# Structure and magnetic properties of $RFe_{11}TiN_x$ (R=Y, Sm, and Dy)

L. X. Liao, Z. Altounian, and D. H. Ryan
*Centre for the Physics of Materials and Department of Physics, McGill University, Montréal, Québec, Canada H3A 2T8*

Single phase alloys of composition $RFe_{11}Ti$ with R = Y, Sm, and Dy were prepared by induction melting. The samples were nitrided by thermal cycling to 770 K, at a heating rate of 10 K/min, under an atmosphere of nitrogen in a thermopiezic analyzer (TPA). For $YFe_{11}TiN$ the x-ray diffraction (XRD) patterns give $a = 0.8611$ nm and $c = 0.4802$ nm for the tetragonal structure, space group *I4/mmm*. This represents a 3% volume expansion of the nitrogen-free unit cell. The amount of absorbed nitrogen corresponds to one nitrogen atom per formula unit indicating that $RFe_{11}TiN$ is a true nitrogen compound with the nitrogen atoms occupying the 2*b* site in the structure. The expansion of the unit cell is accompanied by a dramatic increase in the Curie temperature for all compounds.

## I. INTRODUCTION

High performance magnets based on rare-earth iron (R-Fe) systems suffer from low Curie temperatures, $T_c$. The recent discovery of the strong enhancement of $T_c$ in $R_2Fe_{17}$ after nitrogenation[1] motivated us to investigate the effects of nitrogenation in other R-Fe systems. We have studied the tetragonal $RFe_{11}Ti$ alloy system because of its large anisotropy fields, $H_A$. For example, in $SmFe_{11}Ti$, $\mu_0 H_A = 14$ T at 273 K.[2] In addition, the $RFe_{11}Ti$ systems (except for R = Tb) have uniaxial (*c* axis) anisotropy above room temperature.

## II. EXPERIMENTAL METHODS

Alloys of composition $RFe_{11}Ti$ with R = Y, Sm, and Dy were prepared by induction melting appropriate amounts of Fe (99.99%), R (99.9%), and Ti (99.9%) on a water-cooled copper boat under Ti-gettered Ar. To ensure the homogeneity of the ingots, all alloys were melted at least three times. To improve the homogeneity of the $SmFe_{11}Ti$ alloys, we used elemental powders which were pressed into a pellet prior to induction melting. An excess of 2% Sm was added to the sample to compensate the mass loss due to evaporation of Sm during melting. Nitrogenation of the samples was carried out by heating pulverized samples (~40 mg) in a thermopiezic analyzer (TPA)[3] in approximately 1 bar of $N_2$ gas. The nitrogen content of the alloy was determined from the pressure change observed during the nitrogenation process. The structural data on $RFe_{11}Ti$ and their nitrides were obtained by an automated Nicolet-Stöe powder diffractometer with Cu *Kα* radiation. The magnetic transition temperatures, $T_c$, were measured by a thermomagnetic analyzer (Perkin-Elmer TGA-7).

## III. RESULTS AND DISCUSSION

X-ray diffraction scans of all as-made samples showed the single phase nature of the $RFe_{11}Ti$ alloys. The structures are isomorphous with the $ThMn_{12}$-type structure. An example of a diffraction pattern obtained for $YFe_{11}Ti$ is shown in Fig. 1(a). The reaction between nitrogen gas and $RFe_{11}Ti$ intermetallic compounds is very similar to that observed in $R_2Fe_{17}$ alloys.[4] The samples begin to absorb nitrogen at about 720 K, and the maximum absorption rate occurs at around 770 K. The nitrides of $RFe_{11}Ti$ were obtained by heating at 10 K/min to 770 K and held at that temperature for varying times. From the pressure changes during the heat treatment in the TPA, the nitrogen content $x$ in $RFe_{11}TiN_x$ was determined to be $1 < x < 1.6$. A typical example of TPA trace for $YFe_{11}Ti$ is shown in Fig. 2. For some samples, especially after long annealing times at high temperatures, the presence of a relatively high concentration of α-Fe was observed. These samples gave values of $x$

