

A study of the magnetic properties of $\text{LaNi}_{5-x}\text{Si}_x$ alloys and their hydrides

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Received 5 April 2017; accepted 8 June 2017

Abstract:

In this work, we study the influence of the substitution Si for Ni for the magnetic properties of $\text{LaNi}_{5-x}\text{Si}_x$ ($x = 0-0.5$) alloys. The structure of the alloy was tested by X-ray diffraction (XRD) measurements. The magnetic properties of the samples were carried out using a vibrating sample magnetometer (VSM) system. The results showed that when Ni was substituted for Si in alloys and after hydrogen absorption, $\text{LaNi}_{5-x}\text{Si}_x$ alloys retained their CaCu_5 structure. The susceptibility (χ) of the alloys decreased when substituting Ni by Si increased. The original bulk samples showed a Pauli paramagnetism state after hydrogen absorption transformed into a superparamagnetic state. The results obtained showed that although measurements of magnetic characteristics are relatively simple, quantitative information about the microscopic processes occurring in the material was used as the negative electrode in Ni-MH rechargeable battery.

Keywords: hydrogen absorption, LaNi_5 , magnetic properties, nano, Ni-MH batteries.

Classification number: 2.1

Introduction

An investigation of the R - T (R = rare earth, T = transition metal) interaction in $4f$ - $3d$ intermetallic compounds has been the subject of many theoretical and experimental studies [1, 2]. R - T compounds are known to show interesting magnetic properties associated with both localised moments of rare earth atoms and itinerant electrons of the $3d$ atoms [3, 4]. There is considerable interest in the electronic structure of LaNi_5 in regard to both its high capacity for hydrogen absorption and in its feature of having exchange-enhanced susceptibility [5-7]. LaNi_5 possesses the hexagonal CaCu_5 structure (space group $P6/mmm$) with one formula unit (f.u.) per unit cell [8-11].

The LaNi_5 compound is also considered to be at 4.2 K using an exchange-enhanced paramagnet, having a magnetic susceptibility of $\chi = 2.5 \times 10^{-3}$ emu/f.u. or 2.27×10^{-3} emu/f.u. [12]. Since no corrections for the possible presence of magnetic impurities have been made, the above values can be considered as upper limits. The estimated exchange-enhancement factor ($s = 5-6$) is lower than that reported for Laves-phase compounds [13, 14]. Thus, it is of interest to analyse the magnetic behaviour of systems which show exchange-enhancement factors intermediate between those reported for RCO_2 compounds and normal paramagnets [15, 16].

There has been a lot of research to improve the quality of the material in LaNi_5 systems, such as the replacement of La metal by Nd, Er, Y, etc. [17-21], and the replacement of Ni metal with Al, Cu, Fe, etc. [22-24]. Research is continuing to improve performance and extend the lifetimes of Ni-MH batteries. In this paper, we study the effect of the substitution of Si for Ni of the magnetic properties of alloys $\text{LaNi}_{5-x}\text{Si}_x$ used as the negative electrode in Ni-MH batteries recharge. The partial replacement of Ni using Si LaNi_5 materials acts as an antioxidant and increases the lifetime of Ni-MH batteries.

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Experimental

Reagents and MH electrode preparation

The $\text{LaNi}_{5-x}\text{Si}_x$ system alloys were prepared using an arc-melting method in an Ar gas atmosphere from the metal components at a purity of at least 99.9% or more. Here, a slight excess of La was added to compensate for the weight loss during arc melting. The samples were turned over and re-melted several times to attain good homogeneity. Powder samples were created by milling in an agate mortar for 30 minutes to a grain size of about 50 μm . Hydride samples were prepared using a process of charge-discharging per 10 cycles. Electrochemical measurements were conducted in a three electrodes system. The electrolyte was 1M LiOH and 6M KOH, and the positive electrode was $\text{Ni}(\text{OH})_2$, which is a negative electrode material in which we need to study. In charge-discharge capacity measurements, all electrodes are connected to a potential device called a Bi-Potentiostat 366A. The electrodes were fully charged (the over-charged ratio was approximately 30-50%) at the current density of 50 mA/g, and then discharged at the same current density to the cut-off potential of -0.7 V (versus SCE). Electrochemical measurement results have been shown in our previous studies.

Microstructure measurements

The crystalline structure and the phase impurities of the samples at room temperature were examined using X-ray powder diffractometer, using $\text{Cu-K}\alpha$ radiation. The obtained powder XRD patterns were analysed via means of a Rietveld refinement procedure using X'pert High Score Plus in order to determine the type of structure and the lattice parameters.

