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Magnetic and structural properties of melt-spun rare-earth transition-metal intermetallics with $ThMn_{12}$ structure

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The magnetic and structural properties of melt-spun $R_8Fe_{84}Ti_8$ with R = Nd, Sm, Dy, Gd and $R_8(Fe,Co)_{76}[V(Mo)]_{16}$ with R = Nd, Sm have been studied with x-ray diffraction, transmission electron microscopy, and magnetic measurements. The tetragonal $ThMn_{12}$-type structure was found in all alloys after annealing at about 700 °C. The Curie temperature (T_c) of the as-spun amorphous samples was in the range of 40–100 °C. Crystallized $Nd_8(Fe_{1-x}Co_x)_{84}Ti_8$ samples with the 1:12 structure have a T_c around 250 °C for $x = 0$, reaching the value of 660 °C for $x = 0.5$ and then decreasing again to 490 °C for $x = 1$. ac susceptibility studies on Co-substituted samples showed magnetic transitions in the temperature range 100–200 K. The coercivity was found to be strongly dependent on the microstructure. The highest value of H_c (2 kOe) was obtained in Sm-Fe-Ti samples with a grain size about 500 Å. The upper value of H_c is low because of the presence of some α-Fe in crystallized ribbons.

I. INTRODUCTION

The search for iron-rich rare-earth alloys for permanent magnet applications has received added stimulus with the discovery[1] of R-Fe-B magnets with the tetragonal $Nd_2Fe_{14}B$ phase.[2] A new possible candidate for permanent magnet development is a ternary intermetallic compound having a uniaxial crystal structure of the $ThMn_{12}$ type. The ternary $ThMn_{12}$-type compounds occur when iron and rare-earth elements are combined with a small amount of vanadium, titanium, chromium, molybdenum, tungsten, silicon,[3] or aluminum.[9] Magnetic measurements showed that these compounds have relatively high Curie temperatures and some of them have a sufficiently high magnetization and magnetocrystalline anisotropy which allow them to be considered as potential candidates for permanent magnet materials.[4–9]

The purpose of this paper is to investigate the magnetic and structural properties of several melt-spun samples having the $ThMn_{12}$-type structure. In particular, melt spinning was used to prepare fine-grain microstructures that could lead to high coercivities and therefore determine which of the alloys are promising for permanent magnet development.

II. EXPERIMENT

Several samples with composition $R_8Fe_{92-x}T_x$ (R = Sm, Nd, Dy, or Gd and T = V, Mo, or Ti) and $Nd_8(Fe_xCo_{1-x})_{84}Ti_8$ were prepared by arc melting starting materials of at least 99.9% purity under purified argon gas. Pieces of the ingots were then made into ribbons using the melt-spinning technique. The ribbon samples were annealed at about 700 °C for times in the range of 1–15 min. The annealing temperature was determined by differential scanning calorimetry (DSC) which showed an exothermic peak (related to crystallization) at about 650 °C. Samples were studied before and after annealing by x-ray diffraction using Cr$K\alpha$ radiation. The magnetic measurements were made with a vibrating sample magnetometer.

The homogeneity and chemical composition of the samples were also studied with energy dispersive x-ray analysis (EDXA). Transmission electron microscopy was used to examine the microstructure of several samples.

III. RESULTS AND DISCUSSION

A. Crystal structure and microstructure studies

X-ray diffraction studies of as-spun $R_8Fe_{84}Ti_8$ samples showed diffuse rings characteristic of amorphous materials. The amorphousness was also confirmed by DSC and thermomagnetic data. Samples containing V or Mo were microcrystalline in the as-spun state. Similar studies in all the ternary Fe-rich alloys have shown that the tetragonal $ThMn_{12}$-type phase is formed for all crystallized samples studied. The lattice parameters for $Sm_8Fe_{84}Ti_8$ were found to be $a = 8.58$ Å and $c = 4.79$ Å, which are close to those reported by Buschow.[4]

Electron diffraction also confirmed the presence of the $ThMn_{12}$-type phase. Figure 1 shows an example of a selected area diffraction pattern of $Sm_8Fe_{84}Ti_8$, which is in good agreement with the phase with lattice parameters $a = 8.54$ Å

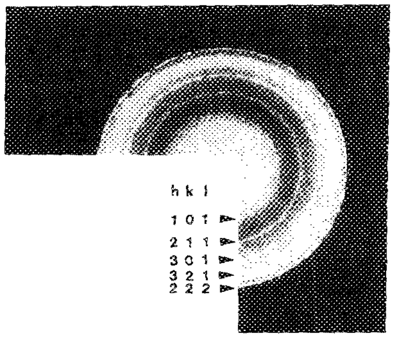

FIG. 1. Selected area diffraction of $Sm_8Fe_{84}Ti_8$ crystallized ribbons having the $ThMn_{12}$-type structure with lattice constants $a = 8.54$ Å and $c = 4.77$ Å.

