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Magnetic properties of commercial metal hydride battery materials

D.P. Broom, M. Kemali, D.K. Ross*

Joule Laboratory, University of Salford, Salford M5 4WT, UK

Abstract

The magnetic properties of two commercial $LaNi_5$-based materials and their variation as a function of hydrogen cycles have been studied using magnetisation measurements. Pure $LaNi_5$ is a Pauli paramagnet, but it has been shown that after hydrogen cycling Ni clusters are formed on its surface. At room temperature these clusters were found to act as superparamagnetic particles. Magnetisation curves have been obtained for a treated $LaMM(Ni_{3.43}Mn_{0.38}Al_{0.29}Co_{0.67})_{4.77}$ sample and similar superparamagnetic behaviour has been identified. Measurements have also been made on a modified alloy, of commercial interest, at a range of high and low temperatures. This sample displays ferromagnetic, as well as paramagnetic and superparamagnetic, behaviour. It has been shown that the response at low field increases dramatically upon heating, demonstrating a large growth in the number of superparamagnetic particles present on its surface.

Keywords: Metal hydrides; Hydrogen storage electrodes; $LaNi_5$; Magnetism

1. Introduction

In recent years metal hydride battery materials have become increasingly popular as an alternative to Ni–Cd. In addition to the environmental benefits, they also have low discharge rates and long cycling stability. Metal hydride batteries are now used extensively in consumer applications, such as lap-top computers and mobile phones. The materials used in these batteries are $LaNi_5$ based. In order to obtain the optimum performance, other transition metals are substituted for the Ni. Many experimental techniques have been used to study the behaviour of hydrogen in these materials [1]. Schlapbach [2] studied the magnetic properties of pure $LaNi_5$ and found that after hydrogen cycling Ni clusters are formed on its surface. These clusters are superparamagnetic [3] at room temperature and ferromagnetic at liquid helium temperatures. In this paper we study the magnetic properties of two commercial $LaNi_5$-based materials and their variation as a function of hydrogen cycles. The formation and behaviour of the Ni clusters will also be discussed.

2. Experimental

All the measurements were made on a Vibrating Sample Magnetometer (VSM), at Manchester University, UK, in the range 0–12 T. A CF cryostat and a furnace enabled measurements to be taken between 3 and 1200 K. The samples measured were heat-treated $LaMM(Ni_{3.43}Mn_{0.38}Al_{0.29}Co_{0.67})_{4.77}$ and a modified alloy, of commercial interest, that had undergone a treatment to enhance the surface Ni (known as HAK treatment) [4]. The samples were placed in a small silica bulb and held in place by a small plug of high temperature cement.

3. Results

Fig. 1 shows the magnetisation curves for the uncycled and cycled heat treated $LaMM(Ni_{3.43}Mn_{0.38}Al_{0.29}Co_{0.67})_{4.77}$ samples, at ambient temperature. The uncycled sample shows a purely paramagnetic response, with a susceptibility of $\chi = 0.179$ emu g^{-1} T^{-1}. The curve for the cycled sample contains an additional superparamagnetic component, which rapidly saturates at low field. This is due to the clustering of Ni atoms on the surface of the material and is consistent with the response observed for pure $LaNi_5$ [2]. The analysis of this response will be discussed later. The value for the paramagnetic susceptibility was taken to be the gradient of a straight line fitted to the high field data. As well as the appearance of a superparamagnetic response upon cycling, there also appears to be an increase in the paramagnetic susceptibility to $\chi = 0.199$ emu g^{-1} T^{-1}.

Fig. 2 shows the magnetisation curves for the uncycled

*Corresponding author.

