



11th International Congress on Metallurgy & Materials SAM/CONAMET 2011.

Study of the thermal stability in air of LaNi₅ by DSC, EDX, TEM and XRD combined techniques

M.V Blanco^{a,b,*}, E. Zelaya^c, M.R Esquivel^{a, c,d}

^a Comisión Nacional de Energía Atómica, Centro Atómico Bariloche, Avda. Bustillo km 9,5 (R8402AGP) S.C. de Bariloche, Argentina

^b Instituto Balseiro (UNCu y CNEA)

^c Consejo Nacional de Investigaciones Científicas y Técnicas

^d Centro Regional Universitario Bariloche, (UNCo), Quintral 1250, (R8400FRF), S.C. de Bariloche, Argentina

Abstract

In this work, the thermal stability in air of LaNi₅ and its reaction products were analyzed. The structural and microstructural parameters were determined by X-ray diffraction and TEM techniques. According to the results of XRD / TEM, the starting material is monophasic with hexagonal structure (*P6/mmm*, $a = 5.019(0) \text{ \AA}$, $c = 3.982(7) \text{ \AA}$). Thermal measurements were made by differential scanning calorimetry, using heating rates between 1 and 25 °C.min⁻¹. The calorimetric curve corresponding to a heating rate of 1 °C.min⁻¹ shows stability of the intermetallic up to (140 ± 1) °C. The thermal decomposition evolves as three successive exothermic global events. According to the measured curve, the maximum peaks are produced at (205 ± 1) °C, (258 ± 1) °C and (391 ± 1) °C, respectively. Thermal evolution lead to the formation at 600 °C of the final products La₂O₃ (*P-3m1*, $a = 3.945(0) \text{ \AA}$; $c = 6.151(0) \text{ \AA}$), NiO (*Fm3m*, $a = 4.178(0) \text{ \AA}$) and LaNiO₃ (*R-3c*, $a = 5.457(3) \text{ \AA}$; and $c = 13.146(2) \text{ \AA}$). The elemental composition was analyzed by EDS.

© 2012 Published by Elsevier Ltd. Selection and/or peer-review under responsibility of SAM/CONAMET 2011, Rosario, Argentina. Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

Keywords : LaNi₅, thermal stability

* Corresponding author. Tel.: +54-0294-4445100; fax: +54-0294-4445299.

E-mail address: vblanco@cab.cnea.gov.ar.

1. Introduction

The intermetallic (IM) LaNi_5 has been extensively studied as a material with various applications related to hydrogen technology (Srivastava and Upadhyaya, 2011). In particular, it has been study as a metal-hydride forming material useful for stationary applications and commercial Ni-MH batteries (Cuevas et al., 2001). LaNi_5 is suitable for hydrogen applications because of its low hysteresis, chemical stability, rapid activation and equilibrium pressures below 10 atm at room temperature.

This IM is particularly promising for applications in schemes of thermal hydrogen compression (THC) (Talagañis et al., 2009; Talagañis et al., 2011). It is because the working temperature-pressure relationship has an operating range between 10 and 90 °C. However, the thermal stability of LaNi_5 in air has not been studied in depth. This analysis will allow knowing the temperature range in which the intermetallic could support air contact without decomposing. In this way, the safety margins for operation in compressors devices before any exposition to air could be established. In addition, the study of the relative stability of the products would help to identify the reversibility of the reaction products and to characterize their structures and properties.

The mechanism of thermal decomposition of the IM under oxygen atmosphere can be done by calorimetry. At the present time, lanthanum and nickel oxides, such as La_2O_3 , LaNiO_3 and NiO have been earmarked to hydrogen production processes, more specifically in the development of catalysts (Gallego et al., 2011; Pechini, 1967). However, due to the characteristics of the microstructure of the oxides obtained by annealing of LaNi_5 , these products may have additional advantages that could make them suitable for other applications of hydrogen technology.

