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INVESTIGATION ON THE THERMODYNAMIC ANALYSIS, PREPARATION AND CHARACTERIZATION OF $LaNi_5$ – HYDROGEN STORAGE ALLOY BY MAGNESIOTHERMIC REDUCTION DIFFUSION PROCESS

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Abstract

The present investigation focuses on the preparation of $LaNi_5$ intermetallic compound by "Metallothermic reduction diffusion process". Experiments were carried out using oxides and chlorides of La and Ni metal powders as the raw materials with granular Mg powder as the reductant. The thermal reduction process was carried out at 900 ºC for 9 hrs in Ar atmosphere. After the completion of reaction, the contents were purified by treating with dilute acetic acid followed by de-ionized water. Thermodynamic feasibility studies were carried out to determine the probabilistic nature of formation of the desired compound. Thermal analysis was carried out to find the dissociation and decomposition temperature of the reactants. The phase purity and the elemental composition of the alloy were assessed by XRD and EDX analyses. The morphological features of the prepared powders were examined by SEM. From this study, it has been concluded that LaNi5 alloy can be prepared with an appreciable purity by the Metallothermic reduction diffusion process.

Key words: *Materials Processing; Intermetallic compound; Metallothermic reduction; XRD and SEM*

1. Introduction

A demand for more competent power sources has augmented the interest in diverse fields of new technology, such as fuel cells by means of hydrogen or hydrocarbon as fuel [1, 2, 3]. Hydrogen storage alloys (HSAs), the main materials in the negative electrodes of nickel/metal hydride (Ni–MH) secondary batteries, have been widely premeditated for many years because of their principal role in the battery applications [4]. Rare-Earth AB_5 type $LaNi_5$-based and Zr–Ti–V-based laves phase (AB_2) HSAs have been extensively used as negative electrode materials for the commercial production of Ni–MH batteries [5, 6]. Structure dependence of the host metal, hydrogen atoms take up the tetrahedral or octahedral interstices of the metallic sub lattice. AB_5's have a hexagonal crystal structure represents the most commercial family on the market. The AB_2's seem to be more sensitive to gaseous impurities than the AB_5's [7] hence the advantage of $LaNi_5$ intermetallic compound is that they exhibit low hysteresis, are moderate to gaseous impurities and are effortlessly hydrogenated in the initial cycle after manufacture [8]. Conventionally, the metal hydride materials have been prepared by arc melting [9-11] , induction melting [12], mechanical alloying [8, 13-15] electro chemical synthesis [16, 17], solid state reduction method [18].The preparation of Rare Earth metals and alloys production from its ores has not yet full-fledged in India .Therefore the production processes of Rare Earth based functional materials are found to be considered as a insightful area of research. The Reduction-Diffusion (R-D) process involves reduction of cheaper raw materials such as lanthanum oxide (La_2O_3) by calcium and simultaneous diffusion in nickel [19-21] forming the intermetallic compound. The process is based on the relative thermodynamic stability of oxides. From the thermodynamic calculations of reactants, the free energy of formation of CaO at 1200K is 245 Kcal/gfw, which is lower than that of La_2O_3, 205 Kcal/gfw [22], hence we can say that the so-called calciothermic reduction process is possible to reduce lanthanum oxide by calcium metal to prepare single phase $LaNi_5$ [19]. Although many methods have been attempted for the preparation of $LaNi_5$, to our knowledge no one has attempted to prepare this alloy by reduction-diffusion technique using magnesium (Mg) as the reductant. Hence, we have made an attempt to prepare this alloy by reduction- diffusion technique using magnesium as the reductant. The results of the above investigation

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have been presented in this paper.