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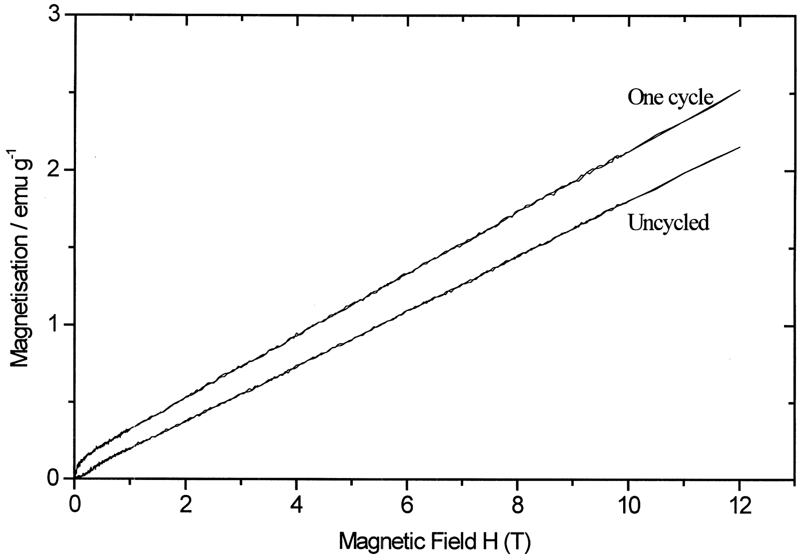

Fig. 1. Magnetisation curves for the uncycled and cycled heat treated LaMM($Ni_{3.43}Mn_{0.38}Al_{0.29}Co_{0.67}$)$_{4.77}$ sample at 300 K.

and cycled HAK treated samples at ambient temperature. The uncycled sample shows a spontaneous ferromagnetic response at low field and a paramagnetic response at higher fields. It is assumed that the ferromagnetic response is from free Ni produced in the HAK treatment process. It can be seen that the cycled sample shows an increased magnetisation at low fields. This is believed to be a result of the addition of a superparamagnetic component, due to the formation of Ni clusters, as described above. There is a significant increase in the curvature of the shoulder on the cycled samples curve, which strongly suggests the presence of this component. It is possible that the ferromagnetic component also increases, but further analysis is necessary to confirm this. It is also possible that the uncycled sample contains a small superparamagnetic component, although the shoulder on the curve is thought to be a saturation of the ferromagnetic component. It can also be seen that the paramagnetic susceptibility decreases upon cycling, from 0.233 to 0.209 emu g^{-1} T^{-1}. This decrease suggests an increase in the number of free Ni atoms in the bulk of the material.

Fig. 3 shows magnetisation curves for the uncycled HAK treated sample from 3 to 300 K. It can be seen that the data for 100 and 200 K have a similar shape to 300 K except for a higher gradient in the high field region, corresponding to an increase in the paramagnetic susceptibility. In Fig. 4 these data are compared with Schlapbach's data for uncycled pure $LaNi_5$. The susceptibility increases from 0.05 emu g^{-1} T^{-1} for $LaNi_5$, independent of temperature, to values that decrease from 0.509 to 0.233

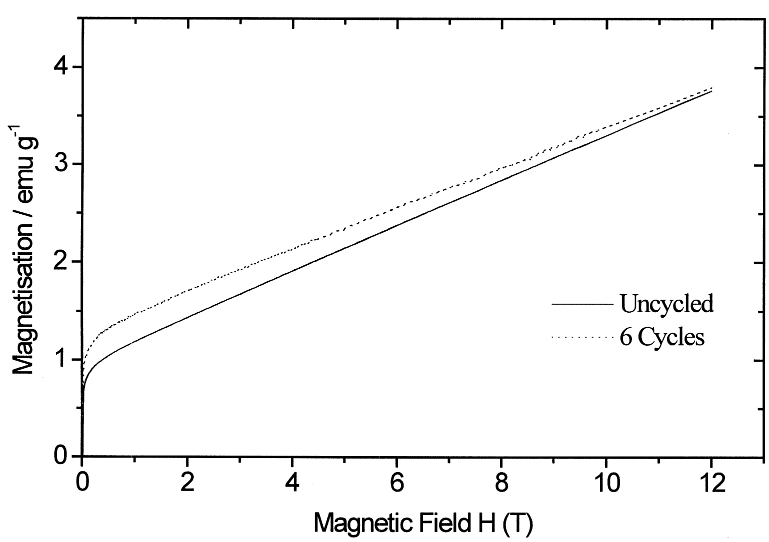

Fig. 2. Magnetisation curves for the uncycled and cycled HAK treated samples at 300 K.

