Lanthanum and its alloys, especially those combined with other rare earth elements like cerium and neodymium, exhibit excellent hydrogen absorption capabilities. This makes them ideal materials for use in hydrogen storage systems. Lanthanum alloys can efficiently store hydrogen at high pressures and low temperatures, enabling hydrogen storage for later use in energy applications. Given the growing demand for materials used in hydrogen technologies, there is an increasing focus on the recycling of these metals. Recycling lanthanum and its alloys is crucial for sustainability, as rare earth elements are limited, and their mining can have negative environmental impacts. Effective recycling not only conserves natural resources but also reduces the environmental burden associated with the extraction and production of these materials. Rare metal recycling technologies can significantly contribute to the development of sustainable energy, which is vital for the future of clean and renewable energy.

Keywords: Hydrogen storage, Energy applications, Lanthanum, Recycling, Alloy production

1. Introduction

The increasing emphasis on reducing the carbon footprint and transitioning to sustainable energy sources has accelerated the development of technologies capable of storing and releasing hydrogen efficiently, particularly in conjunction with renewable energy systems. [1] Among the most prominent materials used for reversible hydrogen storage, the intermetallic alloy LaNi5 has been extensively studied due to its structural stability, strong hydrogen affinity, efficient sorption kinetics, and reliable cyclic performance during hydrogen absorption and desorption at moderate pressures and temperatures. [1-3] Hydrogen technologies based on materials capable of safely and efficiently handling hydrogen are regarded as a key enabler of the "green transformation" of the energy sector, as they allow bridging temporal and spatial gaps between renewable energy generation and its immediate utilization. [3-5] LaNi5-based alloys offer significant safety improvements and reduced energy losses compared to conventional hydrogen storage methods (compression/liquefaction), thereby facilitating the transition toward widespread implementation of a hydrogen economy. [1-3, 5]

LaNi5 is a hexagonal intermetallic alloy of the CaCu5 type, whose crystal structure enables the reversible incorporation of substantial amounts of hydrogen as a hydride. The material can be synthesized either by melting under a protective atmosphere or by subsequent mechanical processing. Precise control of the microstructure is crucial: ball milling produces a high fraction of nanoparticles and induces atomic disorder. Although these features generally enhance sorption kinetics and increase the specific surface area—both of which are desirable for hydrogen storage—they may, over extended cycling, negatively impact the maximum storage capacity and structural durability due to the higher energy barrier associated with hydriding. [1-3, 6]

Prolonged mechanical milling (≥100 h) ultimately reduces sorption capacity and increases plateau pressure, because the altered lattice parameters and increased defect concentration reduce the material's affinity for hydrogen. Subsequent annealing can only partially restore atomic ordering and cannot fully recover the original structural state. [2]

Alternatively, the sorption properties and mechanical stability of LaNi5-based alloys can be optimized through appropriate substitution of metallic components—for instance, by partially replacing nickel with another metal. Such modifications allow tuning of the operational hydrogen absorption/desorption pressure range, enhancing the alloy's longevity and cyclability while enabling more flexible industrial application across various storage systems. [3,7]

Industrial-scale preparation of LaNi5 requires high-purity metallic precursors (La, Ni), melting under oxidation-free conditions, typically in an argon atmosphere or under vacuum, and controlled solidification (casting into molds, ingot formation, or powdering for subsequent surface treatments or mechanical processing). [1,2] One highly desirable method involves casting into molds with simultaneous control of the cooling rate, allowing the formation of an optimally fine-grained microstructure with a high density of active sites for hydrogen chemisorption.

The production process can be further tailored through various mechanical or thermal treatments depending on the intended final application (e.g., solid-state storage, powdered material for fuel cells, sorption membranes, etc.). Importantly, modern industrial methods allow recycling of LaNi5 at the end of its lifecycle without significant loss of sorption properties, in line with circular economy principles. [1, 3, 5]

LaNi5 is capable of reversibly absorbing substantial amounts of hydrogen (1–1.4 wt%) under moderate pressures (1–2 MPa) and temperatures (20–80°C), making it advantageous for practical deployment in both stationary storage systems and mobile applications, including vehicles, fuel cells, and hybrid energy systems. [1-5]

Compared to other hydrogen storage methods (high-pressure cylinders, cryogenic liquid hydrogen), LaNi5 offers several significant advantages: enhanced safety, as it operates without extreme overpressure, explosion risk, or liquid phases; reduced energy losses during charging and discharging of the storage system; ease of handling due to rapid absorption/desorption and an almost isothermal reaction profile; and material recyclability with environmentally friendly production that avoids emissions of hazardous substances. [1-3,8,9]