2. Thermodynamic Analysis

Thermodynamic models have been elaborately studied for La-Ce, La-Nd, La-Nd alloys [23]. Mixing enthalpies of liquid Co-Ce, Co-La alloys has been calculated [24] and the thermodynamic models have been proposed. Thermodynamic properties of Dy-Ni intermetallic compound has been studied [25]. The formation mechanism La of $LaNi_5$ [26], $DyFe_2$ [27], $TbFe_2$ [28] by R-D process has been presented. Based on the above model theories and taking account of the previous work done in R-D process, a thermodynamic feasibility study has been carried out and discussed briefly in the following section. Thermodynamic analysis has been carried out for the preparation of $LaNi_5$ using oxides and chlorides of La and Ni metal powders with granular Mg powder at 900 °C. Raoult's law approximation has been put forth and ΔG^{mix} corresponds to negative value favoring the A-B type bonding rather A-A and B-B type bonding [31]. Unreacted core model [27, 28] and standard thermodynamic properties [29, 30] have been taken into account for carrying out this feasibility analysis.

$$La_2O_3 + 10Ni + 3Mg \rightarrow 2LaNi_5 + 3MgO \quad (1)$$

$$2LaCl_3 + 10\,Ni + 3Mg \rightarrow 2LaNi_5 + 3MgCl_2 \quad (2)$$

Equations 1and 2 exhibit the fundamental reactions describing the preparation of $LaNi_5$ alloy. Gibbs free energy of formation (ΔG) and Equilibrium constant (K) of the above equations explore the possibilities and the nature of the chemical reactions taking place in the process.

$$La + 5\,Ni \rightarrow LaNi_5 \quad (3)$$

$$La_2O_3 + 3Mg \rightarrow 2La + 3MgO \quad (4)$$

$$2LaCl_3 + 3Mg \rightarrow 2La + 3MgCl_2 \quad (5)$$

$$Mg\,(l) \rightarrow Mg\,(g) \quad (6)$$

Equations 1, 2 can be analyzed by splitting into elemental equations 3, 4 and 5. Based on the above equations, Mg has been considered as the reductant to form rare earth alloys, which has been illustrated in the theory of unreacted core model [27, 28]. Specific heat capacity (C_p) values are assumed to follow standard quadratic equation [29, 30] and the ΔG values can be determined using elemental equations [31]. Table.1 represents ΔG° for equations 1 and 2, signifying the non spontaneity [31] of the reaction. Hence, the reaction has to be carried out at 900°C for a longer time (say 9h.) [32-34]. This may be performed by allowing the precursors to reduce and diffuse among themselves simultaneously to form the respective alloy. The characteristic features of the process appear to be dawdling in reality. Hence the idealistic approximation is reasonable form of approach to understand the thermodynamic behavior of the process [26-28].

Table.1. *Free energy of reaction and Equilibrium constant values for equations 1 and 2*

Equation No.	Free energy of reaction DG° (J/mol-K)
1	-4,220,582
2	-3,049,204

3. Experimental

3.1 Preparation of ($LaNi_5$) intermetallic compound by Reduction- Diffusion (R-D) Technique

For the preparation of $LaNi_5$ alloy, La_2O_3, $LaCl_3.6H_20$, Ni (99% purity, Merck, India) were used as the raw materials. Fine granular magnesium (Mg) powder was used as the reductant. The above reactants were mixed using a pestle and mortar. The mixed salts were placed in a high density alumina crucible. The layers of reactants were sandwiched with granular magnesium powder. The crucible was then placed in an inconel reactor which had provisions for the purging of argon gas and for the release of exhaust gases. The whole assembly was positioned in an electrical resistance furnace. The thermal reduction was performed at 900 °C which is above the melting point of Mg metal for about 9 hrs. During the process, the inconel reactor was flushed with high purity argon gas. During the course of reaction, Mg burnt and instantaneously gave high energy, which was utilized for the formation of $LaNi_5$ intermetallic compound. After the thermal reduction, the residuals in the alumina crucible was removed and treated with 5% acetic acid and followed by deionised water. The dull gray powder was obtained which was further cleaned with acetone. The purified powders were calcinated at 450°C for 2 h to get the fine crystalline$LaNi_5$ powders.

