Magnetic Properties of Monodisperse NiH_x Nanoparticles and Comparison to Those of Monodisperse Ni Nanoparticles

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We produced, for the first time, monodisperse NiH_x nanoparticles with particle diameters of 7.0 nm and investigated their magnetic properties. We also produced monodisperse Ni nanoparticles with nearly the same particle diameters as those of NiH_x nanoparticles as a comparison. The magnetic properties of NiH_x nanoparticles were quite different from those of Ni nanoparticles. We observed two compositional phases in NiH_x nanoparticles, similar to bulk material: one is the nearly pure Ni phase with the blocking temperature (T_B) of 11 K and the other is the hydride phase. We observed T_B of 40 K in Ni nanoparticles.

1. Introduction

Nickel hydride NiH_x and other metal hydrides have been considered to be important materials that can be used for hydrogen storage for both fuel cells and electrodes in batteries.^{3–7} As a solid, NiH_x has an advantage over gas in both handling and application. In addition to these important technological applications, NiH_x has attracted much attention from scientists because both their physical and thermodynamic properties largely depend on *x*.

There exist both theoretical and experimental studies on the magnetic properties of NiH_x for both gas-phase clusters^{8,9} and bulk materials such as films.^{10–20} The magnetic properties of bulk materials changed from ferromagnetism to paramagnetism with increasing *x*. Interestingly, it had been found that NiH_x consists of two magnetic phases,^{10,11,14–20} originating from the limited solubility (~70%) of H atoms in Ni.²⁰ They are the ferromagnetic α -phase (the nearly pure Ni phase, *x* < 0.03) and the paramagnetic β -phase (the hydride phase, *x* > 0.7). The magnetic moments of NiH_x decreased with increasing *x* and eventually became zero (i.e., paramagnetic) when *x* > 0.7. In the case of gas-phase nickel hydride clusters, the magnetic moments were small but nonzero.⁹

In this work, we prepared, for the first time, monodisperse NiH_x nanoparticles with particle diameters of 7.0 nm and investigated their magnetic properties. We also produced monodisperse Ni nanoparticles with the same particle diameters within the experimental limit to see the difference in magnetic

properties between the NiH_x and the Ni nanoparticles. We found that the magnetic properties of NiH_x nanoparticles were quite different from those of Ni nanoparticles. We observed two compositional phases in NiH_x nanoparticles, similar to bulk material.

2. Experimental Procedure

2.1. Preparation. To produce the monodisperse NiH_y nanoparticles, we prepared two solutions in separate flasks, i.e., one with 9 mL of hydrazine (1.0 M solution in tetrahydrofuran) in 8 mL of oleylamine solution and the other with 0.15 g of $Ni(acac)_2$ (acac = acetylacetonate) in 10 mL of oleylamine solution. All chemicals were purchased from Aldrich and used as received. The solutions were magnetically stirred while argon gas flowed. At the solution temperature of 90 °C, the Ni(acac)₂ solution was quickly injected into the other solution. After this, the solution temperature increased to 110 °C and stayed at that temperature for 3-4 h, during which the solution color changed from dark green to thick brown. The solution temperature further increased to 160 °C and stayed at that temperature for about 30 min, during which the solution color changed from thick brown to black. After the solution was cooled to room temperature, a mixture of 15 mL of chloroform and 15 mL of methanol was added to the product solution. After 1 day, the nanoparticle precipitate was separated from the solution. The nanoparticles were diluted with ethanol and then separated from the solution through centrifugation. This process was repeated three times. However, a further heating at 160 °C provided the monodisperse Ni nanoparticles due to dehydrogenation. The dehydrogenation leads to the volume contraction and, thus, the particle diameter

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Figure 1. TEM micrographs of (a) multilayer and (b) monolayer assemblies of NiH_x nanoparticles and (c) multilayer and (d) monolayer assemblies of Ni nanoparticles.

decrease.¹¹ However, nucleation also occurs simultaneously. For the present experimental condition (i.e., \sim 1 h and 30 min heating at 160 °C), the particle diameter did not change. However, a longer heating will certainly yield nanoparticles with larger particle diameters. We summarize the main part of the reaction as follows. That is, as the reaction progresses, the following reaction occurs:

 $Ni(acac)_2 + N_2H_4 \rightarrow NiH_x$ nanoparticles \rightarrow Ni nanoparticles

2.2. Characterization. We characterized the diameters with a transmission electron microscope (TEM) (200 keV, Philips CM200), the structure with an X-ray diffractometer (XRD) (Philips, X-PERT, Cu K α lines, $\lambda = 1.5418$ Å), and the magnetic properties with a Squid magnetometer (Quantum Design, MPMS 7). For the TEM measurements, the nanoparticles were dispersed into benzene solvent. For the magnetic property measurements, the nanoparticles were weighed and then filled into capsules in an inert gas environment. After this, the capsules were sealed with paraffin wax to prevent nanoparticles from air oxidation.

