Preparation and characterization of the $NdFe_{10}T_2N_x$ (T=Mo,V) compounds with the $ThMn_{12}$ tetragonal-type structure

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The dramatic changes in the magnetic properties observed in the R_2Fe_{17} alloys upon nitrogen absorption have also been observed in the $NdFe_{10}T_2N_x$ (T = Mo,V). The nitrides, prepared at $T = 773$ K and $2\frac{1}{2}$ atm pressure of N_2, showed an increased anisotropy $H_A > 5$ T at RT compared to the $H_A = 0$ for the non-nitrogenated materials. The Curie temperatures increase about 44% and the observed volume expansion is 3.6% for Mo and 2.8% for the V compound although the structure remains the same. A coercive field of 0.97 and 0.45 T has been observed at 4.2 K for $NdFe_{10}Mo_2N_x$ and $NdFe_{10}V_2N_x$ compounds, respectively.

INTRODUCTION

A new series of ternary nitrides has been prepared recently based on the 1:12 structure with general formula $RFe_{10}Mo_2N_x$,[1] where R = rare Earth. The compounds have the same $ThMn_{12}$ tetragonal structure but the lattice constants are increased resulting in about a 4% increase of the unit cell volume. The Curie temperature increases from 80% in Lu to 28% in Gd making these compounds to have T_c suitable for permanent magnet applications.

We report here on the structural and magnetic properties of $NdFe_{10}Mo_2N_x$ and $NdFe_{10}V_2N_x$ which are important since the two compounds have big c-axis anisotropy. For example $NdFe_{10}Mo_2N_x$ has an anisotropy field of 10.3 T at 4.2 K. More important is that the nitrogenated as cast powder presents a coercivity of 0.97 T at 4.2 K and 0.1 T at RT for $NdFe_{10}Mo_2$ and 0.45 T at 4.2 K and 0.08 T at RT for $NdFe_{10}V_2$, respectively.

EXPERIMENT

The $NdFe_{10}Mo_2N_x$, $NdFe_{10}V_2N_x$ compounds were prepared by arc melting the constituents, all 99.99% pure, followed by an annealing in vacuum at 1173 K for a week.

X-ray diffraction showed these samples to be single phase with the 1:12 tetragonal structure. The annealed samples were grounded in a very fine powder $< 10\ \mu$m and heated in an atmosphere of purified N_2 gas for $2\frac{1}{2}$ h at 773 K.

X-ray patterns of the samples were taken in a Siemens D-500 diffractometer with Cu $K\alpha$ radiation. From the x-ray diagrams of the nitrided samples we conclude that the nitrogenation reaches completion since the diffraction peaks of the nitrides were shifted considerably to lower diffraction angles, relative to those of the original $NdFe_{10}T_2$ compounds and remain unchanged for longer nitrogenation times.

The Curie temperatures were determined with a thermomagnetic balance and magnetization curves were measured with a vibrating sample magnetometer on powders oriented in an epoxy resin applying a magnetic field of 2 T. The maximum magnetic field used for the measurements was 2 T.

RESULTS AND DISCUSSION

In Fig. 1 we give the thermomagnetic data for the Mo and V nitrides. From these curves we determine the T_c of the new compounds to be 577 and 885 K, respectively. We observe that the magnetization does not go to zero above the T_c due to α-Fe existing in the samples. Also there is a small kink (see arrows) of the magnetization curves around the T_c of the nitrogen-free compounds (at 410 and 605 K, respectively) showing us that we have traces of the original compounds in our samples.

The structure of the two nitrides is the $ThMn_{12}$ structure with $a = b = 8.671$ Å and $c = 4.870$ Å for the $NdFe_{10}Mo_2N_x$ and $a = b = 8.628$ Å and $c = 4.823$ Å for the $NdFe_{10}V_2N_x$. In Fig. 2 we see (a) the x-ray pattern of $NdFe_{10}Mo_2$ powder as well as (b) the patterns of the nitrided sample not oriented and (c) oriented in an applied field parallel to the plane of reflection. The almost missing (002) reflection and the reduced intensity of the (hkl) reflections which have nonzero l (they should totally disappear if the orientation was perfect) reveal that the c axis of the grains is parallel to the plane of reflection and it proves the uniaxial c-axis anisotropy of the material. The stronger peak of the α-Fe phase also existing in the nitrides coincides with the (330) reflection of our phase. The increased background existing at the lower angles is due to