The use of LaNi5-based solid-state storage is directly linked to the reduction of greenhouse gas emissions, as the stored hydrogen can be produced electrolytically from renewable sources such as solar and wind energy [3-5]. Moreover, hydrogen can also be stored in the form of chemically bound ammonia (NH_3), further enhancing the safety and efficiency of the overall energy chain [1]. LaNi5 also enables the development of decentralized low-emission energy systems, including backup power for renewable power plants and applications in clean mobility. [3-5]

Importantly, hydrogen storage in solid alloys addresses a key limitation of renewable energy: temporal and geographical mismatches between production and demand. [3-5] The ecological benefit of LaNi5, namely by reducing reliance on energy- and resource-intensive high-pressure or cryogenic storage systems, positions it as one of the most promising materials for the hydrogen infrastructure of the future.

A new direction in hydrogen storage research focuses on nanostructured and hybrid materials, where substitution and compositional modifications (e.g., $LaNi5_{-x}Sn_x$ or hybrids with Mg, Si, etc.) allow further optimization of material properties for specific applications, thereby enhancing both versatility and environmental performance. [3, 6, 7] Studies indicate that combining a fine microstructure with an optimized working pressure range is critical for the development of safe, low-emission energy storage systems. [3, 7]

2. Experimental description

Melting lanthanum alloys, including LaNi5, in a vacuum furnace is a modern metallurgical process that produces exceptionally pure and homogeneous materials with precisely defined compositions. Vacuum melting is typically used for reactive, easily oxidizable metals such as lanthanum and its alloys. In a vacuum induction furnace, the raw materials (metals or pre-alloyed ingots) are placed in a graphite or ceramic crucible enclosed within a sealed vacuum chamber. The applied vacuum (typically 10^{-3} to 10^{-5} Pa) prevents the ingress of atmospheric oxygen and nitrogen, thereby avoiding oxide and nitride formation as well as unwanted absorption of hydrogen and other gases. [10, 11] Melting is achieved by electromagnetic induction, electric arc, or, in specific cases, electron beam heating. Induction heating generates eddy currents within the metal, providing uniform heating and complete melting of the charge.

Once the vacuum is stabilized and the target temperature is reached, the process can be monitored through viewing ports equipped with anti-deposition protection or controlled automatically to regulate the melt composition and temperature. After thorough mixing and optional homogenization, the melt can be cast directly within the chamber or, under vacuum or an inert atmosphere, into the appropriate casting device. A primary objective of the process is producing larger quantities of nickel–lanthanum alloy. For the melting, an electric induction vacuum furnace (Leybold Heraeus) with a chamber volume of 112 liters and crucible capacities ranging from 0.5 to 1.2 liters was used. The vacuum furnace is shown in Figure 1, and examples of melting crucibles are presented in Figure 2.

Fig. 1. Internal chamber of the Leybold Heraeus electric induction vacuum furnace

Fig. 2. Examples of crucible sizes

2.1. Foundry experimental parameters

For vacuum melting of lanthanum, it is necessary to reach a temperature of approximately 920°C, corresponding to the melting point of lanthanum. In vacuum furnaces, slight overheating (around 930–950°C) is typically applied to ensure melt stability and adequate mixing, while the deep vacuum or inert gas atmosphere prevents oxidation of this highly reactive metal. [12]

For alloys with higher lanthanum content, such as LaNi5, the melting points of the other components and the potential formation of eutectics must also be considered. The fundamental principles of vacuum melting of LaNi5 can be divided into three main areas:

Charge: The starting materials are high-purity lanthanum and nickel in a stoichiometric ratio (La:Ni = 1:5), or a pre-alloyed ingot doped with lanthanum. These elements are placed into a ceramic or graphite crucible resistant to the aggressive melt. [7]

Vacuum: The process is conducted under a deep vacuum (typically 10^{-3} to 10^{-5} Pa) to prevent oxidation of the highly reactive lanthanum. In some applications, the vacuum can be replaced by an argon atmosphere with very low oxygen content.

Heating: An induction coil generates eddy currents, providing uniform melting of the material. The melting temperature is slightly above the melting point of LaNi5 (optimally 1350–1450°C, depending on exact composition and processing), ensuring thorough homogenization and complete alloying of the components. During melting, the process can be visually monitored through a furnace viewport, as shown in Figure 3.