In a recent study, $\text{La}_{0.25}\text{Ce}_{0.52}\text{Nd}_{0.17}\text{Pr}_{0.06}\text{O}_2$ dioxides obtained by thermal decomposition of $\text{La}_{0.25}\text{Ce}_{0.52}\text{Nd}_{0.17}\text{Pr}_{0.06}(\text{OH})_3$ were identified and characterized (Esquivel and Zelaya, 2011). In that case, the presence of nanopores in the oxide surface was observed, giving the possibility of designing materials for applications in gross purification of hydrogen. In this paper, we analyze the processes related to thermal decomposition in air of LaNi_5 and its reaction products. These oxides obtained could be applied to gross purification process of hydrogen. This objective aimed the presentation of this work

2. Experimental

Commercial LaNi_5 (Reacton, 99.999%) was placed in steel chamber and processed by mechanical milling in a medium-energy ball mill (Pulverisette 6, Fritsch) for 15 minutes. The process was carried out under Ar atmosphere, maintaining a constant ball/ sample mass ratio (6.28). The product was annealed in air at 600 °C for 24 h. Structural and microstructural parameters were established using X-Ray Diffraction (Philips diffractometer, PW 1710/01, Cu $K\alpha$ radiation and graphite monochromator), and Transmission Electron Microscopy (Philips CM200-UT, operated at 200 kV). The thermal stability of the compounds was studied by Differential Scanning Calorimetry (DSC TA 2910 calorimeter). Non isothermal calorimetric measurements were performed in air at a heating rate of 1 °C.min⁻¹. The temperature range was from room temperature to 570 °C. Isothermal calorimetric measurements were done by combined heating of sample in Ar to avoid material decomposition at 25 °C.min⁻¹. After closing Ar supply, an isothermal measurement in air was done. From these results, the isothermal enthalpy changes and isothermal degree of reaction were found. Morphology, particle size distribution and composition of the samples were determined by Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM 515, Philips Electronic Instruments associated with EDAX Genesis 2000 probe).

3. Results and discussion

3.1 LaNi_5 characterization

The starting IM was analyzed by XRD, TEM and SEM. Figure 1a presents a SEM image of a LaNi_5 particle which presents smooth surfaces and well defined edges. This morphology is typical of AB_5 's obtained at high equilibrium temperatures. The XRD measurement of this IM is presented elsewhere (Blanco and Esquivel, 2012). The ring diffraction pattern was obtained by TEM (Fig. 1b). The reflections were indexed according to the structure of LaNi_5 . The structure corresponds to the $P6/mmm$ space group, La occupies the Wyckoff position $1a$ and Ni occupies the Wyckoff positions $2c$ and $3g$. The values of the parameters resulted $a = 5.019(0)$ Å, $c = 3.982(7)$ Å. As can be observed in the area examined of the particle, there is preferential orientation, indicated by the presence of very bright spots in the rings corresponding to 101 and 110 reflections.

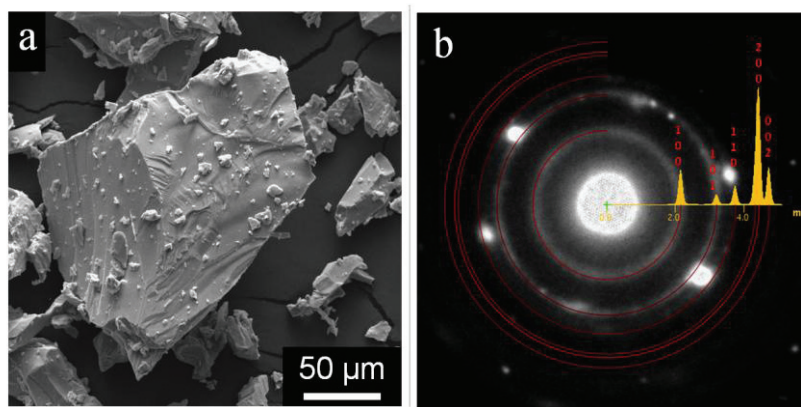


Figure 1- (a) LaNi_5 particle (b) Ring diffraction pattern of LaNi_5 .

The sample composition was analyzed by energy dispersive spectroscopy (SEM/TEM). In both cases, the average values for the composition of the starting intermetallic were 75% Ni, 25% La (error associated to SEM and TEM $\pm 2\%$ at). The presence of traces of another element could not be detected in any of the two cases. Therefore, the sample is monophasic to the detection limits of TEM/XRD.

3.2 Thermal decomposition of LaNi_5

The IM thermal stability was analyzed by DSC. A non isothermal measurement was performed in air at 1 °C.min⁻¹ (Fig.2). For this measurement, the intermetallic showed structural stability up to (140 ± 1) °C. At this temperature the onset initiates, and it is almost completed at (491 ± 1) °C. Three overall exothermic events could be distinguished. Measured peaks corresponds to the following temperatures (205 ± 1) °C, (258 ± 1) °C and (391 ± 1) °C, and are related to the decomposition and subsequent oxidation of LaNi_5 .