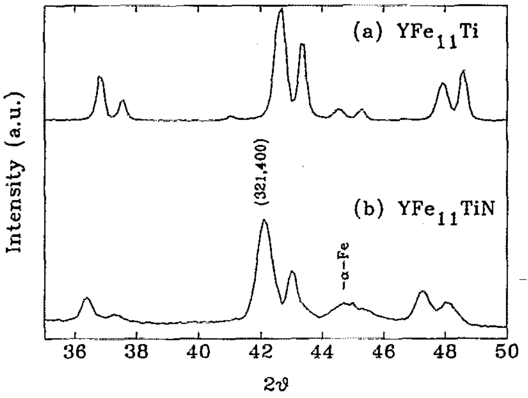

FIG. 1. X-ray diffractometer scans for $YFe_{11}Ti$ (a) before and (b) after nitrogenation.

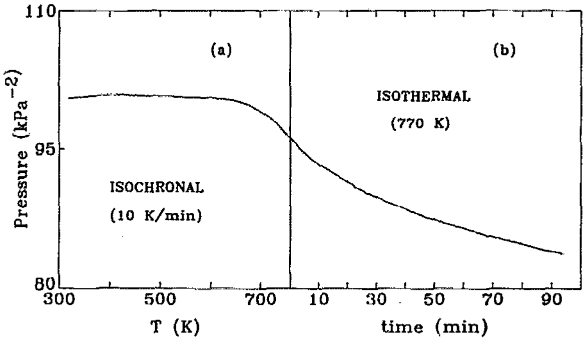

FIG. 2. TPA traces for $YFe_{11}Ti$ in 1 bar of $N_2$ gas. (a) Isochronal heating to 770 K at 10 K/min and (b) isothermal annealing at 770 K for 100 min.

TABLE I. Structure and magnetic data for $RFe_{11}Ti$ and $RFe_{11}TiN$.

| Compound | $a$ (nm) | $c$ (nm) | $V$ ($nm^3$) | $\Delta V/V$ (%) | $T_c$ (K) |
|---|---|---|---|---|---|
| $YFe_{11}Ti$ | 0.8499 | 0.4783 | 0.3455 | | 521 |
| $YFe_{11}TiN$ | 0.8611 | 0.4802 | 0.3560 | 3.06 | 756 |
| $DyFe_{11}Ti$ | 0.8484 | 0.4772 | 0.3434 | | 548 |
| $DyFe_{11}TiN$ | 0.8576 | 0.4805 | 0.3534 | 2.9 | 760 |
| $SmFe_{11}Ti$ | 0.8552 | 0.4782 | 0.3497 | | 595 |
| $SmFe_{11}TiN$ | 0.8647 | 0.4821 | 0.3604 | 3.06 | 743 |

as large as 1.6 implying that decomposition had already occurred during the thermal treatment during which extra nitrogen was absorbed in the formation of RN.

The nitrides were examined by x-ray diffraction and TGA. The diffraction results show that the nitrided samples retain mainly the $ThMn_{12}$ structure with an expanded lattice. In addition, it was found that small amounts of solid solution of $\alpha$-(Fe,N) and poorly crystallized rare-earth nitride were present in all alloys suggesting the metastable nature of these nitrides. Figure 1(b) shows a diffraction scan of $YFe_{11}TiN_x$. The expansion of the unit cell is clearly seen [compare with Fig. 1(a)]. The lattice constants for $RFe_{11}TiN_x$ calculated from the x-ray diffraction patterns are listed in Table I. The relative cell volume increase $\Delta V/V$, also shown in Table I, shows a consistent $\sim 3\%$ volume expansion over the nitrogen-free unit cell for all the compounds.

Curie temperatures of $RFe_{11}Ti$ and their nitrides were determined using TGA in a small field gradient. Examples of these measurements are shown in Fig. 3. Figure 3(a) shows a TGA scan of $SmFe_{11}Ti$ and Fig. 3(b) shows a TGA scan after nitrogenation. A small amount of $SmFe_{11}Ti$ phase is still present after nitrogenation. It is evident that the nitrogen uptake results in a dramatic increase in Curie temperature (Table I). For $SmFe_{11}Ti$, nitrogenation increases the Curie temperature from 595 to 743 K. In many R-Fe systems, $T_c$ is very sensitive to the Fe-Fe distance, therefore the $T_c$ increase after nitrogenation is attributed to the reduction of the negative exchange interactions associated with the Fe-Fe configurations.