3.2 Characterization of $LaNi_5$ intermetallic compound

Before the thermal reduction, the decomposition and the thermal dissociation reactions of the reactants have been determined Thermo Gravimetric Analysis (TGA) using a thermal analyzer (instrument model SDT Q600500 PL, Thermal Sciences, version V4.30 analyzer). The TGA curves were recorded from room temperature to 900°C in N_2 atmosphere at a heating rate of 10 °C min^{-1}. The phase purity of the product was assessed using a Philips 8030 X-ray Diffractometer. The unit cell lattice parameters were obtained by least square fitting method of the d spacing and the hkl values. The morphological features of the prepared powders were scrutinized by

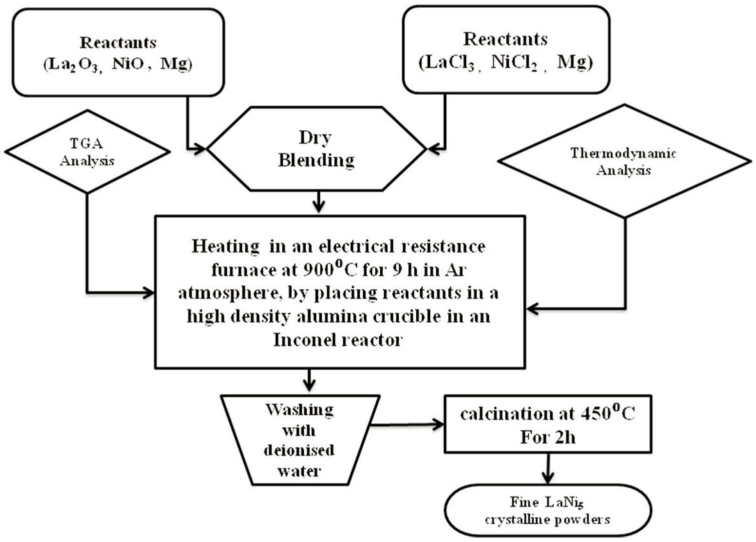

Figure 1. *Experimental procedure for the preparation of* $LaNi_5$ *intermetallic compound*

SEM (JEOL JLA-3.5 CF-Japan). The results of the above investigation will be presented in the following section.

4. Results and Discussion

4.1 Thermal Analysis

4.1.1 TGA Analysis for oxide and chloride systems

The first weight loss accounts to 3.34% occurs between 58.19 ºC to 351.92 ºC is ascribed for the dehydration of water molecules in oxide system and a weight loss of 36.50% amid 93.94 ºC and 151.65 ºC has been concerned for chloride system respectively . The loss in weight between 305.19 ºC to 606.55 ºC which may be due to the transformation of reactants into the desired product $LaNi_5$ compound in oxide system and subsequent to 249.87 ºC, there is a spiky variation in TGA curve may be endorsed to the renovation of reactants and crystallization of the product $LaNi_5$ in chloride system respectively. Beyond 809.68 ºC, the TGA curve does not show any prominent exothermic reaction, with a declining curve indicating the progressive transformation of reactants into a single phase $LaNi_5$ from their compounds as far as oxide precursors are concerned and an trivial weight loss of 0.27% has been noticed between 675.21 ºC and 900 ºC can be attributed to the evaporation of the melt at high temperature region of the oxide precursors.

