Original Article

Synthesis and hydrogen storage of La\textsubscript{23}Nd\textsubscript{7.8}Ti\textsubscript{1.1}Ni\textsubscript{33.9}Co\textsubscript{32.9}Al\textsubscript{0.65} alloys

Priyanka Meena\textsuperscript{a,b,c,}, Mukesh Jangir\textsuperscript{a}, Ramvir Singh\textsuperscript{c}, Vishnu Kumar Sharma\textsuperscript{b}, Indra Prabh Jain\textsuperscript{a}

\textsuperscript{a} Centre for Non-Conventional Energy Resources, University of Rajasthan, Jaipur, India
\textsuperscript{b} Metallurgical and Material Engineering Department, MNIT, Jaipur, India
\textsuperscript{c} Physics Department, University of Rajasthan, Jaipur, India

\textbf{A R T I C L E  I N F O}

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SEM
EDS
TGA
Hydrogenation/dehydrogenation

\textbf{A B S T R A C T}

The present work investigates structural and hydrogen storage properties of first time synthesized La\textsubscript{23}Nd\textsubscript{7.8}Ti\textsubscript{1.1}Ni\textsubscript{33.9}Co\textsubscript{32.9}Al\textsubscript{0.65} alloy by arc melting process and ball milled to get it in nano structure form. XRD analysis of as-prepared alloy showed single phased hexagonal LaNi\textsubscript{5}-type structure with 52 nm average particle size, which reduces to about 31 nm after hydrogenations. Morphological studies by SEM were undertaken to investigate the effect of hydrogenation of nanostructured alloy. EDX analysis confirmed elemental composition of the as-prepared alloy. Activation energy for hydrogen desorption was studied using TGA analysis and found to be $-76.86$ kJ/mol. Hydrogenation/dehydrogenation reactions and absorption kinetics were measured at temperature $100^\circ$ C. The equilibrium plateau pressure was determined to be $2$ bar at $100^\circ$ C giving hydrogen storage capacity of about $2.1$ wt%.

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1. \textbf{Introduction}

Metal hydride alloys have become very important for hydrogen storage and applications. Due to ease in storage and transportation, metal hydrides have become useful for a variety of technological applications. Hydrogen as a clean fuel is an excellent energy carrier to be used in automobiles, space, domestic and many other applications [1,2]. Hydrogen produced from renewable energy sources is a potentially attractive, pollution-free alternative to fossil fuels. The rapid development of advanced materials for hydrogen production, storage, and utilization has opened up a new avenue for the conversion and utilization of hydrogen as energy [3]. The problems of energy shortage and environmental contamination encouraged scientists using sustainable and clean energy sources. Although hydrogen is an attractive source of alternative fuel, but it is only an energy carrier unlike oil, gas or natural gas [4,5]. Amongst the conventional hydrogen storage methods, metal hydrides are promising materials due to high hydrogen content and many applications [6]. Nickel-based rare earth AB\textsubscript{5} (LaNi\textsubscript{5}) type alloys have attracted considerable interest in the last decades as hydrogen storage materials due to their advantages such as large reversible hydrogen storage capacity, proper hydriding pressure and fast absorption/desorption kinetics [7–10].

\* Corresponding author.
E-mail: priyankameena34@gmail.com (P. Meena).

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In rare earth metal hydrides family LaNi₅-based alloys are important due to their better hydrogen storage capacity, fast kinetics, reversible sorption properties and low equilibrium plateau pressure of 1–3 MPa at room temperature [11]. However, studies on such alloys are rare in literature. The effect of hydrogen absorption/desorption of LaNi₅₋₆AlₓMnₓ alloy was reported by Li et al. [12] who found that the shapes of PCT (Pressure–Composition–Temperature) isotherms even after 300, 2000 and 3500 cycles were similar to that of initial activation. Gao et al. [13] investigated hydrogen storage properties of La–R–Mg–Ni-based alloy electrodes which exhibited good activation characteristics with excellent high rate discharge capability. The term Mischmetal ‘Mm’ is used for research papers of other authors cited in this paper. It consists mainly of Lanthanum, Cerium, Praseodymium, Neodymium and Samarium in different compositions by different authors. Therefore, the term “Mm” is defined for Mischmetal, which will be used in many references in text of this paper.