In order to analyze the characteristics of the reaction three isothermal measurements were carried out. The selected temperatures were 258 °C, 310 °C and 570 °C. The three temperatures corresponds to different oxidation processes. The first temperature (258 °C) is associated to the decomposition of LaNi_5 and partial oxidation of La to La_2O_3 . The isothermal measurement at 258 °C is shown in Figure 3.a. As can be observed the heat evolution starts immediately when the flow of Ar is interrupted. The second isotherm temperature is associated to LaNi_5 decomposition and complete oxidation of La to La_2O_3 . The third temperature is 570 °C,

and is related to the LaNi_5 decomposition, complete La oxidation to LaNiO_3 and Ni oxidation to NiO.

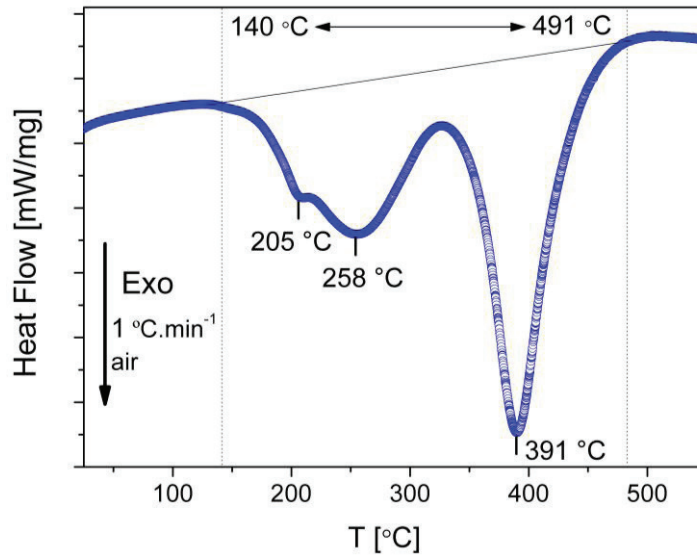


Figure 2- Calorimetric curve belonging to the thermal decomposition of LaNi_5 at a heating rate of 1 °C.min⁻¹.

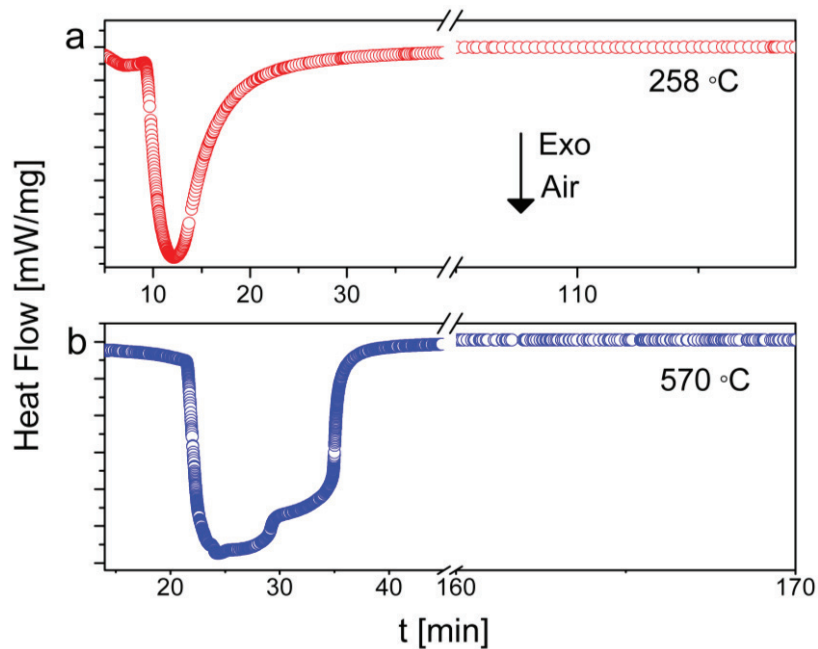


Figure 3- a) Isothermal evolution of LaNi_5 oxidation a) 258 °C and b) 570 °C.