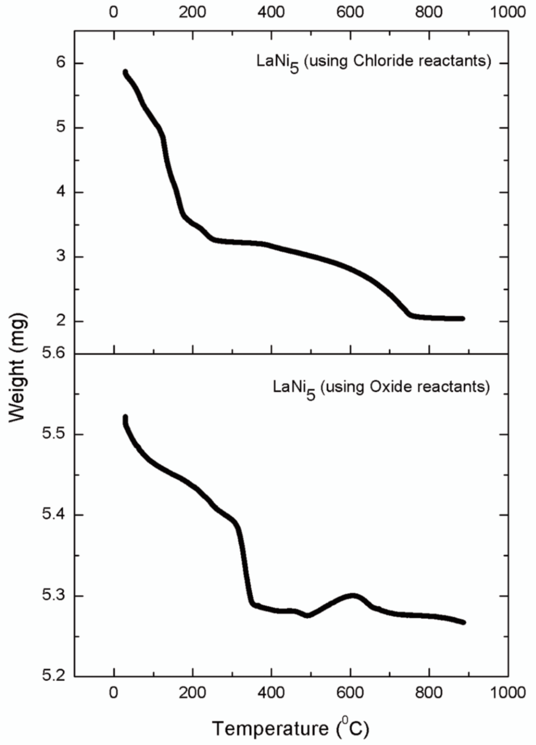

Figure 2. *TGA curves for* $LaNi_5$ *through oxide and chloride reactants*

4.2 X-ray Diffraction (XRD) studies

Figure 3 shows the XRD pattern of prepared $LaNi_5$ alloy by reduction diffusion technique using magnesium as the reductant for both oxide and chloride precursors. XRD spectrum indicates the well defined peaks match well with the standard HCP $LaNi_5$ alloy (space group *p6/mmm* and a = 5.0160 Å, C = 3.9820 Å). The calculated values of a = 4.992 Å, and C = 3.978 Å, which are in good agreement with the standard data and reported values [11, 17, 18]. From the XRD data, we have calculated the average crystalline size via line broadening analysis and by using Scherer's formula. The calculated average crystalline size of the prepared powders is lying between 1.8 μm to 2.2μm. The appearance of weak diffraction peaks appeared in the spectrum indicates that the presence of minor amounts of impurities such as magnesium oxide, lanthanum oxide and nickel oxide in the product.

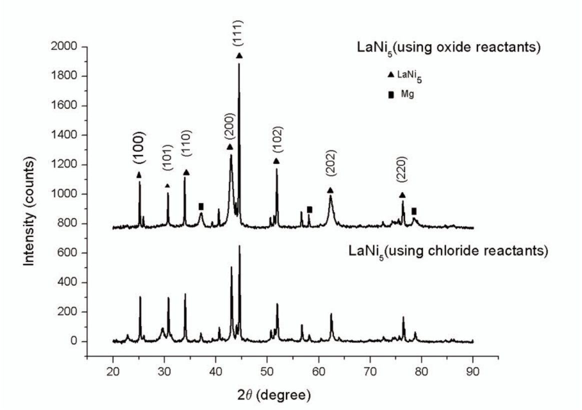

Figure 3. *XRD analyses of $LaNi_5$ intermetallic compound*

4.3 Energy dispersive spectroscopy analysis using X-rays (EDX)

Fig.4 (a, b) shows the EDX profile of the prepared $LaNi_5$ powders by oxide and chloride routes. The spectra ascertain the presence of La, Ni ions in approximately closed to the phase of LaNi i.e $La_{0.9}Ni_{4.8}$ in the case of chloride route and $La_{0.76}Ni_{4.6}$ in the case of oxide route. Traces of impurities such as Mg, Cl and O are also noticed from the EDX spectra.

4.4 Morphological analysis

Fig. 5(a, b) shows the scanning electron micrographs (SEM) of the prepared $LaNi_5$ powders through oxide and chloride routes. The SEM images reveal that the particles are uniformly distributed with regular size and shape. The average particle size of the powders is found to be in the range of 1.8μ - 2μ for both oxides and chloride routes.

