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Magnetic properties of the $LaNi_5$–H system

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Abstract

We simultaneously measured the H/M atomic ratio and the magnetization, M, of $LaNi_5$–H while it was activated and then cycled many times, at 100 °C and then 26 °C. The overall magnetization of the sample rose steadily as cycling precipitated Ni. In addition, however, M exhibits a large degree of magnetic hysteresis between the absorption and desorption isotherms. The magnetization in both the pure α and β phases is very sensitive to the H concentration. Furthermore, we found that the intrusion of the intermediate γ phase, $LaNi_5H_{\approx 3}$, also profoundly altered the magnetic properties of the sample. It is proposed that the ferromagnetism occurs by exchange between clusters of fcc Ni spins, via polarization of the conduction electrons.

Keywords: Hydride; Magnetism; Ferromagnet

1. Introduction

$LaNi_5$ is a Pauli paramagnet. Cyclic absorption and desorption of hydrogen by $LaNi_5$ causes superparamagnetic Ni clusters to precipitate near the surface of the metal particles by a mechanism which is well understood [1,2], involving the uptake of oxygen from the gas supply (absorption) and from gases back-streaming through the vacuum pump (desorption). Continued cycling eventually leads to ferromagnetism of the desorbed intermetallic [1].

Our interest in the magnetic properties of $LaNi_5$–H_x was twofold. First, we wished to investigate the properties of the cycled hydride in situ. It was thought that the precipitated Ni might have an amplifying effect on the intrinsic properties of the hydride matrix, depending on the role played by the Ni clusters. Second, we wished to explore the magnetism, if any, of the intermediate γ phase, $LaNi_5H_{\approx 3}$, which intrudes when the material is cycled at temperatures above about 60 °C [3].

In this paper we present some of the results of a comprehensive study in which a single sample of $LaNi_5$ was hydrogen cycled more than 70 times under a wide variety of experimental conditions, always with simultaneous measurement of the changes in sample weight due both to the changing magnetic moment and to the absorption of interstitial/impurity atoms.

2. Experimental

The measurements were made with a computer operated isochoral gravimetric hydrogenator based on a Sartorius microbalance. Following the addition of a system of solenoids to generate a magnetic field and field gradient, this instrument also functions as a Faraday magnetometer. By careful design of the solenoids, the problem of mechanical stability with ferromagnetic samples inherent in the Faraday technique has been overcome [4]. Measurements were made with the field gradient in nominally forward and reverse directions. Because the magnetic component of the sample weight reverses with the gradient, but the component due to the absorption of interstitial H, C or N atoms does not, taking the sum or difference of the two data sets extracts simultaneous measurements of the magnetic moment and absorbed interstitial concentration.

In this study with interstitial H, the sample was held in a quartz bucket, approximately 10 mm long by 4 mm internal diameter. To prevent ferromagnetic fine powder particles escaping from the sample under the influence of the magnetic forces exerted by the magnetometer, a spring-loaded frit was used to seal the sample bucket. In this way, the 24% volume expansion due to H absorption was accommodated with minimal change in the demagnetization factor. The data were not corrected for demagnetization effects.

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the magnetization, M, of $LaNi_5$–H (Nucor Research Chemicals alloy #1241, $LaNi_{4.93}$) while it was activated and then cycled many times, initially at 100 °C, then under various other conditions of temperature, pressure and ambient atmosphere. Although the γ phase has been reported in experiments with very pure gas, an explicit comparison between samples loaded with H from sources of different purity [5] suggested that some impurity level is necessary to stabilize this phase. Therefore, every absorption was made with a fresh charge of H_2, of purity 99.999%. In each desorption, the H_2 was exhausted through the vacuum pump. Thus, the cumulative impurity load gettered by the sample increased steadily throughout the duration of the experiment.

3. Results

The sample was activated (by which we mean the exposure of virgin intermetallic to H_2) at 100 °C, then cycled a further 15 times at the same temperature. The magnetization of the sample was initially very small, consistent with its accepted Pauli paramagnetism. During the first absorption of H (cycle 1), which occurs at considerably higher pressure than subsequent absorptions and is accompanied by decrepitation of the sample and profuse dislocation generation, M was not detectably dependent on H/M (the hydrogen-to-metal atomic ratio). During desorption, however, a slight increase in magnetic moment was already discernible, evidently owing to the precipitation of Ni clusters as proposed by Schlapbach [1].

