Ferromagnetic Order in the Intermetallic Alloys $\text{LaNi}_{5-x}\text{Mg}_x$

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The influences of the substitution of Ni with Mg on crystallographic and magnetic properties of the intermetallic alloys $\text{LaNi}_{5-x}\text{Mg}_x$ ($x \leq 0.4$) were investigated. The X-ray diffraction patterns showed that all samples were of single phase, and the lattice parameters, a and c , decreased slightly upon chemical doping. LaNi_5 is well known as an exchange-enhanced Pauli paramagnet. Interestingly, in $\text{LaNi}_{5-x}\text{Mg}_x$, the ferromagnetic order existed even with a small amount of dopants; the Curie temperature reached the value of room temperature for $x = 0.2$, and enhanced with increasing x .

Key words: hydrogen storage materials; chemical substitution; crystallographic and magnetic properties; X-ray diffraction

The intermetallic alloys of general formula RM_5 (R: rare earth or transition metal; M: transition metal) are able to store large amounts of hydrogen to form metallic hydrides, in which LaNi_5 can absorb or desorb more than 7H per formula unit at room temperature. Thus LaNi_5 , which crystallizes in a hexagonal structure of CaCu_5 type (space group $P6/mmm$ — (Wernick & Geller 1959; Guegan, Lartigue & Achard 1985), is a very attractive and now well known as a hydrogen storage material (Barnes *et al.* 1976; van Vucht, Kuijpers & Bruning 1970). In order to improve the hydrogen storage capacity, the stability of the hydride phase, or the alloy corrosion resistance of LaNi_5 , the effects of replacing by other metals have been extensively studied (Kielbik *et al.* 2000; Latroche *et al.* 1995; Luo *et al.* 1995; Tai *et al.* 2003; Mendelsohn, Gruen & Dwight 1977; Lartigue,

Guegan & Achard 1980; Sakai *et al.* 1990). It was reported that the partial substitution of Ni with Al, Mn, and Co can improve the cycling performance and decrease the plateau pressure of hydrogen without reduction of hydrogen storage capacity (Mendelsohn, Gruen & Dwight 1977; Lartigue, Guegan & Achard, 1980), and significantly extend the cycle life (Sakai *et al.* 1990), respectively. Interestingly, upon chemical doping, the electronic structure of alloys changed leading to some new magnetic properties which however has not been fully understood. On the other hand, one of the most promising hydrogen storage materials mentioned is Mg (Jains *et al.* 2009). Mg can store large quantities of hydrogen, and is relatively inexpensive. The effects of Mg doping on Ni site was reported in sample $\text{LaNi}_{4.8}\text{Mg}_{0.2}$ (Giza *et al.* 2008). The

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hydrogen capacity of $\text{LaNi}_{4.8}\text{Mg}_{0.2}$ is about 6.0. This suggests $\text{LaNi}_{4.8}\text{Mg}_{0.2}$ can be used as negative MH electrodes in the Ni/MH batteries. Based on researches on LaNi_5 -based alloys, we investigated properties of the intermetallic alloys LaNi_5 doped with Mg. In this paper, the results of experiments on crystallographic and magnetic properties of the $\text{LaNi}_{5-x}\text{Mg}_x$ are discussed.

MATERIALS AND METHODS

A series of polycrystalline $\text{LaNi}_{5-x}\text{Mg}_x$ samples with x in the range $x \leq 0.4$ were prepared from nominal compositions by arc-melting the constituents La, Ni and Mg (all 3N purity) under high-purity argon atmosphere in a water-cooled copper crucible. A slight excess of La was added to compensate the weight loss during arc-melting process. The samples were turned over and re-melted several times to attain good homogeneity. The crystalline structure and the phase impurity of the samples at room

temperature were examined by X-ray powder diffractometer, using Cu-K_α radiation. The obtained powder XRD patterns were analyzed by means of a Rietveld refinement (Rietveld 1969) procedure using X'pert High Score Plus in order to determine the type of structure and the lattice parameters. The magnetic properties of the alloys $\text{LaNi}_{5-x}\text{Mg}_x$ were measured on a Quantum Design SQUID magnetometer in magnetic fields up to 5 T and in the temperature range from 5 K and 300 K.

X-ray diffraction normally is one of useful route to examine the crystal structure and determine lattice parameters of materials. In *Figure 1*, we showed the XRD patterns of the $\text{LaNi}_{5-x}\text{Mg}_x$ system. The data confirmed that all the samples were single phase, and to be crystallized in the hexagonal CaCu_5 -type structure. We could not detect any secondary phases within the 1% error of measurements. *Figure 2* represents the lattice parameters

Figure 1. The XRD patterns at room temperature of the intermetallic alloys $\text{LaNi}_{5-x}\text{Mg}_x$ (with $x \leq 0.4$).

determined for the samples with $x \leq 0.4$ by using the Rietveld refinement analysis, together with literature data for pure LaNi_5 (Tai, pers. comm., nd). Upon partial substitution of Mg for Ni, both parameters, a and c , slightly decrease, however they did not change as much as compared with those for LaNi_5 . We realized that the obtained value for $x = 0.2$ was in good agreement with the only literature values reported (Giza *et al.* 2008). The unit cell volume $\Omega = 86.68 \text{ \AA}^3$ for LaNi_5 followed Vegard's law (Vegard 1921) and reduced linearly at a rate of $0.5112 \text{ \AA}^3/\text{at.}\% \text{ Mg}$.