Once the isotherm in air atmosphere was reached, two hours were required to ensure complete oxidation. A larger value of heat reaction is reached in the isotherm stabilized at 570 °C due to partial Ni oxidation and to the complete oxidation of La to LaNiO_3 . According to XRD results, the heat reaction determined in Figure 3a

corresponds to LaNi_5 decomposition and La partial oxidation to La_2O_3 .

The degree of progress of the LaNi_5 decomposition was evaluated by taking the following considerations about the theoretical heat of reaction:

At 258 °C

$$Q_T^{258} = m_{\text{LaNi}_5} \Delta H_{\text{LaNi}_5}^d + m_{\text{La}} \Delta H_{\text{La}_2\text{O}_3}^f \quad (1)$$

At 570 °C

$$Q_T^{570} = m_{\text{LaNi}_5} \Delta H_{\text{LaNi}_5}^d + m_{\text{La}} \Delta H_{\text{LaNiO}_3}^f + m_{\text{Ni}} \Delta H_{\text{NiO}}^f \quad (2)$$

Experimental values for the heats of reaction were obtained from the curves presented in figures 3a and 3b.

Table 1 presents the heats of reaction calculated at 258 °C, 310 °C and 570 °C.

Isotherm Temperature	Q_T [kJ]	Q_E [kJ]	Maximum α
258°C	-0.041±0.004	-0.014±0.001	0.340
310°C	-0.041±0.004	-0.021± 0.002	0.503
570°C	-0.068±0.007	-0.048± 0.005	0.700

The degree of progress, defined as $\alpha = \frac{Q_{\text{exp}}}{Q_T}$ was determined at each time for each measurement. The results are plotted in Figure 4.

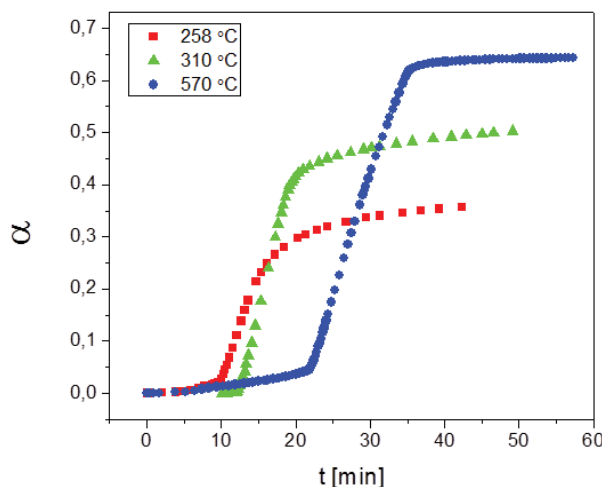


Figure 4- Evolution of the degree of reaction associated to LaNi_5 oxidation process at three different temperatures.

The degree of reaction marks a partial conversion of the thermal decomposition of LaNi_5 . At 258 °C, the intermetallic decomposes but only part of La is converted to La_2O_3 . At higher temperatures, the curve accelerates and a higher conversion is reached due to partial oxidation of Ni combined with a larger oxidation of La. At 570 °C, the reaction is quicker and a higher amount of LaNi_5 is oxidized. Despite this high temperature value, not all Ni is converted to NiO. Therefore, no maximum α value is reached.

3.3 Analysis of the reaction products

Figure 5 shows the diffraction pattern corresponding to LaNi_5 annealed in air at 600°C for 24 h. This treatment was done to favor the formation of end products and increase the crystallite size. As shown in the Figure, the following structures are detected La_2O_3 ($P-3m1$, $a = 3.945(0)\text{ \AA}$, $c = 6.151(0)\text{ \AA}$), NiO ($Fm3m$, $a = 4.178(0)\text{ \AA}$) and LaNiO_3 ($R-3c$, $a = 5.457(3)\text{ \AA}$ and $c = 13.146(2)\text{ \AA}$).