By cycle 6 at 100 °C, the characteristic split desorption plateau indicative of γ-phase formation was apparent. By cycle 16 there was also a clear split in the absorption plateau, and the magnetic moment of the desorbed sample was about 12 times larger than that measured before any hydrogen exposure.

The sample was then desorbed by pumping and cooled to 26 °C, where further cycling took place. The steps in both the absorption and desorption plateaux remained, and were quite stable against further cycling at room temperature.

Fig. 1 shows typical pressure–composition and magnetization–composition phase diagrams, recorded at 26 °C during cycle 46. The intrusion of the γ phase in desorption is signalled, perhaps even more clearly than in the pressure–composition data, by a peak in M in the $\beta+\gamma$ two-phase region. This peak appeared when the split desorption plateau was first observed, and its height eventually saturated while the sample magnetization grew. Hence it appears to be particularly associated with intrinsic magnetism of the γ phase. The corresponding feature in the absorption M–M/H isotherm is much smaller.

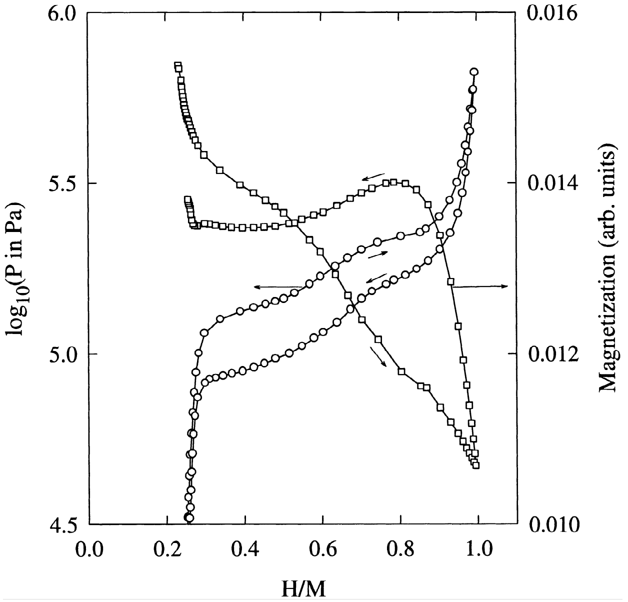

Fig. 1. Pressure–composition and magnetization–composition isotherms, recorded simultaneously at 26 °C after cycling at 100 °C then 26 °C. The steps in the absorption and desorption p–c isotherms, and the peak in the desorption M–c isotherm, are associated with the formation of the γ phase.

Following cycle 62 the sample was heated to above 500 °C and then cooled to room temperature while measuring the magnetization. The result is shown in Fig. 2. The Curie temperature is very close to that of bulk fcc Ni (627 K). This treatment annealed the sample, making reactivation necessary. Absorption–desorption cycling at 26 °C quickly re-established the magnetic properties measured

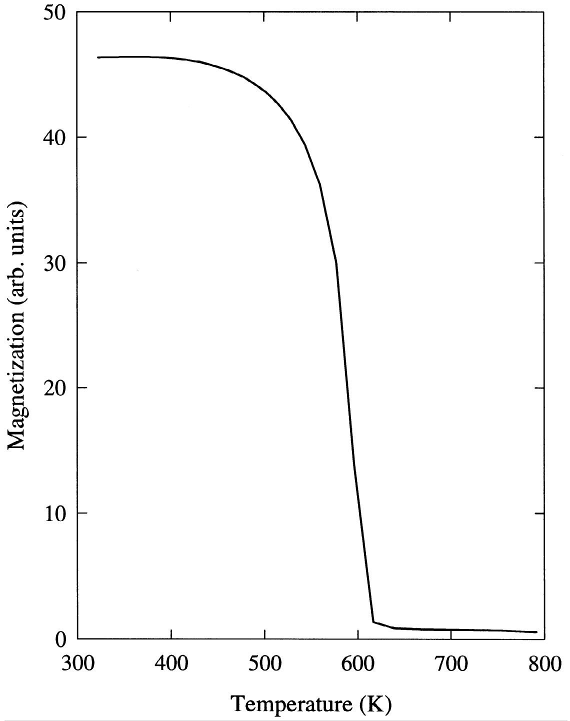

Fig. 2. Magnetization of the sample during cooling from above the Curie temperature, which is very close to that of bulk fcc Ni.

