Two-fold materials for hydrogen energy applications: synthesis and characterization

M. R. Esquivela, E. Zelaya, J. J. Andrade-Gamboa and S. Obregón

Abstract

In this work, two-fold materials are synthesized and characterized. The materials are designed for applications in both hydrogen gross purification and hydrogen compression. The synthesis unifies steps of the different unitary process to lower costs. (La,Ce,Nd,Pr)Ni₅ intermetallics are obtained by mechanical alloying. The structural and hydrogen sorption properties are improved by treatment in Ar. The material is stable from room temperature up to 600 °C. This material is applied to a one-stage hydrogen compression scheme. The same material is treated under air. It decomposes at 120 °C. As a result, an intimate mixture of oxides is obtained. This product is designed to be applied to hydrogen gross purification. Applications of the materials for the hydrogen technology are discussed along to the structural properties.

© 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.

Hydrogen, Hydrogen Compression, Hydrogen Purification, Two-fold materials

1. Introduction

The transition from hydrogen economy to hydrogen civilization demands significant changes (Goltzov and Veziroglu, 2001; Goltzov, 2002). These changes include the search of new materials to be applied in the
hydrogen technology. These applications are intended to substitute the ones based on fossil-fuels by following a global strategy that allows a complete replacement of the fossil-fuel-based technology by the hydrogen-based one. This announcement suggests that the development of materials applied to the hydrogen-based technology not only involves the research itself but also includes an integral treatment. This treatment should be applied to all stages from synthesis to final deposition of the residues. This strategy should be beneficial for the environment.

Briefly, the stages of the hydrogen technology include the following unitary operations: production, gross purification, purification, transportation, compression, storage, supply to services and final deposition of the residues, some of them identified by Sandrock, 1999. In this work, it is proposed a methodology of synthesis of two-fold materials applied to two hydrogen stages: gross purification (Sandrock, 1999; Esquivel and Zelaya, 2011) and thermal compression (Sandrock, 1999; Cerón-Hurtado and Esquivel, 2010).

The synthesis involves two steps. In the first one, the material is synthesized by mechanical alloying (MA). After this step is achieved, there is a thermal treatment (TT) involving two options. The first option is annealing the material at low temperature (T = 600 °C) in Ar. It is applied to thermal hydrogen compression (THC). The second option is decomposing the material in air at low temperatures (T < 600 °C). This one is involved in the design of materials applied to gross purification of hydrogen.

This work was motivated by the possibility of developing a cheaper methodology that includes the synthesis and further improvement of two-fold materials applied to two stages of the hydrogen technology.

2. Materials and Experimental Procedures

An intermetallic of the AB5-type of composition La_{0.62}Ce_{0.27}Nd_{0.08}Pr_{0.03}Ni_{4.70}Al_{0.30} was obtained by low energy mechanical alloying from a mixture of La_{0.25}Ce_{0.52}Nd_{0.17}Pr_{0.06}Ni_{5} and LaNi_{4.60}Al_{0.40}. A Uniball-mill II from Australian Instruments was used. A sample mass/balls ratio of 17.3 was selected. The mixture was milled 100 h by using the same procedure reported elsewhere (Esquivel and Rodriguez, 2009). Handling of reactants and products was done in glove box (Mbraum Instruments) under controlled atmosphere (Ar, ppm O_{2} < 0.01 and ppm H_{2}O < 0.01). A portion of the sample was annealed under Ar at 600 °C for 24 h. The other portion of the sample was heated in air at 600 °C for 24 h. The hydrogen sorption properties were measured in a device designed ad-hoc in our laboratory. The thermal stability of the intermetallic was analyzed by differential scanning calorimetry (DSC, TA Instruments DSC 2970 calorimeter) between room temperature and 570 °C. Nanostructure was studied by Transmission Electron Microscopy (TEM). Characterization was carried out using a FEI Tecnai G2 microscope operating at 200 keV. The particles size distribution and morphology were analyzed by scanning electron microscopy (SEM, FEI SEM 515). The composition was analyzed by energy dispersive spectroscopy (EDS, EdaX Genesis-FEI SEM 515). Structure was studied by X-Ray Diffraction. Measurements were done in PW diffractometer (PW1701-Philips Instruments) using a graphite monochromator with CuK\alpha radiation. Diffractograms were refined by the Rietveld method using the DBWS program (Young et.al, 1995).