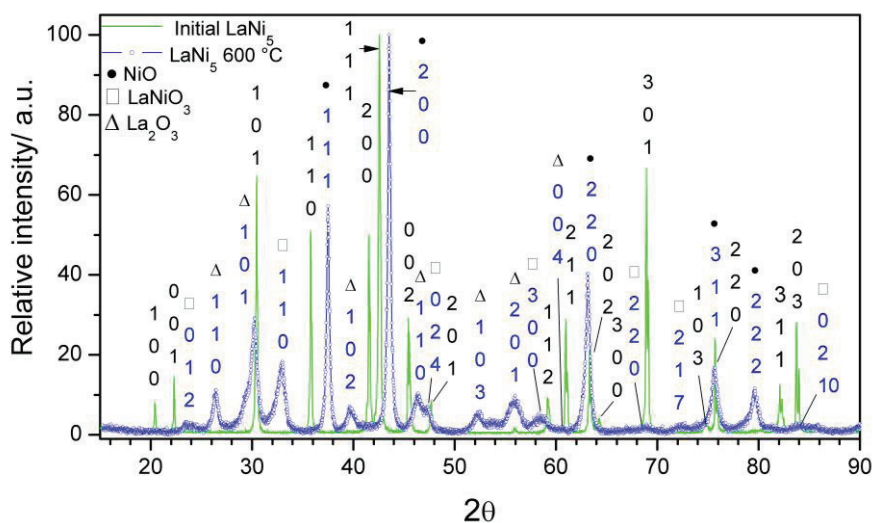


Figure 5- Diffractogram portion of starting of LaNi_5 (green line), diffractogram of LaNi_5 heated in air atmosphere at 600°C for 24 h (blue line) LaNiO_3 (ICSD 67717), La_2O_3 (ICSD 24693), NiO (ICSD 9866)

Compositional analysis was performed by energy dispersive spectroscopy; the results are detailed in Table 2. The elements present are La, Ni and O. According to the observed values can be seen that the distribution of La and Ni is, within the detection limits of the technique, similar throughout the sample. None of the examined particles consisted entirely of Ni, attributable to NiO or La, assignable to La_2O_3 .

Table 2- Compositional analysis of the reaction products of LaNi_5 annealed in air

Sample	Particle size ($\mu\text{m} \times \mu\text{m}$)	Elemental Percentages (At $\pm 2\%$)	
		La	Ni
Reaction products of LaNi_5	70 x 100	17	83
annealed in air atmosphere	30 x 20	17	83
	30 x 20	16	84
	30 x 20	17	83

This would indicate that the reaction products are intimately mixed. The Ni/La ratio for the particles presented in Table 2 (~5) does not correspond to the atomic ratio between these elements for the LaNiO_3 compound (~1).

3.4 Mechanism of decomposition of LaNi₅ in air

The reaction mechanism is represented by more than a global stage. The LaNi₅ disproportionation would happen at temperatures above 140 °C. This event is endothermic, $\Delta H = 26.3 \text{ kJ}\cdot\text{mol}^{-1}$ (Watanabe and Kleppa, 1983). With the available results is not yet possible to determine whether the decomposition occurs instantaneously at this temperature. This first event is followed by the selective oxidation of the decomposition products leading to the formation of the oxides presented in Figure 4. The formation of decomposition products is associated with global exothermic events related to the formation of the corresponding oxides. The sequence of the three thermal events observed in Figure 3a would indicate that the products are obtained in series. According to the literature the enthalpy of formation for La₂O₃ has a value of $-1794.2 \text{ kJ}\cdot\text{mol}^{-1}$ (Gordienko et al., 1979). The required heat for the formation of LaNiO₃ has a value of $-1236.0 \text{ kJ}\cdot\text{mol}^{-1}$ (Weast et al., 1964), whereas the formation of NiO requires a heat of $-237.7 \text{ kJ}\cdot\text{mol}^{-1}$ (Bannikov et al., 2006). In the analysis of these processes is currently under study the presence of reaction intermediates reported in this system as LaOOH and La(OH)₃, since the reaction:



is reversible in the presence of humid atmosphere (Neuman and Walter, 2006).

After analyzing the data obtained by XRD, SEM and DSC, the following thermal decomposition reaction is proposed:



The mechanism of decomposition could be described by the following steps:



According to the literature, the reaction enthalpy of (4) has a value of $\Delta H = -99.2 \text{ kJ}\cdot\text{mol}^{-1}$ (Weast et al., 1964).

4. Conclusions and summary

The thermal stability of LaNi₅ air was analyzed. It was found that is stable up to $(140 \pm 1) \text{ }^\circ\text{C}$. This result is important because this intermetallic is used in hydrogen thermal compression schemes, where operating temperatures are between 10 and 90 °C. This temperature value is a limit that separates LaNi₅ applicable to THC from materials applicable to other stage of hydrogen technology: gross purification. At temperatures above 140 °C, the thermal evolution of intermetallic in air has 3 overall exothermic peaks indicative of a irreversible destabilization of the intermetallic with formation of individual and mixed oxides, suggesting a complex process in parallel and in series. The reaction products, La₂O₃, LaNiO₃ and NiO were determined by

various techniques. The analysis of the same for gross purification of hydrogen along with the discrimination of the reaction mechanisms is under current development.