Magnetization measurements

Magnetic properties of the alloys $\text{LaNi}_{5-x}\text{Si}_x$ were measured using a vibrating sample magnetometer (VSM) in magnetic fields up to 1.3 T. The temperature dependence of the magnetization $M(T)$ of hydride samples was measured in a nitrogen gas environment; and the temperature ranged from 300 K to above 700 K. The maximum applied field was 0.1 T. During the measurement, the temperature was raised at a rate estimated to be about 5 K.

Results and discussions

Crystal structure analysis

X-ray diffraction normally is one of the most useful routes to examine the crystal structure and to determine lattice parameters of materials. When replacing a part of Ni by Si in LaNi_5 alloy, crystal characteristics of the alloy remains unchanged compared to the LaNi_5 original material, although the Si atoms are smaller than the Ni atoms, this result is shown in Fig. 1. Fig. 2 shows the $\text{LaNi}_{4.5}\text{Si}_{0.5}$ alloy before and after cycling 10 cycles; the alloys remains as a CaCu_5 structure. Characteristics of the sample crystal decreased, which was

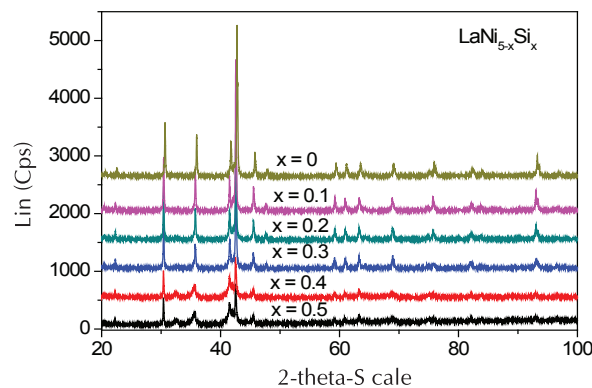


Fig. 1. The X-ray diffraction spectrum of the LaNi_5 and $\text{LaNi}_{5-x}\text{Si}_x$ ($x \leq 0.5$) alloys.

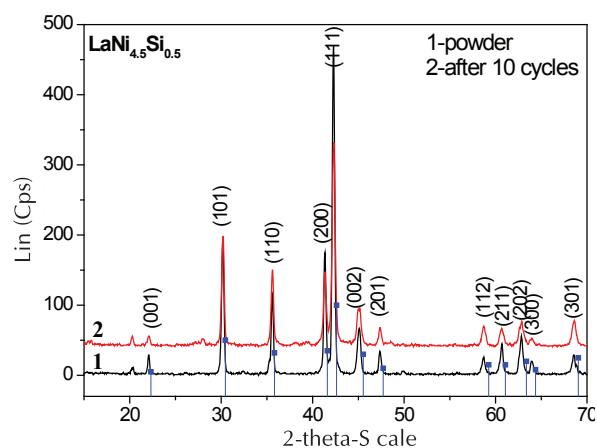


Fig. 2. The X-ray diffraction spectrum of the alloy $\text{LaNi}_{4.5}\text{Si}_{0.5}$ after 10 cycles.

presented for the expanded diffraction peaks and decreased in diffraction peaks intensity. This is because the hydrogen absorption process can cause stretch lattice, but not by much. The volume expansion on hydriding, $\Delta V/V$, decreases almost linearly with increasing silicon content, the decrease being almost proportional to the decrease in hydrogen content of the hydrides.

The magnetic properties

Measurements are carried out on the bulk samples, the powder samples after ground (not to absorb hydrogen) and powder samples were taken after charge-discharge at 10 cycles for the whole system. The magnetisation curves of the bulk samples and the powder samples after grinding are shown in Fig. 3. The magnetisation curve of bulk LaNi_5 and $\text{LaNi}_{5-x}\text{Si}_x$ samples is a straight line passing through the origin of this is characteristic of Pauli paramagnetic with magnetic susceptibility are listed in Table 1.

From the table above, we have clearly seen that the value of magnetic susceptibility of the compound $\text{LaNi}_{5-x}\text{Si}_x$ reduced when the mass or the Si composition increased. It is understandable that the elemental Si is not magnetic, while an increase in the element Si, decrease the magnetic element Ni, and it leads to a reduction of magnetic susceptibility.

Table 1. Magnetic susceptibility of the sample LaNi_5 and $\text{LaNi}_{5-x}\text{Si}_x$.