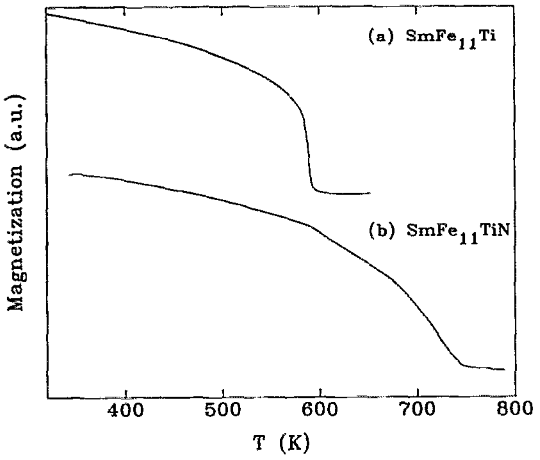

FIG. 3. Thermomagnetic scans of $SmFe_{11}Ti$ (a) before and (b) after nitrogenation.

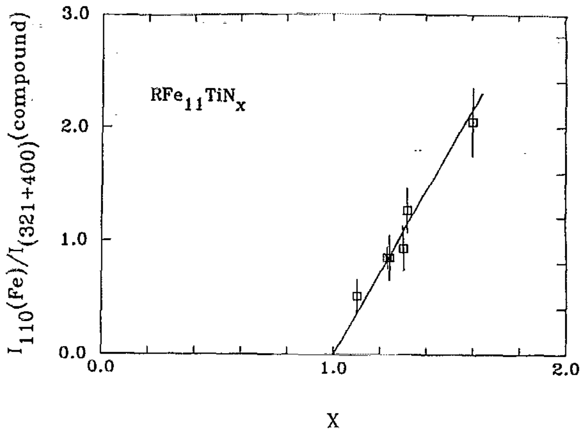

FIG. 4. X-ray intensity ratio of the $\alpha$-Fe (110) line to that of the (321) and (400) lines of the tetragonal compound as a function of total absorbed nitrogen.

An interesting and common feature of these alloys is that they always give the same Curie temperature and the same unit cell for each rare-earth system irrespective of the thermal treatment involved in the nitrogenation process. This implies that the nitrides are true compounds. The presence of $\alpha$-(Fe,N) diffraction peaks in the nitrided samples suggested some RN formation as well.[4] In Fig. 4, we have plotted the x-ray intensity ratio of the $\alpha$-Fe (110) diffraction line to that of the (321) line of the tetragonal compound against total absorbed nitrogen, $x$, as measured directly by the TPA. The data suggests that the single phase compound, free from $\alpha$-Fe and RN, should have $x = 1$. Therefore, we propose that the composition of the nitrides be represented by $RFe_{11}TiN$. For the $R_2Fe_{17}N_x$ for $R = Y$ compounds, the cell expansion is about 7% and $x = 2.6$ (Ref. 4) consistent with our cell expansion of 3% and $x = 1$. The only available site for two nitrogen atoms per unit cell in the $I4/mmm$ space group is the $2b$ site. Assuming a R-N close atomic contact we obtain a value of 0.08 nm for the radius of N. This is in good agreement with the value of 0.075 nm for the covalent atomic radius of nitrogen.

## IV. CONCLUSIONS

We have shown that the nitrides of composition $RFe_{11}TiN$ can be prepared by the reaction of $RFe_{11}Ti$ and nitrogen gas at 770 K in a thermopiezic analyzer. The nitrided samples mainly retain the $ThMn_{12}$-type structure with an enlarged unit cell and with the nitrogen atoms occupying the $2b$ site. The volume expansion of the nitrogen-free unit cell was 3% for all compounds. This expansion of the unit cell is accompanied by a dramatic increase of the Curie temperature.

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