3. Results and Discussion

3.1. Synthesis of the AB5 compound by MA and improvement for use in THC.

The reduced diffractogram of the as milled sample is shown in Figure 1.a. The diffractogram is shown reduced to appreciate fully the main features of the structures present in the sample. The composition of the AB_{5} is La_{0.62}Ce_{0.27}Nd_{0.08}Pr_{0.06}Ni_{4.70}Al_{0.30} as obtained by EDS. The main peaks corresponding to the AB_{5}
structure are labeled. The peak of Ni present in the range is indicated with a full black circle. As observed, the profile shows wide peaks and both AB$_5$ and Ni. This feature is clearly observed in the 40-50 2θ range were the peaks of index 111 of both structures are superimposed. The sample was milled 100 h. Based on previous results, this milling time is long enough to reach final stage (Lu and Lai, 1998). This means that further milling does not increase the amount of AB$_5$. Only a further refinement of the sample is reached (Lu and Lai, 1988; Cerón-Hurtado and Esquivel, 2010). Further milling may even be a drawback because recent investigations indicate that mechanical milling during long periods might induce chemical destabilization of the main AB$_5$ structure leading to the formation of minor lanthanide-nickel based intermetallics (Blanco and Esquivel, 2010). Although low energy mechanical alloying is advantageous because the material is obtained at temperatures lower than 150 °C (Cerón-Hurtado and Esquivel, 2010), the material needs to be annealed at low-intermediate temperatures (T = 600 °C) in order to be used in thermal compression of hydrogen (Esquivel and Rodriguez, 2009, Cerón-Hurtado and Esquivel, 2009).

The sample milled and annealed is shown in Figure 1.b. Annealing conditions under Ar were T = 600 °C and t = 24 h. If figures 1.a and 1.b are compared, it is clearly deduced that the peaks in figure 1.b are narrower. The signal to noise ratio is increased and a general increment of the peaks resolution is observed. As an example, these features are observed in the 2θ range between 40 and 46 °. Only two peaks are resolved in figure 1.a while four peaks are seen in figure 1.b. The improvement is related to an increment on the crystallite size due to grain growth. No recrystallization processes are observed during annealing of samples obtained by low energy mechanical alloying because not sufficient energy is impinged to the particles to produce amorphous phases (Cerón-Hurtado and Esquivel, 2010; Esquivel and Rodriguez, 2009). The improvement is also related to a reduction of strain of the particles. As an example, these microstructural parameters were calculated for the hkl direction 110 for both samples. The values are summarized in Table 1.

The annealed sample was refined using the Rietveld method. The fitting data is presented in hollow circles. The difference between observed and calculated intensities are shown in the same figure. $R_{wp}$ value stands for the goodness of the fit. A summary of results obtained using this method is presented in Table 1. As observed,
the main phase is the AB₅ and the minor one is Ni. Up to the detection limit of the technique, no other phases are observed.

Table 1. Structure and microstructure

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>Cell parameters</th>
<th>Mass %</th>
<th>Rwp %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealed (Fig 1.b)</td>
<td>AB₅ (P6/mmm)</td>
<td>a (Å) 4.978(4)  c (Å) 3.997(4)  α, γ 90, 120</td>
<td>88 ± 2</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>Ni (Fm3m)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fig 5.a</td>
<td>ABO₃ (R-3c)</td>
<td>a (Å) 5.46(0)  c (Å) 6.57(0)  α, γ 90, 120</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>AO₂ (Fm3m)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NiO (Fm3m)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Microstructure (*) the annealed sample is used as reference

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>hkl</th>
<th>Crystallite size (Å) ± 10</th>
<th>Strain (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As milled (Fig 1a)</td>
<td>AB₅</td>
<td>110</td>
<td>300</td>
<td>3</td>
</tr>
<tr>
<td>Annealed (Fig 1b)</td>
<td>AB₅</td>
<td>110</td>
<td>550</td>
<td>1</td>
</tr>
</tbody>
</table>

The SEM images of as milled and annealed samples are presented in Figures 2.a and 2.b, respectively. The surface of as milled sample presents traces of fracture and cold welding. These effects are indicated with hollow white circles and hollow white squares, respectively. These morphologies are typical of powders obtained by mechanical alloying (Cerón-Hurtado and Esquivel, 2010). If the annealed sample is compared to the as milled one almost no differences are observed. Particle morphology and size distribution remains similar. It means that grain growth occurs as observed in Figure 1 but the lower temperatures involved during annealing produce no particle size increment as observed in Figure 2. This feature is an advantage of the low energy mechanical alloying – low temperature annealing synthesis-improving method because the final intermetallic is obtained as a powder with a microstructure appropriate to be used in the diverse sorption schemes of THC (Esquivel and Rodriguez, 2009, Cerón-Hurtado and Esquivel, 2012, Kim et.al, 2008).