Figure 3 shows the applied magnetic field dependence of magnetization of $\text{LaNi}_{5-x}\text{Mg}_x$ measured at fixed temperatures between 5 K and 300 K. Here we plotted the normalized magnetization, $M/M(1\text{ Tesla})$ as a function of applied magnetic field. The data taken at $T = 5 \text{ K}$ is represented in Figure 3a. For $x = 0.1$, the $M(H)$ curve exhibited a S-shape charactering for a like-superparamagnetic behaviour. This suggested a hint of ferromagnetic order in samples with a small amount of doping content,

Mg. In the literature, LaNi_5 is well known as a Pauli paramagnet via the measurements down to 1.6 K (Nasu *et al.* 1971). With increasing x , the ferromagnetic order was enhanced as corroborated by the the symmetric loop with visible remnant moments M_r and coercive fields H_c . The inset in Figure 3a displays a typical hysteresis loop of the sample with $x = 0.4$, measured at 5 K in the magnetic field of $-0.1 \text{ T} \leq B \leq 0.1 \text{ T}$. The values of M_r and H_c are obtained for $0.01 \mu_B/\text{f.u.}$ (formula unit) and 6 mT, respectively. This classified the sample as a weak ferromagnet. The values of magnetic moments at 5 Tesla were $0.02 - 0.13 \mu_B$ for $x = 0.1 - 0.4$, respectively. For experiments carried out at higher temperatures $T = 100$ and 200 K (Figures 3b and c), for $x = 0.1$ the normalized magnetization linearly depended on the applied fields with a small slope of dM/dH , and no hysteresis effects were observed, indicating a paramagnetic state. Thus we predict that the sample with $x = 0.1$ has the Curie temperature T_C around 10 K. $M(H)$ curves still remain in the S-shape for $x > 0.1$. Figure 3d demonstrates

Figure 2. Lattice parameters of $\text{LaNi}_{5-x}\text{Mg}_x$ as a function of the Mg concentration x measured at room temperature. Notice: the data for $x = 0$ are taken from Rietveld (1965).

Figure 3. Magnetization vs. applied magnetic field $M(H)$ curves of $\text{LaNi}_{5-x}\text{Mg}_x$ alloys measured at different temperatures (a) $T = 5$ K, (b) 100 K, (c) 200 K, and (d) 300 K. Mg concentrations are (from bottom to top) $x = 0, 0.1, 0.2, 0.3$ and 0.4 . Notice: the vertical axes represent the normalized magnetization (M divided to M at 1 Tesla). Inset: Hysteresis loop of $\text{LaNi}_{4.6}\text{Mg}_{0.4}$ in a small scale of the horizontal axis measured at $T = 5$ K.

the data measured at 300 K. For $x = 0.2$, the magnetization trends towards a linearly variation with magnetic fields, however, the data show a small curvature through origin as a sign of a ferromagnetic component. Nevertheless, it is believed the sample has a transition from ferromagnetic to paramagnetic state near 300 K. For $x = 0.3$ and 0.4 samples, the magnetization data clearly reveal the existence of ferromagnetic ordering, which means the samples have T_C above 300 K.

On the study concerning the magnetic properties of LaNi_5 -based alloys, in which Ni is partially replaced by other metals, such as Co, Mn, Fe, Al, etc., the long-range ferromagnetic

ordering exists in $\text{LaNi}_{5-x}\text{Fe}_x$ alloys. The net magnetization is induced by magnetic Fe atoms, and increases with the Fe content. This is attributed to the enhanced Fe-Ni exchange interaction, and is confirmed by the increase of the Curie temperature in $\text{LaNi}_{5-x}\text{Fe}_x$ (Cullity 1972; Tai *et al.* 1999; Yang *et al.* 2000). Both Fe and Ni are 3d electron metals, and hence their electronic structures are similar. Ni can be replaced with Mg, due to the difference in the electronic structure of the two elements. Therefore the origin of ferromagnetism in $\text{LaNi}_{5-x}\text{Mg}_x$ is openly discussed. It needs more evidence from both experiments and theories (*i.e.* to calculate the total density of state (DOS) of $\text{LaNi}_{5-x}\text{Mg}_x$) to clarify this phenomenon.

CONCLUSION

In conclusion, we have investigated the crystallographic and magnetic properties of the intermetallic alloys $\text{LaNi}_{5-x}\text{Mg}_x$ ($x \leq 0.4$). The XRD patterns provided evidence of the single phase and crystallizing in the hexagonal CaCu_5 -type structure in all the samples. The lattice parameters calculated by the Rietveld method, both a and c , slightly decreased with increasing Mg concentration. The magnetization data showed the existence of ferromagnetism and enhanced upon chemical doping. This is corroborated by the typical S-shape of hysteresis loops characterizing specifically for weak ferromagnetic materials. The Curie temperature was suggested to be around 10 K for sample with $x = 0.1$, and rapidly to be increased up to room temperature for higher Mg concentration $x > 0.1$. For further studies, we will focus on measurements, which help to determine exactly the Curie temperature and also to determine the origin of ferromagnetism of $\text{LaNi}_{5-x}\text{Mg}_x$.

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