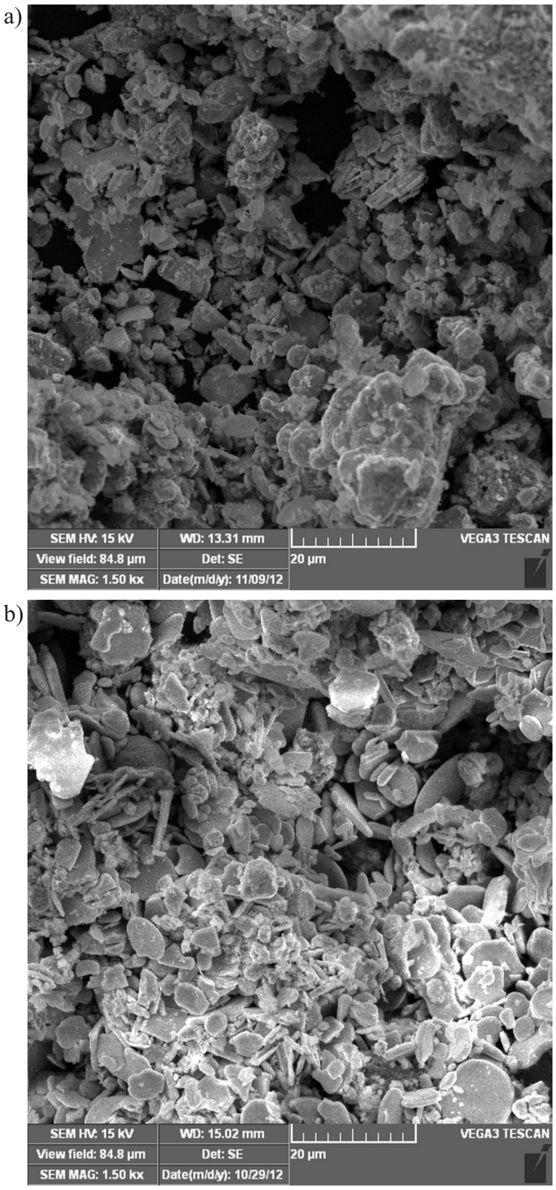

***Figure** 5. SEM images of $LaNi_5$ powders: (a) by oxide reactants, (b) by chloride reactants*

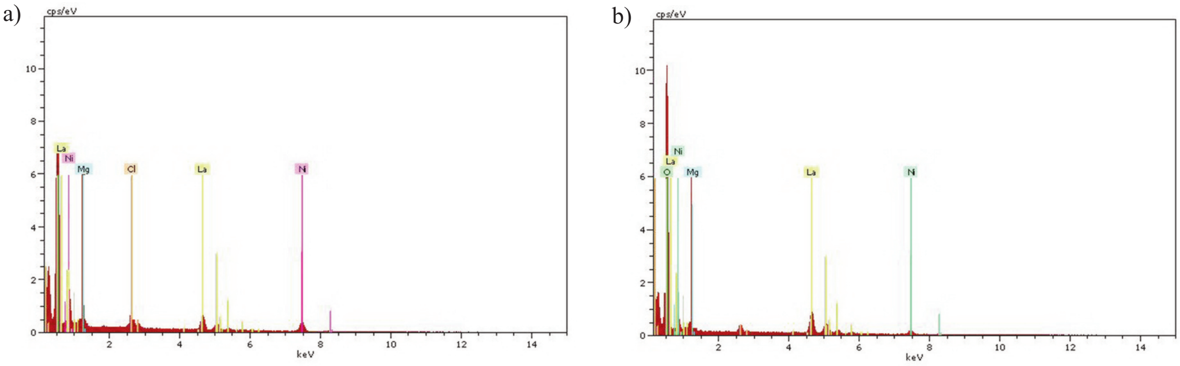

Figure 4. *EDX Spectra of $LaNi_5$ powders (a) by oxide reactants, (b) by chloride reactants*

5. Conclusions

It has been accomplished that the preparation of $LaNi_5$ alloy powders can be possible by R-D process using Mg as the reductant. The process is sluggish due to low kinetics in thermal reduction process. The preparation of $LaNi_5$ intermetallic is found to be more favorable in the case of chloride process than the oxide route. The results have also shown that the prepared intermetallic is close to the appropriate stoichiometry of $LaNi_5$. The XRD data confirms the presence of hexagonal crystals of $LaNi_5$ with minor impurity phases. SEM micrographs reveal that the powders are in irregular morphology with aborted size and shape. Attention is needed in several investigations involving concepts of diffusion and rate kinetics, structure-property relationship pertaining to the reaction proceedings are unsettled, are to be carried out in our upcoming work.

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