Fig. 2. (a) As milled sample; (b) As milled + annealed in Ar; (c) As milled + annealed in air

3.2. Application to a THC scheme

The application of the material to a THC scheme is presented in Figure 3.a. The figure schematizes the application of the material to a linking stage between two different thermal compressors (Esquivel and Rodriguez, 2009). According to the scheme, the THC cycle starts in point A in the linking stage pressure compressor. As hydrogen is injected into the system, the hydride is formed reaching point B at 25 ° C. At this point, all the hydride is formed. The standard pressure is the middle point between A and B. This value is
1550 kPa. At this moment, the supply of H₂ to the system is ceased. After that, temperature is increased to 90 °C. The system evolves to point C. At this moment, the H₂ is removed from the system. The desorption isotherm is followed and the system reaches point D. Now, the system is isolated and cooled down to 25 °C reaching point A. The THC cycle is now complete. As a global result, a change in the ratio of pressure or compression is obtained. A new cycle can be restarted by supplying fresh H₂. In this case, the ratio of compression (R_c) is 1.45. This scheme may be used as a one-stage compressor or joins two different compressors (Esquivel and Rodriguez, 2009; Cerón-Hurtado and Esquivel, 2012, Dehouche et. al., 2005).

3.3. Genesis of a two-fold material. The synthesis of a composite of metal-oxides by thermal decomposition and further characterization for gross purification of hydrogen.

The lack of moving parts and mechanical isolation are the major advantages of thermal compressors of hydrogen over traditional gas compressors. Despite that, the first ones operate with new and fresh supply every time a new compression cycle is started. This feature implies that there are at least two valves needed to allow the supply and removal of the hydrogen. By hazard, the opening of these valves might introduce air into the system. Therefore, it is important to analyze the thermal stability of the intermetallic in air. The calorimetric curve is shown in Figure 4. No appreciable thermal event is observed up to 120 ± 1 °C, the onset of the thermal decomposition. At higher temperatures, the curve departs from the baseline. This result is relevant because THC schemes normally operate between 10 and 90 °C because of the use of water as cooling/heating fluid (Au and Wang, 1993; Cerón-Hurtado and Esquivel, 2012). This assessment indicates that there is a security margin of 30 °C over the maximum temperature of operation.

As temperature rises, three clear exothermal events occur, reaching maximum temperatures of 281 ± 1 °C, 373 ± 1 °C and 458 ± 1 °C, respectively. The thermal decompositon of AB₅ intermetallics was previously reported in our group for other compositions: La₀.₂₅Ce₀.₅₂Nd₀.₁₇Pr₀.₀₆Ni₄.₇₀Sn₀.₃₀ (Cerón-Hurtado and Esquivel, 2010), La₀.₂₅Ce₀.₅₂Nd₀.₁₇Pr₀.₀₆Ni₅, and La₀.₂₅Ce₀.₅₂Nd₀.₁₇Pr₀.₀₆Ni₅.₅Alₓ (Obregón et al, 2012). In these references, no formation of mixed oxides involving the Lanthanide +3/+4 and Al +3 or Sn +2/+4 cations was observed. The main mechanism of thermal decomposition was reported in these works. The thermal decomposition presents marked similarites for these intermetallics. Nevertheless, no strict similarities are observed with the thermal decomposition of the AB₅ analyzed in this work. It is presented in Figure 4. The DSC curve of the
La$_{0.25}$Ce$_{0.52}$Nd$_{0.17}$Pr$_{0.06}$Ni$_{4.70}$Sn$_{0.30}$ (Cerón-Hurtado and Esquivel, 2010) is displayed in Figure 4. The thermal evolution is not exactly the same to that of La$_{0.62}$Ce$_{0.27}$Nd$_{0.08}$Pr$_{0.06}$Ni$_{4.70}$Al$_{0.30}$. Although both curves present various thermal events, the one of Cerón-Hurtado and Esquivel presents a wide large peak involving more than one exothermal event. This curve is different from the one of the present work which presents three well observed thermal events. The diffractograms of the reaction products are presented in Figure 5.