Electrochemical properties of the AB₅-type LaMmNi₅₋₆AlₓMnₓ alloy modified with carbon used as anodic materials in boro hydride fuel cells was studied by Lota et al. [14] Hydrogenation of MmNi₅₋₆AlₓMnₓ alloy was undertaken by Zarei et al. [15] who found its hydrogen content of about 2 wt% at 20 °C. Frommen et al. [16] in 2015 showed that lanthanum-containing composite released about 2.1 wt% hydrogen between 300 and 350 °C.-phase structure and electrochemical properties of La₀.₆Gd₀.₄Mg₀.₂Ni₁₅₋₁₋ₓCo₀.₂₅Al₀.₅Mnₓ (x = 0–0.3) alloys prepared by induction melting were studied by Li et al. [17]. Volodin et al. [18] estimated the hydrogen diffusion coefficient (D₁₁) in Laₓ₁₋ₓNd₀.₅MgNi₉ alloy electrode and found that the D₁₁ changes with hydrogen content having a maximum of ca. 2×10⁻¹¹ cm²/s at ca. 85% of discharge. Srivastava et al. [19] studied MmNi₅₋₆AlₓMnₓ alloys for hydrogen storage by ball milling with transition metal Co/Ni/Mn/Fe in which hydrogen content was found to be 1.68, 1.64, 1.56, 1.52 wt%, respectively. It has been reported by Lv et al. [20] that La₀.₇₇Mg₀.₂₃Nd₀.₅ alloys reversibly absorb and desorb hydrogen at 25 °C having 1 wt% of hydrogen at 0.074 MPa plateau pressure. Cui et al. [21] determined the HRD (high-rate dischargeability) performance of MmNi₅₋₆AlₓMnₓCo₀.₂₅Ni₀.₅Al₀.₃ alloy for hydrogen storage by adding graphene nanoplatelets (GNPs) resulting in the capacity retention rate of the alloy electrode to be 53.0% after ball milling and 68.3% after further addition of GNPs, which is 3.2 times that of original alloy electrode (21.5%). In the present work structural, morphological, thermal and hydrogen storage properties of La₂Nd₄₋₆Th₁₋₁Ni₃₋₃₋₆Co₀₂₋₆₋₆Alₓ₋₆₋₆ alloy are investigated using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), EDS (Energy Dispersive X-ray Analysis) and Thermo Gravimetric Analysis (TGA) techniques.

2. Experimental

2.1. Alloy preparation

La₂Nd₄₋₆Th₁₋₁Ni₃₋₃₋₆Co₀₂₋₆₋₆Alₓ₋₆₋₆ alloy was prepared using Arc-melting method in argon atmosphere by re-melting 3 times the stoichiometric amounts of 99.5% purity of elements to get homogeneous composition.

Small ingots of constituent metals in the form of a pile were kept in carbide crucible placed on a water-cooled copper hearth. The temperature was maintained at 1550–1600 °C for alloy melting. Before melting the chamber was pumped to get vacuum of 10⁻⁵ mbar and then high purity argon gas at 0.4 bar pressure was flushed three times to get rid of oxygen and other reactive gases. The oxygen content in the chamber was further reduced by applying arc on titanium getter and increasing argon pressure to 0.53 bar. After keeping the getter melted for a couple of minutes the arc was directed towards the pile of elements and finally turned off once they had melted. Samples were cool down to room temperature after which removed from crucible and were weighed to ensure that there were no material losses.

2.2. Annealing

Annealing of the alloy was done in sealed evacuated quartz tube which were cleaned by aqua regia for two hours, rinsed with deionized water, dried in a furnace and sealed in one end. The crushed samples were pressed into pellets and placed in the prepared fused silica tubes, which are sealed to form an ampoule. The ampoule was heated to 900 °C for one week, after which it was crushed to get alloy for study.