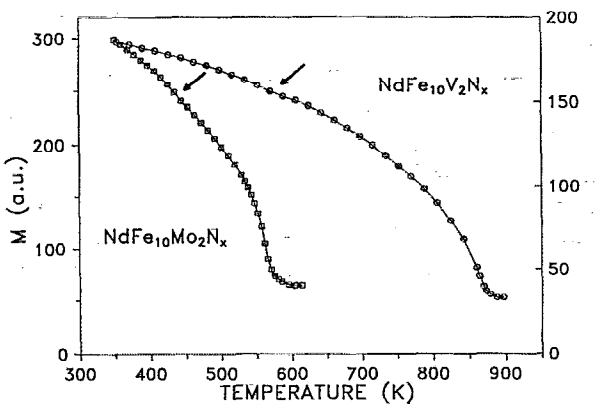

FIG. 1. Thermomagnetic data for the T_c determination of $NdFe_{10}Mo_2N_x$ and $NdFe_{10}V_2N_x$ samples.

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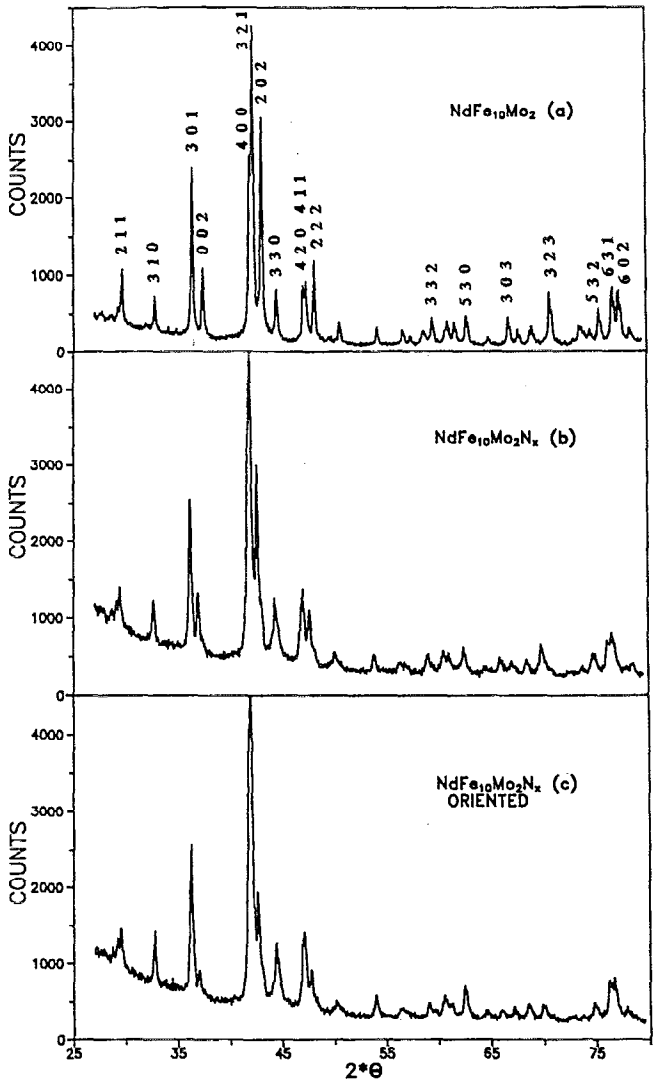

FIG. 2. X-ray powder patterns of (a) $NdFe_{10}Mo_2$, (b) $NdFe_{10}Mo_2N_x$ nonoriented, and (c) $NdFe_{10}Mo_2N_x$ oriented in a field parallel to the plane of reflection.

the glass holder for the nitrogen free sample. Additional background contribution comes from the epoxy resin mixed with the nitride powders. The resin is necessary to make the oriented sample and also is used in the non oriented sample for easy comparison between the two patterns (b), (c). Similar results were observed for the $NdFe_{10}V_2N_x$ sample.

Magnetization curves (Fig. 3) measured parallel and perpendicular to the easy axis of orientation show the large

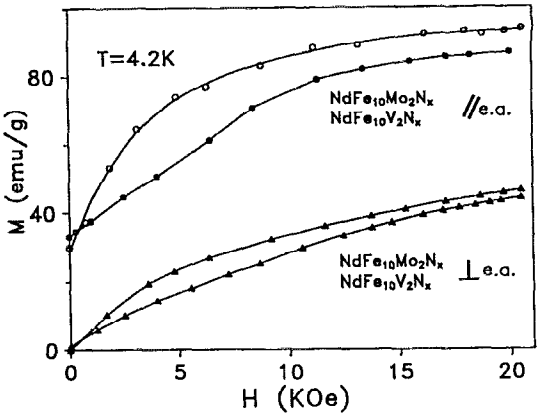

FIG. 3. Magnetization curves of the two compounds measured parallel and perpendicular to the easy axis of magnetization at 4.2 K.