3. Results and Discussion

3.1. TEM Micrographs. Figure 1a,b represents the TEM micrographs of NiH_x nanoparticles. As can be seen in the TEM micrographs, the nanoparticles are monodisperse with particle diameters of 7.0 nm. Also, we present the TEM micrographs of Ni nanoparticles in Figure 1c,d. As can be seen in Figure 1c,d, the Ni nanoparticles are also monodisperse with particle diameters of 7.0 nm.

3.2. XRD Patterns. Figure 2 represents the XRD patterns,²¹ which show that both the NiH_x and the Ni nanoparticles possess the face-centered-cubic (fcc) structure with lattice constants of a = 3.75 and 3.54 Å, respectively. These values are consistent with the corresponding bulk values, respectively.^{10,22–24} The larger lattice constant of NiH_x nanoparticles than that of Ni nanoparticles confirms the volume expansion due to hydrogens, as observed in bulk materials.^{11,24} Here, it is known by neutron diffraction that hydrogen atoms in the NiH_x occupy the octahedral interstitial sites.²⁴ Using Scherrer's formula²⁵ and the



Figure 2. XRD patterns of (a) NiH_x and (b) Ni nanoparticles. The asterisk (*) originates from the glass substrate. The assignments are the Miller indices (*hkl*).



Figure 3. Zero field cooled (ZFC) (\bullet) and field cooled (FC) (\bigcirc) magnetization curves versus temperature of (a) NiH_x and (b) Ni nanoparticles at an applied field of 100 Oe.

full widths at half-maximum (fwhm's) of the peaks, we estimated the average particle diameters for both the NiH_x and the Ni nanoparticles to be ~ 4 nm, which are consistent with the ones observed in the TEM micrographs, respectively.

3.3. Magnetic Properties. We measured the magnetic properties by recording the temperature-dependent magnetization curves (M-T curves) at an applied field of 100 Oe and the hysteresis loops (M-H curves), which are shown in Figures 3 and 4, respectively. From the M-T curves, we estimated the blocking temperatures ($T_{\rm B}$'s). Both the M-T and the M-H curves of Ni nanoparticles show behaviors typical for ferromagnetic materials. The $T_{\rm B}$ and the coercivity at 5 K of Ni nanoparticles were estimated to be 40 K and 270 Oe, respectively. Above the $T_{\rm B}$ of 40 K, the Ni nanoparticles are superparamagnetic.

For NiH_x nanoparticles, there is clearly a $T_{\rm B}$ at 11 K. Based on the magnitude of the magnetic moment, this blocking temperature corresponds to a ferromagnetic to superparamagnetic phase transition. Above 11 K, the magnetic phase relevant to this $T_{\rm B}$ is superparamagnetic. The coercivity at 5 K was measured to be 210 Oe. However, unlike that of Ni nanoparticles, the field cooled (FC) curve of NiH_x nanoparticles deviates from the zero field cooled (ZFC) curve at ~220 K, far above the $T_{\rm B}$ of 11 K, which is further discussed below.



Figure 4. Hysteresis loops of (a) NiH_x and (b) Ni nanoparticles at 5 and 300 K.



Figure 5. FC–ZFC difference curves of NiH_x (\bullet) and Ni (\bigcirc) nanoparticles. The scale in the FC–ZFC difference is arbitrary.

As noticed above, the M-T curve of NiH_x nanoparticles looks somewhat complex. That is, the field cooled (FC) curve deviates from the zero field cooled (ZFC) curve near \sim 220 K, far above the $T_{\rm B}$ of 11 K, whereas the FC curve of Ni nanoparticles deviates from the ZFC curve just above the $T_{\rm B}$ of 40 K, like typical ferromagnetic materials. This unusual behavior in the M-T curve in NiH_x nanoparticles may be more clearly seen in the FC-ZFC difference curve, as shown in Figure 5. In Figure 5, the FC-ZFC difference curve of Ni nanoparticles shows a behavior typical for ferromagnetic materials, i.e., it quickly drops to zero after the $T_{\rm B}$ of 40 K, whereas that of NiH_x nanoparticles shows an additional slow decay between 20 and 220 K after a quick drop up to 20 K. This implies that there should exist another magnetic phase relevant to this slow decay. Looking at the magnitude of the magnetic moments of this unusual magnetic phase in the ZFC curve (Figure 3a), its magnetic moment is not negligible. That is, this unusual magnetic phase corresponds to a very weakly ferromagnetic phase. The upper bound of the $T_{\rm B}$ for this unusual magnetic phase is estimated to be 220 \pm 30 K from the deviation point of the FC curve from the ZFC curve in Figure 3a.