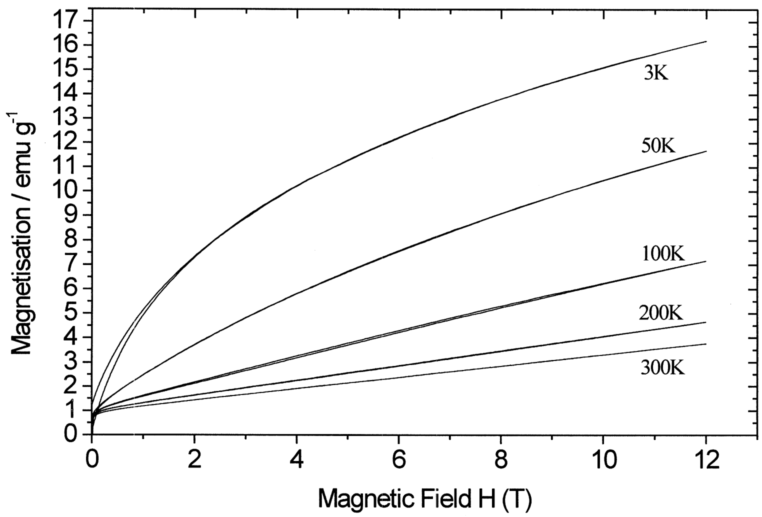

Fig. 3. Magnetisation curves for the uncycled HAK treated sample at various sub-ambient temperatures. The measurements were taken at decreasing temperature.

emu g^{-1} T^{-1} between 100 and 300 K, for the HAK treated material, with little difference between the cycled and uncycled samples. The temperature-independent behaviour of the $LaNi_5$ data would suggest Pauli susceptibility due to the conduction electrons of $LaNi_5$, while the roughly $1/T$ behaviour observed for the HAK material would suggest that the susceptibility of unpaired localised electrons dominates in this case. Our measurements on the $LaMM(Ni_{3.43}Mn_{0.38}Al_{0.29}Co_{0.67})_{4.77}$ sample yield a susceptibility that is comparable to the HAK material so we can assume that this spin susceptibility is probably due to the magnetic ions in the mischmetal used in these alloys. At 3 and 50 K, the observed response for the HAK treated sample shows some saturation of the paramagnetic component.

Fig. 5 shows the magnetisation curves for the uncycled HAK treated sample for temperatures between 300 and 800 K. The 400 K data have a similar shape to the 300 K data except for the smaller gradient, which should vary as $1/T$. However, at higher temperatures, while the gradient continues to fall as $1/T$, the intercept increases and hysteresis begins to appear. Finally, at 800 K, the intercept magnetisation largely disappears while the susceptibility increases again. The comparison of the 700 and 800 K data would strongly suggest that the Curie temperature lies somewhere between these temperatures. This is above the Curie temperature of Ni and would suggest that the clusters contain Co, from the bulk, alloyed with the Ni.

Fig. 6 shows the magnetisation curves for the uncycled HAK treated sample, at 400 K, before and after it was heated up to 800 K. The time interval between these measurements was in the region of 6 h. It can be seen that the magnetisation is increased by at least an order of magnitude and that this mainly occurs in the low field

