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Journal of Alloys and Compounds 468 (2009) 11–14

Journal of ALLOYS AND COMPOUNDS

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Magnetostriction and thermal expansion of interstitially modified $NdFe_{10}V_2Z_x$ (Z = N, H) compounds

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Received 24 October 2007; received in revised form 22 December 2007; accepted 2 January 2008
Available online 14 February 2008

Abstract

$NdFe_{10}V_2$ composites were prepared and the influence of H and N interstitial modifications on their structural and magnetoelastic properties were studied. By hydrogenation, the thermal expansion trace is markedly affected so that hydrogen-induced modification can be proposed as an effective method for monitoring the thermal expansion coefficient of $NdFe_{10}V_2$. Besides, nitrogenation does not have pronounced effect on the thermal expansion behavior of the $NdFe_{10}V_2$ compound. Below the spin reorientation temperature $T_{SR} = 130$ K, the anisotropic magnetostriction $\Delta\lambda$ of the hydride is negligible, while above T_{SR} the saturation value of $\Delta\lambda$ considerably decreases by hydrogenation. Our results show that below $T_{SR} = 130$ K nitrogenation changes the sign of the anisotropic magnetostriction, while above T_{SR} the thermal behaviour of $\Delta\lambda$ is similar to that of the host compound. These results are discussed as due to the influence of interstitial modifications on both the magnetic anisotropy and the magnetization.
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PACS: 75.80.+q; 75.30.Gw

Keywords: Thermal expansion; Magnetostriction; Gas–solid reaction

1. Introduction

With respect to the familiar $Nd_2Fe_{14}B$-type compounds, though the iron-rich $RE(Fe,M)_{12}$ intermetallics (RE = rare earth element, M = non-magnetic element such as Ti, Mo, V, Cr, W or Si) have similar anisotropy field and slightly lower magnetization, they exhibit much higher Curie temperatures and a simpler crystal structure. Because of these attractive properties, they have been widely studied in recent years [1–8]. It is clear that the magnetic properties of $RE(Fe,M)_{12}$ compounds can be considerably improved by insertion of interstitial atoms such as H, N and C [1–3]. For instance, the Curie temperature and the spontaneous magnetization at room temperature of the $NdFe_{10}V_2$ compound are enhanced by about 175 K and 1.22×10^5 A/m, respectively, and the anisotropy field considerably increases from 0.67 to 8 T by nitrogenation [1]. Moreover, it is well established that in some $RE(Fe,M)_{12}$ intermetallic compounds which exhibit a spin reorientation transition, interstitial modification drastically affects this transition due to changes induced in the RE magnetic anisotropy sub-lattice [4].

However, effects of the interstitial modifications on the magnetoelastic properties such as thermal expansion and magnetostriction have been less considered until now. Following our investigations on magnetoelastic properties of the $REFe_{10}V_2$ (RE = Y and Nd) compounds [5], we have studied the impact of H and N interstitial atoms on thermal expansion and magnetostriction characteristics. Recently, we have reported results on the magnetoelastic properties of $YFe_{10}V_2Z_x$ (Z = N, H) compositions [9]. In the present paper, we report on the effect of insertion of H and N interstitial atoms on the thermal expansion and magnetostriction of $NdFe_{10}V_2$.

2. Experimental

$NdFe_{10}V_2$ ingots were prepared by high frequency melting of the constituting elements under purified-argon atmosphere. Then, as-cast ingots were

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doi:10.1016/j.jallcom.2008.01.004

wrapped in tantalum foils and annealed at 960 °C in a 10^{-7} Torr evacuated furnace for 24 h. After complete removal of the outer oxidized layers by sand paper, the alloys were crushed into powders in ethanol to a size less than 200 μm. The hydrogenation and nitrogenation treatments of powders have been executed in an autoclave for 48 h duration under $P = 6$ and 20 bar gas pressures at $T = 250$ and 400 °C, respectively. The amount of interstitial element inserted in the metal matrix was estimated to be $x(H) = 0.9$ and $x(N) = 2.3$ by weighting the samples before and after the gas–solid reactions. Phase identification of the samples was carried out by using a X-ray diffractometer with Fe Kα radiation and a 0.051° step angle.

For magnetostriction measurements, homogeneous and isotropic disk-shaped samples (of 8 mm diameter and 2 mm thickness) were prepared by embedding powders into epoxy resin with the epoxy to alloy powder weight ratio of 5:100. Then the mixtures were compacted as disks under 2 GPa pressure. The epoxy resin was fully dried by post-annealing of the compact mixtures at 150 °C for 2 h. No creep has appeared during magnetostriction measurements.