2.3. Ball milling

The alloy was mechanically milled for 10 h at 300 rpm under 0.1 MPa Ar pressure using a FRITSCH P7 ball milling apparatus with a 15 min work and 5 min rest pattern. The ball to powder ratio was about 10:1 to avoid the oxidation and hydrogenation all the samples before and after milling were handled in a high purity Ar (99.99%) filled glove box with oxygen and a moisture contents maintained at <0.1 ppm.

2.4. Activation of Alloy for hydrogen absorption

In the present study, 2 g of alloy was kept in sample holder made out of 1” diameter Cu tube having thermocouple fixed on it and the heater was placed around the thermocouple. In the first cycle the alloy was evacuated to 10⁻⁵ mbar vacuum, flushed to 99.95% pure hydrogen at 1.01 bar pressure, again evacuated to 10⁻⁵ mbar vacuum and heated to 100 °C for 2 h. At this point cool the sample, introduced hydrogen and heat it to 100 °C for 2 h in hydrogen environment. Again evacuating alloy to 10⁻³ mbar pressure and cool it to room temperature. Considerable time was allowed to heat the sample till an equilibrium temperature is reached.

In the second cycle after cooling the alloy to room temperature, hydrogen at 2 bar again introduced in the cell where the alloy start absorbing hydrogen resulting in decrease in pressure in the cell. This process was repeated for five cycles till the activation process complete and the pressure in the reactor comes to a constant value showing the formation of the hydride material with full saturation [22].

2.5. Alloy characterization

Structural characterization was done by X-Ray diffractometer (Panalytical X Pert Pro) using CuKα, emission (operated at 45 kV,
Results and discussion

3.1. Structural characterization by XRD

XRD studies of La$_{23}$Nd$_{7.5}$Ti$_{11.1}$Ni$_{32.9}$Co$_{22.9}$Al$_{0.65}$ alloy shows homogeneous single phase and all peaks are assigned to hexagonal LaNi$_5$-type structure (with space group: P6/mmm; JCPDS/PDF No.: 00-050-0777) as shown in Fig. 1.

Table 1 presents the results of XRD analysis using X’Pert High Score Plus software. This table lists the values of lattice parameters, unit cell volumes, overall broadening at half maximum (FWHM) of the main peak (111), average crystallite size ($D_{avg}$) and d-spacing of the samples. It is seen that lattice constants a for alloy decreased slightly while that of c slightly increased as shown in Table 1 and the cell volume of as-prepared sample is slightly smaller than that of activated sample. The increase in unit cell volume on activation is due to hydrogen absorption which decreases density of alloy resulting in decrease in lattice constant. Hydrogen absorption increases volume of alloy resulting in decrease in density as shown in Fig. 2, resulting in increase in lattice constants. While desorption of hydrogen the material takes original shape, showing the increase in density that is decrease in lattice constant.

FWHM increases in activated sample, causing peaks to be slightly broadened after activation, which may be due to lattice strain generated during cycling and reduction in crystallite size (Table 1) [23,24] and peak broadening. The average crystallite size was calculated using Debye Scherrer formula,$D = \frac{\lambda}{\beta \cos \theta}$ where $\lambda$ is the X-ray wavelength, $\beta$ is the line broadening at half the maximum intensity in radian, $\theta$ is the Bragg angle. Using Debye Scherrer formula the values of average crystallite sizes for the as-prepared and hydrogen activated sample La$_{23}$Nd$_{7.5}$Ti$_{11.1}$Ni$_{32.9}$Co$_{22.9}$Al$_{0.65}$ are estimated to be about 52 nm and 31 nm respectively (Table 1). The average crystallite size was decreased during activation which indicates that disintegration of the alloy takes place during the first few cycles and thereafter only slightly because the first cycle play an important role in pulverization of such type of powder samples. This means that the hydrogen absorption/desorption process leads to alloy pulverization and the same has been confirmed by SEM results (Fig. 3).