Order number	Sample	χ (10^{-6})
1	LaNi_5	3.700
2	$\text{LaNi}_{4.9}\text{Si}_{0.1}$	2.813
3	$\text{LaNi}_{4.8}\text{Si}_{0.2}$	2.571
4	$\text{LaNi}_{4.7}\text{Si}_{0.3}$	2.326
5	$\text{LaNi}_{4.6}\text{Si}_{0.4}$	2.157
6	$\text{LaNi}_{4.5}\text{Si}_{0.5}$	1.531

Figure 3 also shows magnetisation curves of $\text{LaNi}_{5-x}\text{Si}_x$ powder samples after milling to a grain size of about $50\ \mu\text{m}$. The figure we see for all $\text{LaNi}_{5-x}\text{Si}_x$ powder samples shows super - magnetism. After milling, the magnetism of the samples increased, which was represented in the increasing moments of the sample since the magnetic field was tested. The reason is that the Ni particles are disorbed out from the surface of the particles due to La oxidation by oxygen and water vapour in the air during charging-discharging. The concentration of Ni particles on the surface of the material increases, which Ni is ferromagnetic elements thereby changing the magnetic state of the material.

Magnetisation curves of $\text{LaNi}_{5-x}\text{Si}_x$ samples taken after charge-discharge 10 cycles are shown in Fig. 4. We see that the magnetic moment of the samples increases remarkably. The reason for that is that the nanometer-scale Ni particles are disorbed out the surface of the particles due to La oxidation by oxygen and water vapour in the air during charging-discharging. The concentration of Ni particles on the

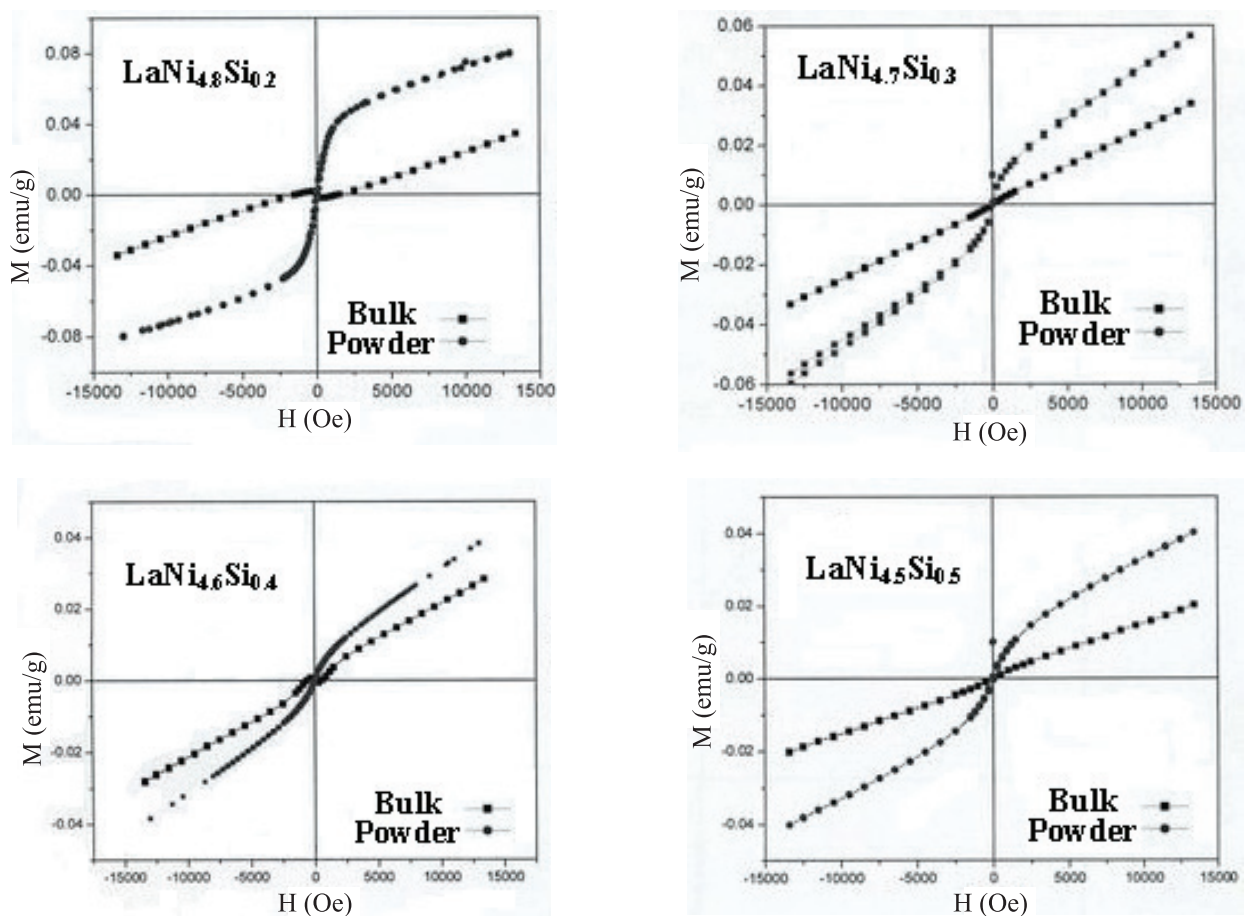


Fig. 3. Magnetisation curves of the powder samples and the bulk samples of $\text{LaNi}_{5-x}\text{Si}_x$.