Magnetostriction and thermal expansion were measured using the familiar standard strain gauge technique. The accuracy of these measurements was better than 2×10^{-6}. By measuring magnetostriction parallel (λ_t) and normal (λ_n) to the applied field direction, the anisotropic ($\Delta\lambda = \lambda_t - \lambda_n$) and volume ($\Delta V/V = \lambda_t + 2\lambda_n$) magnetostrictions were deduced. Thermal expansion coefficients (α) and their average in the 80–300 K temperature interval were obtained by calculating slopes of the experimental curves and the corresponding linear fits.

3. Results and discussion

The X-ray diffraction patterns of the samples revealed the existence of the $NdFe_{10}V_2$ phase belonging to the $ThMn_{12}$ structure, and a small amount of α-Fe as a minor phase. Lattice parameters deduced from the X-ray diffraction analysis (Table 1) were found to agree fairly to literature [6,7]. It is clearly seen that the lattice parameters increase by H and N insertion.

The results of thermal expansion measurements of the $NdFe_{10}V_2Z_x$ (Z = N, H) compounds are presented in Fig. 1. In addition, a thermal expansion trace of the parent alloy is presented for comparison. Indeed the thermal expansion traces of the $NdFe_{10}V_2$ composite and its alloy illustrate that the average thermal expansion coefficient of the host composition ($1.81 \times 10^{-5}\ K^{-1}$) is considerably larger than that of the alloy ($0.52 \times 10^{-5}\ K^{-1}$). This is reasonable because Young's modulus of the resin is much smaller than that of the alloy so that the strains can be more easily transferred to the whole of sample [10].

Moreover, it is obvious that the thermal expansion trace is markedly affected by H insertion, while the thermal expansion behavior of $NdFe_{10}V_2N_x$ is similar to that of the $NdFe_{10}V_2$ host compound. The thermal expansion coefficients at 80 and 300 K are given in Table 1. As it can be seen, the thermal expansion coefficient of $NdFe_{10}V_2H_x$ at room temperature is negative (i.e.

Table 1
Lattice parameters and volume expansion of $NdFe_{10}V_2$ before and after hydrogenation and nitrogenation

Compound	a (Å)	c (Å)	V (Å^3)	$\Delta V/V$ (%)	α ($\times 10^{-5}\ K^{-1}$)	
					80	300
$NdFe_{10}V_2$	8.5610	4.7752	349.977	–	1.16	3.75
$NdFe_{10}V_2N_x$	8.6311	4.7965	357.319	2.1	1.20	4.68
$NdFe_{10}V_2H_x$	8.5686	4.7963	352.148	0.62	1.78	−1.76

Thermal expansion coefficient $\alpha(T)$ at 80 and 300 K.

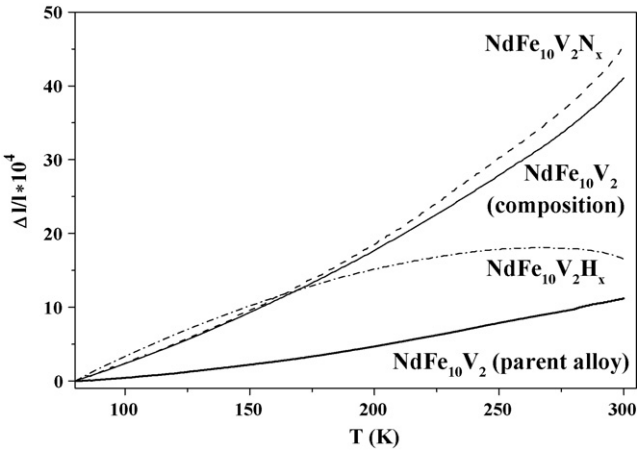

Fig. 1. Thermal linear expansion of $NdFe_{10}V_2$ [5] and $NdFe_{10}V_2Z_x$ (Z = N, H).

clear invar-type behavior) and about −140% smaller than that of $NdFe_{10}V_2$, while thermal expansion coefficient of $NdFe_{10}V_2N_x$ is about 21% larger. Otherwise for temperatures below the spin reorientation temperature $T_{SR} = 130$ K, the thermal expansion coefficient of the interstitially modified compounds are larger than that of the host compound.