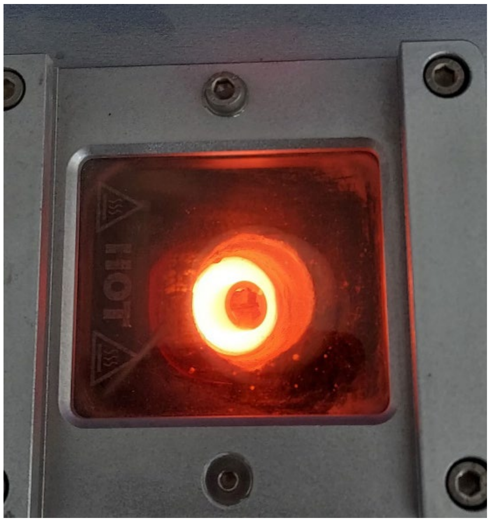

Fig. 3. Visual monitoring of the melting process

2.2. Melting in an electric induction vacuum furnace

Two melting procedures were investigated. The first approach involved simultaneous melting, in which the entire charge was loaded into the crucible prior to melting. In practice, the lanthanum melting temperature is maintained only slightly above its melting point, and the process is carefully controlled. Considering the melting point of pure nickel (1455°C), the temperature must be raised above this threshold. In simultaneous melting, lanthanum melts preferentially, and further temperature increases above its melting point can lead to additional complications that must be accounted for.

The second approach involved a two-step melting procedure, in which the nickel portion of the charge was melted first, followed by incremental addition of lanthanum as the primary alloying component. Based on prior experiments, only zirconia crucibles were used in this method. This procedure proved effective and allowed the production of larger quantities of the alloy with the desired chemical composition.

Simultaneous melting proved unsatisfactory due to significant lanthanum loss; however, several types of crucibles were tested during the experiments. The requirements for crucible properties are demanding, including chemical inertness toward molten lanthanum and LaNi5 alloy to minimize metal–crucible reactions and contamination of the melt. Only a few commercially available crucibles are suitable for melting lanthanum-containing alloys. Thermal stability is critical: the material must withstand prolonged exposure to temperatures around 1400–1500°C (LaNi5 melts at approximately 1350–1455°C) without structural failure or decomposition, while individual components may have even higher melting points. Additionally, low porosity is essential to prevent the crucible from absorbing the reactive metal or its vapors, thereby minimizing potential melt leakage. Several crucible types that could theoretically be used in a vacuum furnace are discussed.

2.3. Primary Requirements for Crucibles for Vacuum Melting of LaNi5

Zirconia crucibles, i.e., crucibles made from zirconium dioxide (ZrO_2), represent one of the most suitable choices for melting highly reactive materials such as lanthanum and LaNi5 alloys in a vacuum furnace. This type of crucible was successfully tested in our furnace, as shown in Figure 4, including the pre-melted portion of the charge. Zirconia offers excellent chemical resistance, being highly inert toward lanthanum, LaNi5, and other metals and their alloys. It practically does not react with the melt even at temperatures exceeding 1500°C, minimizing contamination of the resulting alloy. Its high refractoriness, with a melting point around 2700°C, allows safe operation at all typical LaNi5 melting temperatures.

Furthermore, modern manufacturing techniques produce dense zirconia crucibles with low porosity and high mechanical and chemical stability, which minimize absorption of the molten metal and ensure durability over repeated use. Zirconia crucibles also contribute minimal impurities to the melt, which is essential for achieving high product purity. The main limitations are their higher cost and brittleness: like other oxide ceramics, they are prone to cracking under rapid temperature changes or mechanical shocks, requiring careful handling. The crucible is shown in Figure 4, and its exact composition is provided in Table 1.

Table 1.
Composition of the Zirconia Crucible [13]

Species	Wt. % Typical	Maximum	Minimum
Zirconia ZrO2	93	95	91.5
Alumina Al2O3	0.8	1.5	-
Silica SiO2	1.3	1.8	-
Iron Oxide Fe2O3	0.4	0.8	-
Lime CaO	4	5	3
Magnesia MgO	0.3	0.9	-

Fig. 4. Zirconia crucible with a metallic charge

3. Achieved results

The results are presented here. The vacuum melting procedure for LaNi5 alloy requires careful preparation, precise dosing of components, and strict control of atmosphere and temperature to ensure that the resulting alloy is clean, homogeneous, and exhibits excellent hydrogen sorption properties. A typical two-step melting process can be divided into seven main stages:

A) Charge Preparation:

Accurately weighed stoichiometric amounts of high-purity lanthanum and nickel are combined in a La:Ni ratio of 1:5 (or adjusted according to the desired composition; a slight excess of La is sometimes advantageous to compensate for potential lanthanum loss). The metallic materials are cleaned to remove surface oxides and impurities, either mechanically, chemically, or by brief annealing in a hydrogen or inert atmosphere.