Referring to bulk material, it was found that there existed two magnetic phases, i.e., the ferromagnetic α -phase (the nearly pure Ni phase, x < 0.03) and the paramagnetic β -phase (the hydride phase, x > 0.7).^{10,11,14–20} This phase separation resulted from the limited solubility of H atoms in Ni (i.e., $\sim 70\%$).²⁰ Thus, the existence of the two magnetic phases in NiH_x nanoparticles is also expected because solubility of H atoms in Ni nanoparticles will be also limited as in bulk material. Let us further consider which phase in NiH_x nanoparticles corresponds to which phase in bulk material. The phase with the $T_{\rm B}$ of 11 K



Figure 6. Three repeated measurements (in the order labeled as \bullet , \bullet , and \bigcirc) of the M-T curves of NiH_x nanoparticles at an applied field of 100 Oe. They were measured with time intervals of 1 day.

in NiH_x nanoparticles seems to correspond to the ferromagnetic α -phase in bulk material because both are ferromagnetic. Then, the remaining hydride phase in NiH_x nanoparticles will correspond to the paramagnetic β -phase in bulk material. The former assignment is likely because both are ferromagnetic. The latter assignment is also likely because the paramagnetic behaviors in hysteresis loops in NiH_x nanoparticles were observed. However, another weak ferromagnetism observed in NiH_x nanoparticles as mentioned in the previous paragraph is unusual.

One possibility for the weak ferromagnetism of the unusual magnetic phase in NiH_x nanoparticles may be related to the Ni atoms with hydrogen atom vacancies in the hydride phase. Two kinds of hydrogen atom vacancies may exist. These include the unoccupied octahedral sites by H atoms in NiH_x nanoparticles resulting from limited solubility of H atoms in Ni metal and the superabundant vacancies which are almost exclusively produced at high temperatures (>500 °C) through the coalescence of vacancies formed by the escape of H atoms, as observed by Fukai et al.^{26–28} Since the NiH_x nanoparticles were characterized below room temperature, however, the superabundant vacancies will not be much. In fact, magnetic moments localized to Ni atoms with vacancies had been also noticed in bulk material.¹⁵ From the repeated measurements of the ZFC/ FC curves with time intervals of 1 day, we did not see any increase in the magnetic moments of the curves measured later, as shown in Figure 6. That is, the three M-T curves are identical within the experimental limit, implying that the hydrogen atom vacancies through the dehydrogenation during the measurement of the M-T curves were not produced (or at best, negligibly produced). Thus, the hydrogen atom vacancies in NiH_x nanoparticles, if any were to exist, should be those produced when the NiH_x nanoparticles were synthesized. Another possibility for the weak ferromagnetism may be related to the intrinsic particle size effect of the hydride phase. In fact, unusual ferromagnetisms have been observed in small metal clusters^{29,30} and metal oxide nanoparticles^{31,32} even though their bulk materials are paramagnetic or antiferromagnetic.

The ratio in the amount of the ferromagnetic (i.e., the nearly pure Ni phase) to the paramagnetic (i.e., the hydride phase, 0.7 < x < 1) phases will be much less than 30%, as expected from the x range, i.e., 0.7 < x < 1. This is confirmed from the XRD pattern that even the most intense (111) peak among the peaks arising from the former phase in the XRD pattern is not noticeable (see Figure 2a) even though it seems to weakly occur between the (111) and the (200) peaks of the NiH_x nanoparticles. However, this minor ferromagnetic phase mainly contributed to the magnetic moments in NiH_x nanoparticles as can be noticed from the large magnetic moments observed in both the M-Tand the M-H curves (see Figures 3a and 4a). Although we are not sure, we consider that the nearly pure Ni phase may constitute the core of NiH_x nanoparticles to give the T_B of 11 K.

4. Conclusion

In this work, we produced, for the first time, monodisperse NiH_x nanoparticles (0.7 < x < 1) with particle diameters of 7.0 nm and investigated their magnetic properties. We also produced monodisperse Ni nanoparticles with nearly the same particle diameters within the experimental limit in order to see the difference in magnetic properties between the NiH_x and the Ni nanoparticles. Both NiH_x and Ni nanoparticles possessed the fcc structure. We observed a larger lattice constant in NiH_x nanoparticles, indicating the volume expansion due to hydrogens, as in bulk material. Here, the H atoms are known to occupy the octahedral interstitial sites in Ni. The $T_{\rm B}$ of Ni nanoparticles was estimated to be 40 K. We observed that the NiH_x nanoparticles consisted of two compositional phases, resulting from the limited solubility of H atoms in Ni, as in bulk material. One is the ferromagnetic phase with the $T_{\rm B}$ of 11 K and the other is the paramagnetic hydride phase. Compared to the bulk NiH_x, the former corresponds to the ferromagnetic α -phase (the nearly pure Ni phase, x < 0.03) of bulk material whereas the latter corresponds to the paramagnetic β -phase (the hydride phase, x > 0.7) of bulk material. In addition to these, we observed another weak ferromagnetism in NiH_x nanoparticles. We consider this as due to either the Ni atoms with hydrogen atom vacancies in hydride phase in NiH_x nanoparticles or the intrinsic particle size effect of the hydride phase, or both.

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