before annealing, albeit with a higher overall magnetization owing to further Ni precipitation during heating to and cooling from 500 °C.

4. Discussion

The steady rise in magnetization with cycling, and the closeness of the Curie temperature to that of Ni, show that the basic ferromagnetism of the sample depends on the Ni precipitates. In order to propose a mechanism for the ferromagnetism, we must consider how the Ni clusters are dispersed, and how sufficient interaction occurs between Ni spins to produce a ferromagnetic state which is apparently the same as in bulk fcc Ni metal.

X-ray and neutron diffraction patterns of many samples which have received similar cycling and heat treatments show no sign of Ni Bragg peaks. Furthermore, the total H capacity of samples cycled at 100 °C remains close to $H/M=1$ (Fig. 1). Therefore, only a small fraction of the Ni atoms in the sample have precipitated. In the early stages of precipitation, the Ni clusters appear to be of low dimensionality [6], consistent with surface precipitation. In samples aged at 400 °C, however, the Ni precipitates were found to contribute discernibly to the diffraction pattern, and proved to be aligned with the $LaNi_5$ lattice [unpublished results of Kisi, Gray, et al.]. Particle-size broadening of powder diffraction patterns is consistent with crystallite sizes considerably less than 1000 Å, compared to a typical powder particle size of order microns [7]. Hence there are many crystallites per powder particle, and the Ni must be dispersed to maintain its crystallographic orientation with the $LaNi_5$ matrix, rather than forming a continuous network at the particle surface.

Accordingly, it would be reasonable to expect the sample to be superparamagnetic, unless a strong cluster–cluster exchange is mediated by the $LaNi_5$–H matrix. The very strong effect of H on the sample magnetization suggests that the hydrided matrix does act in this way, presuming that no H is absorbed by the Ni precipitates themselves.

Several exchange mechanisms can be envisaged. The most likely seems to be that clusters of Ni d-spins, internally coupled as in bulk Ni, interact via polarization of the conduction electrons in the matrix. We would expect the conduction-electron polarization to oscillate with distance, so that the rapid change in magnetization with H concentration could be understood as a consequence of the changing electron density and matrix lattice parameters. This mechanism is consistent with the proximity of the Curie temperature of the whole sample to that of ordinary Ni, so long as the intercluster exchange persists to temperatures above the Ni Curie temperature. This hypothesis could be explored by measuring the Curie temperature of the pure β phase. We are as yet unable to do this because of the very high H_2 pressures required.

Strong magnetic hysteresis occurs between absorption and desorption in the pure β phase, even where the pressure–composition isotherm is reversible. Clearly, the internal magnetic field is changing with H concentration, driven not by a changing external field, but by the changing lattice parameters and electron density. It is therefore feasible that this hysteresis is a manifestation of the formation of domain walls, and their interaction with the sample microstructure as they move under the influence of the changing internal magnetic field.

5. Conclusions

The ferromagnetism of hydrogen-cycled $LaNi_5$–H relies on the precipitation of fcc Ni clusters. The origin of the ferromagnetism appears to be exchange between Ni clusters mediated by the metal–H matrix, probably akin to the 3d-conduction electron-3d mechanism of the RKKY interaction in Heusler alloys. Although it is clear that the α and β (and, presumably, γ) phases have distinct magnetic properties, the dependence of the sample microstructure on detailed thermal history makes it very difficult to delineate them. The hysteresis observed in the magnetization–composition isotherm appears to arise because (i) the isotherm was traced below the magnetic ordering temperature of the β phase and (ii) changing the H concentration changes the internal magnetic field, thus mimicking some of the effects of a changing external field.

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