3.2. Morphology of alloy by SEM

SEM images of as-prepared ingots and five cycles activated sample were studied to clarify the effect of hydrogen absorption/desorption on the microstructure of the alloy as shown in Fig. 3(a) and (b). Activation significantly decreases the size of particles compared to as-prepared, which means hydrogen absorption/desorption pulverizes the alloy into fine particles, in agreement with XRD results. It is interesting to observe that no crack was observed on the surface of as-prepared, while some cracks were developed after activation.

Pulverization of the alloy is due to small particles formation during hydrogenation and further breaking by more hydrogen absorption is due to the propagations of micro cracks. It can be observed that during activation process, cracking and pulverization take place. It can easily be understood from SEM image that during pulverization hydrogen atom enters into the interstitial of this lattice and internal stress causes unit cell volume expansion [25]. On activation of alloy cleaved surfaces were generated on the brittle fracture, i.e., occurring with a little plastic deformation [26].

The elemental composition of the alloy has been studied by EDX technique at different sites of the ingots was found almost the same at all the sites as shown in Fig. 4. The elemental percentage of the alloy is shown in Table 2.

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**Table 1 – Structural parameters, FWHM (111), average crystallite size and d-spacing of the sample.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameters</th>
<th>Volume</th>
<th>c/a</th>
<th>FWHM</th>
<th>$D_{avg}$</th>
<th>d-Spacing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a [Å] c [Å]</td>
<td>V [Å$^3$]</td>
<td></td>
<td>(111) [Å]</td>
<td>(nm)</td>
<td>[Å]</td>
</tr>
<tr>
<td>As-prepared sample</td>
<td>5.017 3.98</td>
<td>86.78 0.794</td>
<td>0.1181</td>
<td>52</td>
<td>2.13</td>
<td></td>
</tr>
<tr>
<td>Hydrogen activated</td>
<td>5.016 3.99</td>
<td>86.82 0.795</td>
<td>0.1741</td>
<td>31</td>
<td>2.37</td>
<td></td>
</tr>
</tbody>
</table>
3.3. Kinetic study of the dehydrogenation process

Desorption behaviour of La$_{23}$Nd$_{7.8}$Ti$_{1.1}$Ni$_{33.9}$Co$_{32.9}$Al$_{0.65}$ alloy is studied using TGA technique under 0.1 MPa Ar atmosphere. TG/MS curves for dehydrogenation of the alloy samples with the scanning rate of 5, 10 and 15 °C/min are shown in Fig. 5(a) and (b). TG studies were performed at three different scanning rates (5, 10, and 15 °C/min) as shown in the inset of Fig. 5(a), from which it is found that maximum hydrogen storage capacity is 2.1 wt%. The onset dehydrogenation temperature of the alloy at different heating rate of 5, 10, and 15 °C/min are 190.11, 220.91 and 210.61 °C is shown in Fig. 5(b).

Fig. 5(c) shows Kissinger plot of the hydrogen desorption reaction for samples giving apparent activation energy for the hydrogen desorption. The activation energies were calculated by plotting a curve between ln $k$ and $1/RT_p$ using the
The circles with solid line indicate the areas of (1) and (2).

Table 2 – Results of EDX analysis (in weight) for La$_{23}$Nd$_{7.8}$Ti$_{1.1}$Ni$_{33.9}$Co$_{32.9}$Al$_{0.65}$ alloys.

<table>
<thead>
<tr>
<th>% Weight</th>
<th>La</th>
<th>Nd</th>
<th>Ti</th>
<th>Ni</th>
<th>Co</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>20.21</td>
<td>10.99</td>
<td>1.71</td>
<td>33.29</td>
<td>31.33</td>
<td>0.47</td>
</tr>
<tr>
<td>2</td>
<td>21.85</td>
<td>9.58</td>
<td>1.50</td>
<td>31.69</td>
<td>31.35</td>
<td>0.03</td>
</tr>
<tr>
<td>EDS spot 1</td>
<td>23.56</td>
<td>7.83</td>
<td>1.47</td>
<td>32.60</td>
<td>33.88</td>
<td>0.66</td>
</tr>
<tr>
<td>Present material</td>
<td>23</td>
<td>8.5</td>
<td>1.1</td>
<td>33.9</td>
<td>32.9</td>
<td>0.65</td>
</tr>
</tbody>
</table>

EDX confirms composition of material under study.