These observations can be described as due to the effect of interstitial atoms on the magnetic anisotropy of $NdFe_{10}V_2$ compound for temperatures below and above the spin-reorientation temperature $T_{SR} = 130$ K [1,11–13]. Below T_{SR}, where the magnetocrystalline anisotropy of Nd sub-lattice is dominant, the insertion of the more electronegative N atom at the (0, 0, 1/2) position of the $ThMn_{12}$ structure introduces a positive contribution to the inherently negative second-order crystal field parameter (A_2°), so that the total magnetic anisotropy becomes axial for RE with a negative second-order Stevens factor ($\alpha_J < 0$), such as Nd. Conversely, A_2° remains negative and its magnitude increases by insertion of the more electropositive H atom so that the basal magnetocrystalline anisotropy of Nd sub-lattice is reinforced. On the other hand, above T_{SR} where the magnetocrystalline anisotropy of Fe sub-lattice is dominant, the axial anisotropy weakens (strengthens) by insertion of H (C or N)= atoms. Hence, Fig. 1 emphasizes the direct relationship between variations of the magnetic anisotropy and thermal expansion coefficient, so that at $T < T_{SR}$, where the magnetic anisotropy is reinforced by hydrogenation, the thermal expansion coefficient increases correspondingly. Conversely, at $T > T_{SR}$ where the magnetic anisotropy weakens by hydrogenation, the thermal expansion coefficient of $NdFe_{10}V_2H_x$ decreases. Similarly, the observed changes in the thermal expansion behavior upon nitrogenation, emphasize the similar relation between the magnetic anisotropy parameters and the thermal expansion coefficient.

Fig. 2 shows isothermal traces of the anisotropic magnetostriction of $NdFe_{10}V_2Z_x$ (Z = N, H) compounds versus the applied field at various temperatures. The isothermal traces of host composition are similar to those of parent $NdFe_{10}V_2$ that was studied in our recent paper [5]. Once again, we properly consider the impact of the interstitial modifications in two temperature ranges. Below T_{SR}, the sign of $\Delta\lambda$ changes from

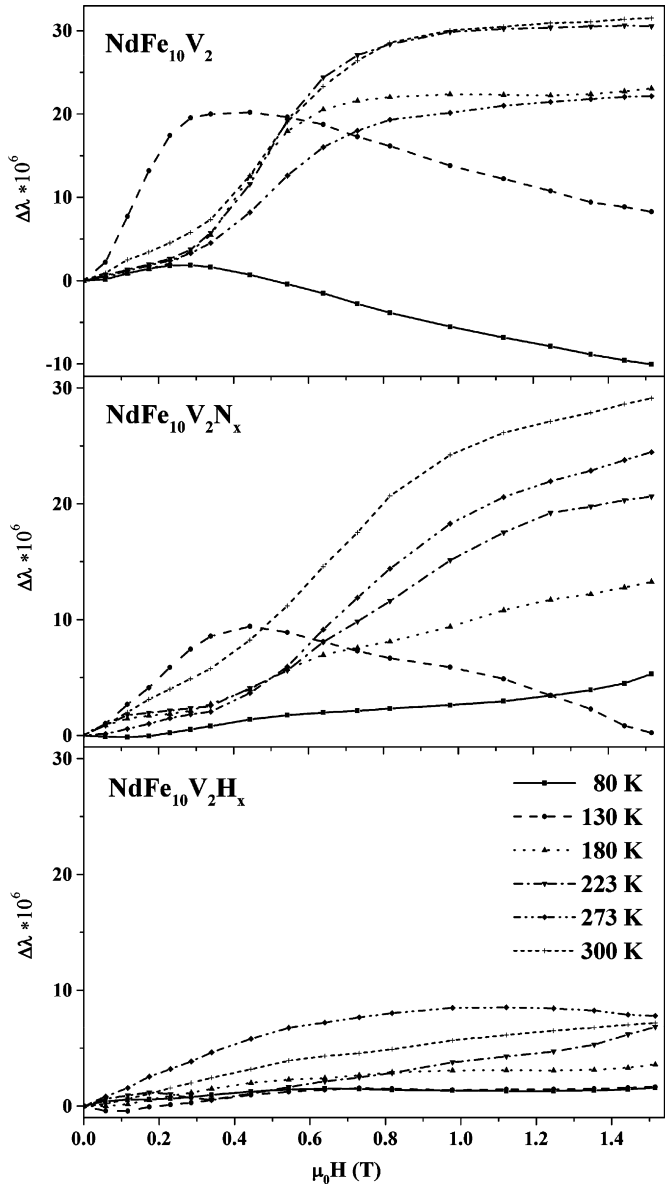

Fig. 2. Anisotropic magnetostriction of the $NdFe_{10}V_2Z_x$ (Z = N, H) interstitials vs. applied fields at typical temperatures.

negative in the host composition to positive for $NdFe_{10}V_2N_x$, besides the magnitude of $\Delta\lambda$ decreases about 50%. However, the anisotropic magnetostriction of the hydride is found to be negligible within our experimental accuracy. Above T_{SR}, the $\Delta\lambda$ traces of the nitride are similar to those of host compound, with a few differences in the saturation trends, while the $\Delta\lambda$ traces of the hydride are very different in magnitude and behavior. It is clear that the initial positive curvature of the $\Delta\lambda$ traces of the host compound is nearly suppressed and that the saturation values of $\Delta\lambda$ considerably decrease after hydrogenation.