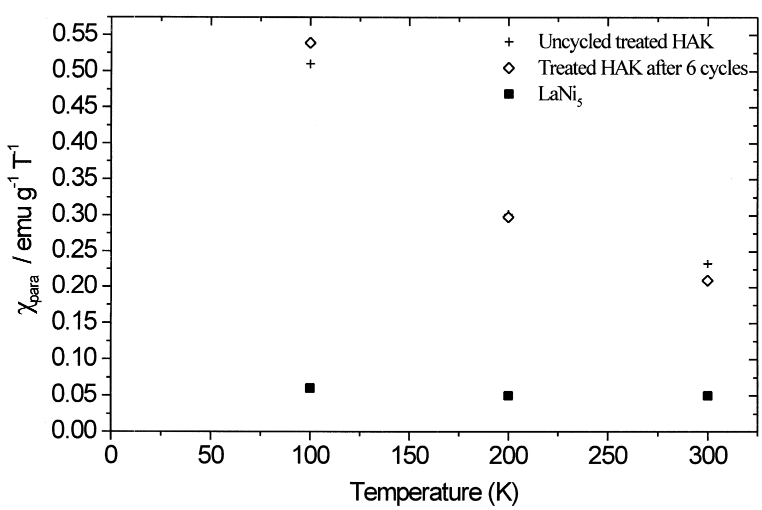

Fig. 4. Comparison of the susceptibilities of cycled and uncycled HAK treated and pure $LaNi_5$ (taken from Schlapbach [2]) at three different temperatures.

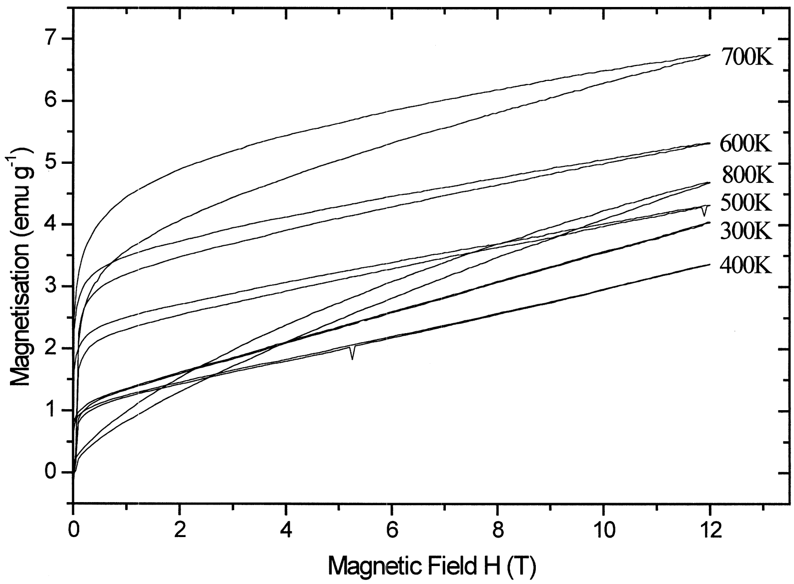

Fig. 5. Magnetisation curves for the uncycled HAK treated sample at various temperatures above ambient. The measurements were taken at increasing temperatures.

region, with a negligible change in the paramagnetic susceptibility. It is inferred that this increase is due to a large growth in the number of Ni clusters by annealing the atomic arrangements, although further analysis will be necessary to confirm this.

In order to determine the size of the Ni clusters, the shape of the superparamagnetic response was analysed at low fields. The normal way to investigate this is to model the magnetisation using the Langevin equation, assuming a Gaussian cluster size distribution, on the assumption that the magnetic moments of all the atoms in the cluster add together to give the magnetic moment of the cluster and that the magnetic moments of the clusters interact independently with the external field.

The Langevin equation is given by

$$M = N_{\mathrm{tot}}\mu\left(\coth\left(\frac{n\mu H}{kT}\right) - \left(\frac{kT}{n\mu H}\right)\right)$$