In the present work only two rare-earth metals are included to see the effect how it is different from misch metal. It is interesting to compare the misch metal and our materials similar to mischmetal. It is interesting to see that hydrogen storage capacity of the present alloy is 2.1 wt% (shown below in Table 3) which is greater than the recent studies of similar alloys.
Table 3 – Comparison of present work with different alloys.

<table>
<thead>
<tr>
<th>Sample (alloy)</th>
<th>Phase</th>
<th>Hydrogen Capacity</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Ref. No./year</th>
</tr>
</thead>
<tbody>
<tr>
<td>La0.8xNd0.2,5Mg0.2Ni13.5Co0.25Al0.15 (x = 0.0–0.4)</td>
<td>(La,Mg)2Ni7, LaNi5</td>
<td>1 wt%</td>
<td>40 °C</td>
<td>2 MPa</td>
<td>[28]/2009</td>
</tr>
<tr>
<td>Ti16Cr23V17Fe6 (x = 2–8)</td>
<td>BCC (main) CHaves (small)</td>
<td>1.42 wt%</td>
<td>25 °C</td>
<td>0.1–1 MPa</td>
<td>[30]/2010</td>
</tr>
<tr>
<td>LaMg0.23Ni23Mg0.15 (M = Ni, Cu, Cr)</td>
<td>La2Mg2Ni, LaMg3Ni, Mg2Ni</td>
<td>1.63 wt%</td>
<td>25°C</td>
<td>1.5 MPa</td>
<td>[15]/2014</td>
</tr>
<tr>
<td>Mn (Ni, Co, Mn, Al)5</td>
<td>LaNi5</td>
<td>0.85 wt%</td>
<td>26–65 °C</td>
<td>1.5 MPa</td>
<td>[15]/2014</td>
</tr>
<tr>
<td>6LiBH4-RECl3-3LiH</td>
<td>LiLa(BH4)3Cl Er(BH4)3</td>
<td>2 wt%</td>
<td>27–77 °C</td>
<td>0.5 MPa</td>
<td>[16]/2015</td>
</tr>
<tr>
<td>La0.7Ni0.32Ni3.5</td>
<td>(La0.25Ni0.75)</td>
<td>0.7 wt%</td>
<td>25 °C</td>
<td>0.074 MPa</td>
<td>[20]/2016</td>
</tr>
<tr>
<td>La2.3Ni5.7Ti1.4Ni13.5Co32.5Al0.65</td>
<td>LaNi5</td>
<td>2.3 wt%</td>
<td>100 °C</td>
<td>0.2 MPa</td>
<td>Present work</td>
</tr>
</tbody>
</table>

4. Conclusions

Structural and morphological properties of a newly developed La23Nd7.8Ti1.1Ni33.9Co32.5Al0.65 alloy were studied before and after hydrogenation/dehydrogenation cycles. Diffraction peaks after activation was found to be slightly broadened but hexagonal LaNi5-type structure of the alloy was maintained. Average crystallites size for the as-prepared and activated alloy La23Nd7.8Ti1.1Ni33.9Co32.5Al0.65 was estimated to be about 52 nm and 31 nm. SEM micrographs confirmed that activation pulverizes the alloy ingot into fine particles. No cracks were observed on the surface of as-prepared particles while cracks were developed after activation. EDX analysis shows that areas 1 and 2 have nearly similar elemental composition. TGA results show that the activation energy for hydrogen desorption was estimated to be ~76.86 kJ/mol with 2 wt% hydrogen content.

Conflicts of interest

The authors declare no conflicts of interest.

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