All the observed changes of $\Delta\lambda$ can be interpreted in terms of the impact of interstitial modifications of magnetic anisotropy and magnetization. Briefly, the main characteristics of these changes and their origins are the following:

(i) The sign reversal of $\Delta\lambda$ at $T < T_{SR}$ after nitrogenation is consistent with the sign reversal of A_2° and the consequent conversion from the basal to axial magnetic anisotropy.

(ii) The increase of the axial anisotropy at $T > T_{SR}$ after nitrogenation affects the saturation behavior of $\Delta\lambda$ so that in spite of the host compound characteristics, the anisotropic magnetostriction of nitride slowly increases when increasing the applied field even up to $\mu_0\mathbf{H} = 1.5$ T.

(iii) The very small magnitude of the $\Delta\lambda$ of hydride sample at $T < T_{SR}$ sounds reasonable considering that the range of fields we can apply (1.5 T) is large enough to rotate effectively the magnetization axis of the hydride taking into account the increased anisotropy field of the Nd sub-lattice.

(iv) The decrease of the saturation value of $\Delta\lambda$ at $T > T_{SR}$ originates from the lowered magnetic anisotropy and saturation magnetization upon hydrogenation with respect to that of host compound [11–14].

Fig. 3 reveals the relation of the interstitial modifications with the volume magnetostriction of $NdFe_{10}V_2$. Below T_{SR}, the sign of $\Delta V/V$ changes after H and N insertion. Here, it is worth to note that the volume magnetostriction of $NdFe_{10}V_2N_x$ is negligible for applied fields below 0.6 T. At room temperature, the volume magnetostriction of $NdFe_{10}V_2N_x$ is similar to that of host compound, with a minimum around $\mu_0\mathbf{H} = 0.9$ T, while the magnitude of the volume magnetostriction of the hydride increases linearly by increasing the applied field. It is obvious that a linear variation is a favored-type behavior for the relative $\Delta V/V$ of all samples when applying fields above 1 T. Concerning magnetization processes [14], one observes a linear correspondence between the magnetostrictive effects and the rotation of the easy magnetization axis against the magnetic anisotropy forces. In parallel, the negligible low temperature volume magnetostriction of the nitride, as observed below 0.6 T, refers to the "non-magnetostrictive" stretching of the domain walls. However, none of the $\Delta V/V$ curves reaches saturation below 1.5 T applied field. In this situation, high field measurements are required before a complete discussion on the variations

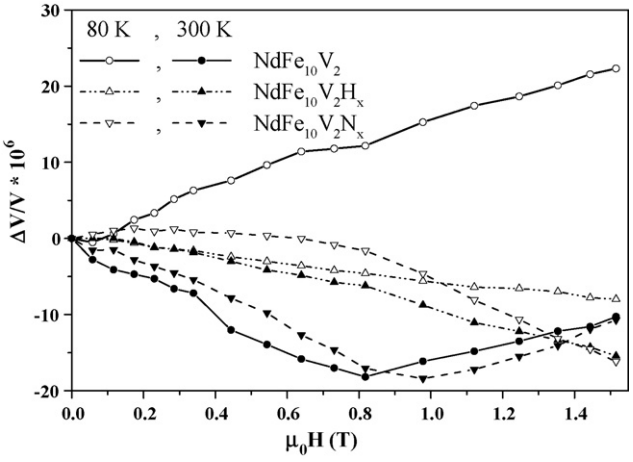

Fig. 3. Typical isothermal traces of volume magnetostriction for the $NdFe_{10}V_2Z_x$ (Z = N, H) interstitials as measured at 80 K (open symbols) and room temperature (solid symbols).

of the volume magnetostriction by interstitial modifications may be provided.

4. Summary

$NdFe_{10}V_2$ parent derivatives were synthesized and the impact of H and N interstitially induced modifications on the crystal structure and the magnetoelastic properties were studied. It is shown that the thermal expansion coefficient of $NdFe_{10}V_2$ compounds is considerably larger than that of the parent alloy, a phenomenon that can be attributed to a lowered stiffness due to the resin matrix. Upon hydrogenation, the thermal expansion curve is markedly affected so that hydrogen modification can be assumed as an effective method to monitor the thermal expansion coefficient of $NdFe_{10}V_2$. In addition, the thermal expansion behavior of $NdFe_{10}V_2N_x$ is similar to that of the $NdFe_{10}V_2$ host compound. All these observations agree fairly with the known effects of interstitial atoms on the magnetic anisotropy of the $NdFe_{10}V_2$ compound.

The present results show that nitrogenation changes the sign of $\Delta\lambda$ below T_{SR} but leaves it similar to that of the host compound above T_{SR}. Moreover, the anisotropic magnetostriction of the hydride is found to be negligible below T_{SR} and the saturation values of $\Delta\lambda$ are considerably decreased by hydrogenation above T_{SR}.

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