where μ is the magnetic moment of each atom involved in

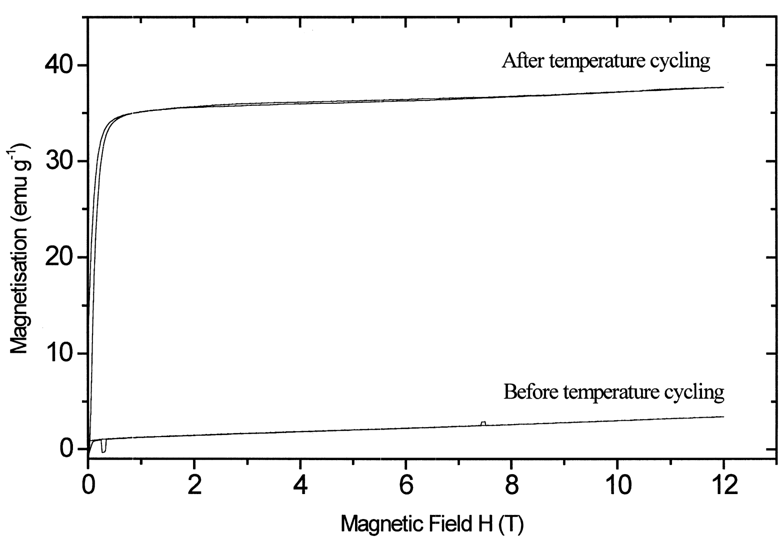

Fig. 6. Magnetisation curves for the uncycled HAK treated sample, at 400 K, before and after the sample was heated up to 800 K (for the measurements shown in Fig. 5).

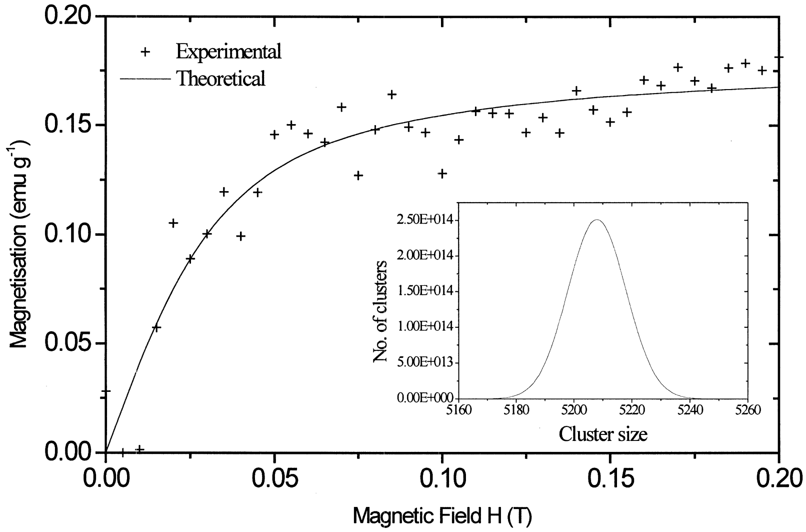

Fig. 7. Least squares fit to the experimental data from the heat treated $LaMM(Ni_{3.43}Mn_{0.38}Al_{0.29}Co_{0.67})_{4.77}$, at 300 K.

the clustering (for Ni, $\mu = 0.6\ \mu_B$), n is the number of atoms per cluster and N_{tot} is the total number of atoms involved in the clustering.

Fig. 7 shows the least squares fit for the $LaMM(Ni_{3.43}Mn_{0.38}Al_{0.29}Co_{0.67})_{4.77}$ sample after one hydrogenation cycle, assuming only Ni is involved in the clustering. The particle size distribution used in this fit is shown in the inset. The mean cluster size obtained from the fit was 5208 atoms with a standard deviation of 10. The value obtained for the proportion of Ni atoms involved in the clustering was ~0.5%.

4. Conclusion

It has been shown that for the heat treated $LaMM(Ni_{3.43}Mn_{0.38}Al_{0.29}Co_{0.67})_{4.77}$, there is nucleation of Ni to the surface after hydrogen cycling. The Ni forms clusters of ~5200 atoms that act as superparamagnetic particles. There is a Gaussian distribution of cluster sizes. The same process appears to occur in the HAK treated sample, although further analysis of the data is necessary. There is also clear evidence of the growth in the number of Ni clusters in the HAK treated sample, at higher temperatures. We therefore intend to make isothermal time-dependent kinetic measurements, to study the growth of these clusters at high temperatures. SEM measurements are currently being carried out, to determine the proportion of Ni on the surface of the samples. Our further work will also include small angle neutron scattering measurements on these samples, which will enable us to study the growth of these Ni clusters. The combination of these techniques will help elucidate our understanding of the behaviour of the Ni in these materials and its role in improving the materials' absorption characteristics.

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