Acknowledgements

The authors thank Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET-Project PIP 0109) for partial financial support. Valeria Blanco thanks CNEA and ANPCyT for Doctoral Fellowship (PRH-PDFT 200-4).

References

- Bannikov, D.O., Safronov A.P., Cherepanov, V.A., 2006, Thermochemical characteristics of $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ oxides, *Thermochimica acta* 451, p. 22..
- Blanco, V. and Esquivel, M.R., 2012, Mechanochemical synthesis of $\text{La}_{0.67}\text{Ce}_{0.52}\text{Nd}_{0.08}\text{Pr}_{0.04}\text{Ni}_{5-x}\text{Fe}_x$ intermetallic compound, *Journal of Advanced Powder Technology*, In Press.
- Christopher, J., Sridhar Kumar, M.P., Swamy C.S., 1990, Thermal studies on high temperature oxidation behaviour of Nickel containing AB_5 type intermetallics, *Thermochimica Acta* 161, p. 207.
- Cuevas, F., Joubert, J.M., Laroche, M., Percheron-Guégan, A., 2001, *Applied Physics A* 72, p.225.
- Deng, X., Sun, J., Yu, S., Xi, J., Zhu, W., Qiu, X., 2008, Steam reforming of ethanol for hydrogen production over $\text{NiO}/\text{ZnO}/\text{ZrO}_2$ catalysts, *International Journal of Hydrogen Energy* 33, p.1008.
- Esquivel, M.R., Zelaya, E., 2011, Synthesis and characterisation of lanthanide-based dioxide, *Advances in Applied Ceramics* 110, p. 219.
- Gallego, J., Sierra, G., Mondragon, F., Barrault, J., Batiot-Dupeyrat, C., 2011, Synthesis of MWCNTs and hydrogen from ethanol catalytic decomposition over a $\text{Ni}/\text{La}_2\text{O}_3$ catalyst produced by the reduction of LaNiO_3 , *Applied Catalysis A: General* 397, p. 73.
- Gordienko S.P., Fenochka, B.V., Viksman, G.S., 1979, Thermodynamics of lanthanum compounds, *Handbook*, p. 191
- H. E. Kissinger, 1957, *Analytical Chemistry* 29, p. 1702.
- Li, J., Liu J., Liao S., Yan R., 2010, Hydrogen-rich gas production by air-steam gasification of rice husk using supported nano- $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ catalyst, *International Journal of Hydrogen Energy* 35, p. 7399.
- Neumann, A., Walter, D., 2006, The thermal transformation from lanthanum hydroxide to lanthanum hydroxide oxide, *Thermochimica acta* 445, p. 200.
- Pechini, R., 1967, US patent No 3330697.
- Srivastava S. and Upadhyaya R.K., 2011, Investigations of AB_5 -type hydrogen storage materials with enhanced hydrogen storage capacity, *International Journal of Hydrogen Energy* 36, p. 7114.
- Talagañis, B.A., Esquivel M.R., Meyer, G., 2009, A two-stage hydrogen compressor based on (La, Ce, Nd, Pr) Ni_5 intermetallics obtained by low energy mechanical alloying-Low temperature annealing treatment, *International Journal of Hydrogen Energy* 34, p.2062.
- Talagañis, B.A., Esquivel, M.R., Meyer, G., 2011, Improvement of as-milled properties of mechanically alloyed LaNi_5 and application to hydrogen thermal compression, *International Journal of Hydrogen Energy* 36, p. 11961.
- Watanabe, S. and Kleppa, O.J., 1983, A thermochemical study of liquid and solid alloys $(1-x)\text{La}+x\text{Ni}$ at 1376 K, *The journal of Chemical Thermodynamics* 14, p. 633.
- Weast, R.C., Selby, S.M., Hodgman, C.D., 1964, A ready-Reference Book of Chemical and Physical Data, *Handbook of Chemistry and Physics*, 45th edi, The chemical Rubbe Co., Cleveland Ohio.