anisotropy of both samples. After linear extrapolation of the high field part of the two curves this anisotropy is approximately determined to be 10.3 T for $NdFe_{10}Mo_2N_x$ and 7.6 T for $NdFe_{10}V_2N_x$. The corresponding values at RT are 7.4 and 5.6 T, respectively. The values of the anisotropy fields determined in such a way are only approximate because it is not certain that the hard axis magnetization remains linear in higher magnetic fields (it could have FOMP transition for example). The M_s values were determined using the law of approach to saturation[2] and are given in Table I. In the same table we give the Curie temperatures as well as summarize the anisotropy fields and the structural constants of the nitrogenated and the parent compounds (the information for the parent compounds was taken from Refs. 3 and 4). Taking into account the Curie temperature of $LuFe_{10}Mo_2N_x$ (T_c = 469 K) we find the exchange integral $J_{Fe\text{-}Fe} = 8.4 \times 10^{-22}$ J between two iron atoms in the $RFe_{10}Mo_2N_x$ series, considering also the T_c of the $NdFe_{10}Mo_2N_x$ compound we find the exchange integral between Nd and Fe atoms $J_{Nd\text{-}Fe} = 8.12 \times 10^{-22}$ J (see Ref. 5). Magnetic loops of the two compounds are given in Fig. 4 parallel and perpendicular to the axis of orientation at 4.2 K. The coercivity is 0.97 T for $NdFe_{10}Mo_2N_x$ and 0.45 T for $NdFe_{10}V_2N_x$. At RT the same values are 0.1 and 0.08 T, respectively.

CONCLUSIONS

The new compounds $NdFe_{10}Mo_2N_x$, $NdFe_{10}V_2N_x$ have big c-axis anisotropy relatively high Curie tempera-

TABLE I. Structure constants, Curie temperatures, saturation magnetizations, and anisotropy fields for $NdFe_{10}Mo_2N_x$, $NdFe_{10}V_2N_x$ as well as for the non-nitrogenated compounds.

	a (Å)	c (Å)	$\Delta V/V$%	T_c (K)	M_s (4.2 K)	H_a (4.2 K)	H_a (300 K)
$NdFe_{10}Mo_2N_x$	8.671	4.870	3.6	577	87 emu/g	103 KOe	74 KOe
$NdFe_{10}Mo_2$	8.589	4.788		410	102 emu/g	...	...
$NdFe_{10}V_2N_x$	8.628	4.823	2.8	885	94 emu/g	76 KOe	56 KOe
$NdFe_{10}V_2$	8.555	4.774		605	128 emu/g	...	...

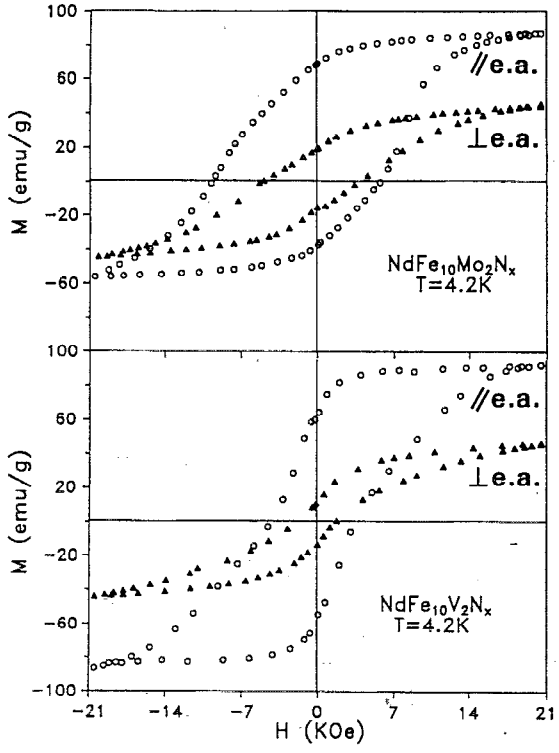

FIG. 4. Magnetic loops parallel and perpendicular to the easy axis of magnetization for $NdFe_{10}Mo_2N_x$ and $NdFe_{10}V_2N_x$ measured at 4.2 K.

tures, and the as-cast powders show high coercivity at 4.2 K. Although they have lower saturation magnetizations than other nitride compounds very likely to be used for permanent magnet applications ($Sm_2Fe_{17}N_{3-\delta}$) they have the potential to be used in applications requiring medium or small energy products.

ACKNOWLEDGMENTS

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