The sample was heated in air at 600 °C for 24 h (Fig. 5.a). The products are compared to the following reference patterns: La$_{0.25}$Ce$_{0.52}$Nd$_{0.17}$Pr$_{0.06}$O$_2$ (Esquivel and Zelaya, 2011) (Fig. 5.b), LaNiO$_3$ (PDF 033-0711) (Fig. 5.c) and NiO (PDF 078-0643) (Fig. 5.d). From a straightforward comparison, it is deduced that the product is composed of NiO and two oxides isostructural to La$_{0.25}$Ce$_{0.52}$Nd$_{0.17}$Pr$_{0.06}$O$_2$ and LaNiO$_3$. In this work, it is supposed that lanthanide cations distribute themselves randomly among the lanthanide dioxides. The cell parameters of the three oxides are summarized in Table 1. The thermal decomposition of an AB$_5$ leading to the formation of mixed oxides isostructural to LaNiO$_3$ was reported in the LaNi$_{4.70}$Al$_{0.30}$-O$_2$ system by Cerón-Hurtado and Esquivel, 2009) while mixed oxides were not observed in AB$_5$-O$_2$ systems with La at % < 50 %. This result suggests that the formation of mixed oxides of the ABO$_3$-type is stabilized at La at % > 50 % in the AB$_5$. The opposite occurs for AB$_2$ with La at % < 50 % were the formation of mixtures of oxides of the AO$_2$-BO type is observed (Obregón et al, 2012, Cerón-Hurtado and Esquivel, 2010).

A SEM image of the sample as-milled and heated in air at 600 °C for 24 h is shown in Figure 2.c. As observed, the mixture of oxides presents a size distribution value lower than that of the as milled sample. It is due to the thermal fracture of the intermetallic. This feature is advantageous for use in gross purification of hydrogen because the material acquires larger surface area which facilitates the contact with the inlet gas and further trapping of the contaminants. In addition, no further treatments are needed to the straightforward use of the material. This last assessment is supported by both the micro and nanostructure. A SEM image of the surface of an AO$_2$ particle is presented in the upper right inset of Figure 5. Surface pores are observed. These pores should be an aid to the catalysis and retention of the contaminant in the inlet stream. These oxides also present surface nano pores as reported previously for La$_{0.25}$Ce$_{0.52}$Nd$_{0.17}$Pr$_{0.06}$O$_2$ (Esquivel and Zelaya, 2011).
A TEM BF image of the mixed oxide is shown in Figure 6.a. The BF shows a nanostructure with a lentil-shaped form. The particle agglomerate has irregular borders. The morphology is defined by the fracture of the former AB$_5$ intermetallic due to the TT. The DF image is presented in Figure 6.b. The crystalline domains are clearly observed. Two size distributions are also detected. One close to 10 nm and the other of ~1 nm. These small crystallite sizes explain the shape of the profile observed in Figure 5.a where wide peaks with low signal/background values are observed for this oxide. It is an advantage for gross purification because nanocrystalline structures offer a larger area to interact and capture contaminants in the inlet gas stream.
4. Summary and conclusions

The findings reported in this work show an innovative strategy that integrates unitary processes for synthesis and further improvement of two-fold materials applied in two stages of the hydrogen technology.

Two unitary operations were integrated: mechanical alloying and thermal treatment. Mechanical alloying was used for synthesis of the La$_{0.62}$Ce$_{0.27}$Nd$_{0.08}$Pr$_{0.03}$Ni$_{4.70}$Al$_{0.30}$ intermetallic. Thermal treatment was used to improve the material structure and microstructure. The thermal treatment was used at low temperatures (T=600 °C). The atmosphere of thermal treatment was selected to fit the material to the application. Air was used for samples applied to THC. In this case, the material was used in a scheme of linking stage or pressure bridge between two hydrogen thermal compressors. Air was used to fit samples for hydrogen gross purification. In this case, the maximum temperature of stability (T < 120 °C) was found. The destabilization of the former intermetallic lead to the formation of a mixture of simple (AO$_2$-BO) and mixed (ABO$_3$) oxides. The nano, micro and structure were characterized. It was found that the oxides present crystallite sizes of the order of 1 to 10 nm and surfaces with micro and nano pores (Esquivel and Zelaya, 2011). The main objectives of diminishing the amount of unitary processes by integrating synthesis and improvement and lowering the cost of processing were reached in this work.

Acknowledgements

The authors wish to thank Consejo Nacional de Investigaciones Científicas y Técnicas of Argentina (CONICET-Project PIP 0109) for partial financial support. Eugenia Zelaya thanks Project FWO-MINCyT / FW/09/03. Sergio Obregón thanks ANPCYT AND CNEA of Argentina for the doctoral grant (PAE-PRH-PDFT-200-4).

References

Blanco, V, Esquivel, M.R., 2010, Chemical unstability of LaNi$_5$ induced by middle energy mechanical milling XXXVII Annual meeting of the Argentinian Association of Nuclear Technology, Buenos Aires, Argentina, paper #036


Cerón-Hurtado, N.M., Esquivel, M.R., 2009, Design of a one-stage of hydrogen compression system based on AB$_5$ intermetallics, XXXVII Annual meeting of the Argentina Association of Nuclear Technology, Buenos Aires, Argentina, paper # 097