B) Crucible and Mold Preparation:

The most suitable zirconia crucible, containing at least 93% ZrO_2 (based on prior experiments), is placed in the furnace, thoroughly dried, and free of any residues from previous melts. A two- or three-part metal mold is also prepared. Mold sizes vary according to the internal cavity shape, e.g., a truncated cone with a bottom diameter of 40 mm, top diameter of 60 mm, and maximum height of 140 mm. The mold must be clean, free from oxidation, and coated with a protective layer; boron nitride (Type EP, 3M) has proven effective in our experiments.

C) Furnace Closure and Evacuation:

The prepared charge is placed into the crucible, which is then inserted into the melting chamber. The alloy is positioned within a special pocket in the furnace roof. The internal space of the chamber with the loaded crucible and coated metal mold is shown in Figure 10. The chamber is then closed and evacuated to a deep vacuum (10^{-4} Pa) to prevent oxidation and nitridation of the metals. In our system, the vacuum can be backfilled with ultra-high-purity argon (6.0) up to atmospheric pressure, which is the procedure adopted in this case.

D) Heating and Melting:

The charge is inductively heated to a temperature above the melting point of nickel, using a graphite sleeve around the exterior of the crucible to provide auxiliary heating. This prevents direct contact between graphite and the charge. Figure 11 shows the heating of the nickel charge. Once the nickel has melted, it is advisable to wait a few minutes before incrementally adding lanthanum as the alloying component. This results in immediate melting and some initial loss due to evaporation. The melt is then stirred by induction for approximately 1.5 minutes to ensure thorough homogenization of the alloy. Prolonged heating, however, requires caution due to increased lanthanum evaporation.

E) Casting and Crystallization:

After homogenization, the molten alloy can either be poured into a preheated mold (if the furnace design allows) or allowed to solidify directly in the crucible. In our procedure, a metal mold at ambient temperature is always used. During cooling, rapid temperature changes must be avoided to prevent cracking of the alloy or crucible; however, if the ingot is subsequently crushed into smaller samples, minor cracking is not an issue. Figure 12 shows a LaNi5 sample after cooling.

F) Removal and Further Handling:

Once fully solidified and cooled below approximately 200°C, the alloy can be safely removed. LaNi5 is stable and does not further oxidize upon exposure to air. Pure lanthanum outside the alloy (e.g., on crucible walls or splashes) reacts with the atmosphere to form highly flammable powder. Figure 5 shows a LaNi5 sample immediately after removal from the permanent mold.

Fig. 5. Cracked LaNi5 alloy sample

G) Crushing, Milling, and Final Processing:

The LaNi5 ingot can be crushed, milled into powder, or machined to the desired dimensions as required. For powder materials, handling under a protective atmosphere is again recommended. Figures 16, 17, and 18 show the prepared LaNi5 alloy samples, ready for further processing and evaluation of their properties.

4. Conclusions

Vacuum melting of LaNi5 alloy is a well-established method for producing a clean, homogeneous, and chemically stable material, which is essential for energy applications—particularly for hydrogen storage. The procedure involves precise weighing of the components, use of an inert crucible, deep vacuum, gentle heating, alloy homogenization, and rapid handling after solidification, all carried out with maximum protection against oxidative contamination.

The correct choice of crucible is critical for vacuum melting of LaNi5. Crucible selection is also an economic consideration: highly inert ceramics are costly but ensure the highest quality of the raw material for hydrogen technologies. LaNi5 contains highly reactive lanthanum, which reacts strongly with common crucible materials, especially at the elevated temperatures required for complete melting with nickel. Zirconia (ZrO_2) crucibles are particularly suitable for both laboratory and industrial vacuum melting of LaNi5, as they provide high purity of the resulting alloy and long service life under repeated use. They are our preferred choice when minimizing contamination and achieving optimal material properties for subsequent hydrogen applications.

The two-step melting procedure was confirmed as the only feasible approach given our technical and technological capabilities. After melting, it is advisable to “stir” the melt (by applying induction for several minutes) to improve the uniformity of both composition and microstructure.

Advantages of Vacuum Melting of Lanthanum Alloys:

Exceptionally high purity, minimizing contamination by gases and trace elements, with minimal impurities that could reduce hydrogen storage capacity.

Precise control over alloy composition due to the absence of unwanted interactions with the atmosphere.

Elimination of metal oxidation and formation of gas inclusions.

Homogeneous microstructure and enhanced chemical reliability of the resulting ingot.

Production of large ingots that can be easily divided into smaller samples or crushed into powder for subsequent processing, such as in metal hydride accumulators.

Disadvantages and Limitations:

Requirement for complex and costly vacuum process technology.

Increased risk of lanthanum evaporation, potentially altering the La:Ni ratio; thus, the formulation may need fine adjustment.

Higher demands on the purity of the charge and careful handling of the raw materials.

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