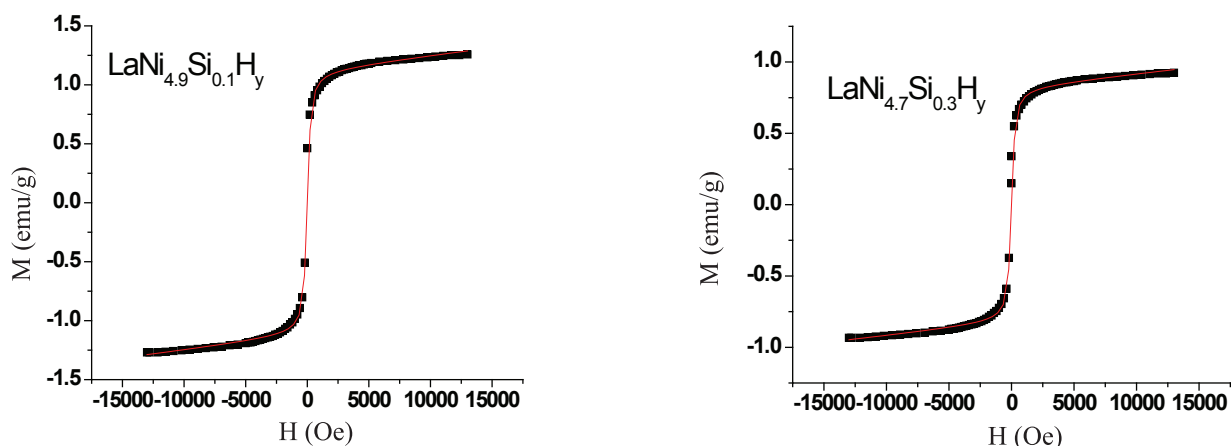


Fig. 4. Magnetisation curve of the sample $\text{LaNi}_{4.9}\text{Si}_{0.1}\text{H}_y$ and $\text{LaNi}_{4.7}\text{Si}_{0.3}\text{H}_y$ after charge-discharge 10 cycles.

surface of the material increases, which Ni is ferromagnetic elements thereby changing the magnetic state of the material. However, if the Ni atoms release too much, it will lead to the destruction of the material structure.

Changes to the characteristic phenomenon before and after hydrogenation by Ni atoms are releasing surface material during the hydrogenation was K. Suzuki analysed via the use of X-ray diffraction diagrams on two LaNi_5 and $\text{LaNi}_{4.7}\text{Al}_{0.3}$ materials systems [25]. The X-ray diffraction spectrum of the LaNi_5 and $\text{LaNi}_{4.7}\text{Al}_{0.3}$ alloys showed after 2000 charge-discharge cycles crystal characteristic reduced, reflected in the expansion and reduce the intensity of the diffraction peaks, have been shown by an appearance of the characteristic peak for the element Ni, which is the element causing a change of state of magnetic materials.

The results are quite consistent with previous studies on the electrochemical properties of the negative electrode materials used in battery recharging of Ni-MH [26]. When the charge-discharge process occurs in a negative electrode, Ni atoms released to constitute clusters of particles on the surface of the material. Therefore, increases the magnetic properties of materials. Through an examination of the nature of the material, the method for fast results and high accuracy, we can evaluate electrochemical process occurs at the negative electrode.

Conclusions

We have investigated the crystallographic and the magnetic characteristics of the intermetallic $\text{LaNi}_{5-x}\text{Si}_x$ ($x \leq 0.5$). The XRD patterns provide evidence of the single phase and crystallising in the hexagonal CaCu_5 -type structure in all

samples. The lattice parameters calculated by the Rietveld method, both a and c , remained mostly unchanged by the replacement of Ni with Si. The bulk sample is characteristic of Pauli paramagnetic. The value of magnetic susceptibility of the compound $\text{LaNi}_{5-x}\text{Si}_x$ reduces when the mass or the Si composition increases. For powder and after charge-discharge 10 cycles samples, the material transfer from the paramagnetic to superparamagnetic state was studied because Ni elements release surface material during charging-discharging. The magnetic susceptibility of the material increases as the number of charge-discharge cycles increase. The analysis showed that although measurements of magnetic characteristics are relatively simple but can give us quantitative information about the microscopic processes occurring in the negative electrode. Such magnetic characteristics measurements can be seen from the analytical method have high sensitivity used to evaluate the quality of the electrode through survey and comparison with standard samples.

ACKNOWLEDGMENTS

This work is partly supported by the Key Project DTKHCN/001/16 of the Ministry of Industry and Trade.

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