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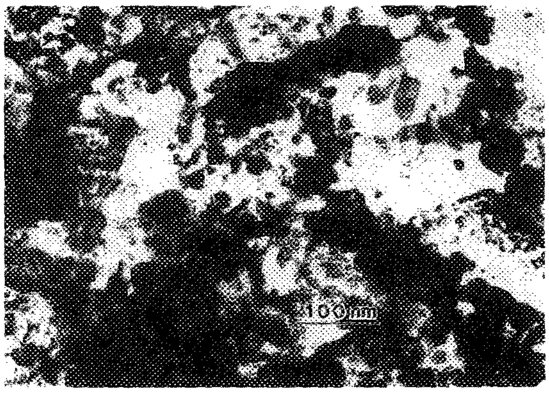

FIG. 2. Typical microstructure found in crystallized ribbon samples, $Sm_8Fe_{84}Ti_8$, with an average grain size of 500 Å.

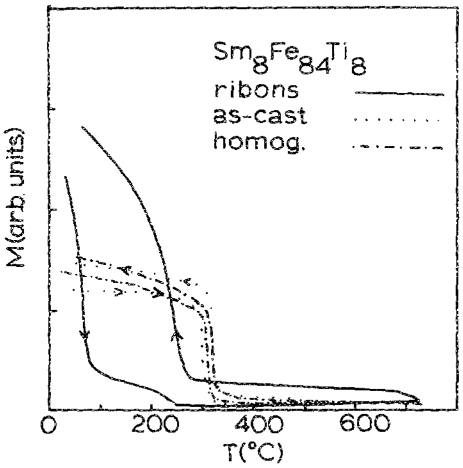

FIG. 4. Thermomagnetic data $[M_H(T)]$ for $Sm_8Fe_{84}Ti_8$ in a field of 300 Oe.

and $c = 4.77$ Å. This way of determining lattice parameters is not as accurate as x-ray diffraction but the c/a ratio is very close to that found by x rays. Transmission electron microscope studies showed a fine-grain structure (Fig. 2) with an average grain size of about 500 Å, similar to that observed in melt-spun R-Fe-B alloys. Detailed microstructure studies on annealed samples showed the presence of α-Fe and possibly a bcc Fe-T alloy (T = V, Mo, or Ti) as also found by De Mooij and Buschow[3,9] in samples with relatively low vanadium concentration. The presence of α-Fe in annealed samples has also been reported by other investigators.[5-8] Samples with smaller grain size had higher H_c values but below 2.5 kOe. Lorentz microscope studies showed domain walls along grain boundaries (Fig. 3).

B. Magnetic measurements

The Curie temperatures of the ribbons were determined from thermomagnetic data $[M_H(T)]$. A heating and cooling rate of approximately 10 °C/min was used in an applied field of 300 Oe. The temperature was held near 700 °C for about 1 min. A typical plot is seen in Fig. 4. The Curie temperature of the amorphous phase is 70 °C for the $Sm_8Fe_{84}Ti_8$ sample; after crystallization the Curie temperature of the 1:12 phase is 254 °C. However, the Curie temperature of the as-cast and homogenized samples is found to be higher (302 °C) than the ribbon samples. This discrepancy may be attributed to differences in chemical composition between the as-cast and melt-spun samples. Energy dispersive x-ray analysis data (EDXA) showed a slightly lower Fe concentration in the ribbon samples than in the as-cast or homogenized samples. This result is in agreement with the results obtained by Buschow and co-workers where T_c is found to increase with increasing in the Fe:T ratio where T = Si, Ti, V, Cr, Mo, or W. However, the small composition difference may not account for the much lower T_c of ribbons. Another possibility is the site occupation of Ti atoms which may be different in ribbons than in bulk samples.

The crystallized ribbons in these samples showed larger coercivities than as-cast or homogenized samples where the coercivities are less than 750 Oe at room temperature. The highest room-temperature coercivity obtained was 2 kOe in a $Sm_8Fe_{84}Ti_8$ sample (Fig. 5), where the as-cast sample of this composition had a coercivity of 750 Oe. The coercivity was found to be strongly temperature dependent (Fig. 6), indicating a strong thermal activation process.

All Sm-containing samples showed higher coercivities. This is consistent with the anisotropy data of Buschow[3] which showed an easy axis for the Sm-Fe-V samples with an anisotropy field $H_A \approx 15$ T. The Nd-containing compounds have an easy plane and that would justify the much lower coercivities obtained in this system.[7] The coercivities ob-

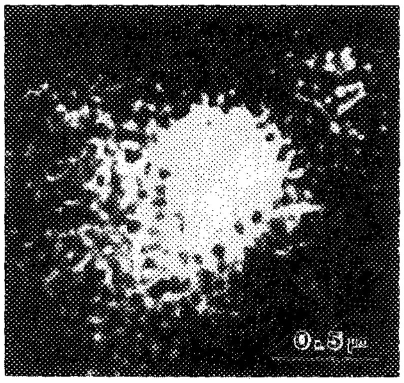

FIG. 3. Magnetic domain walls in Sm-Fe-Ti.

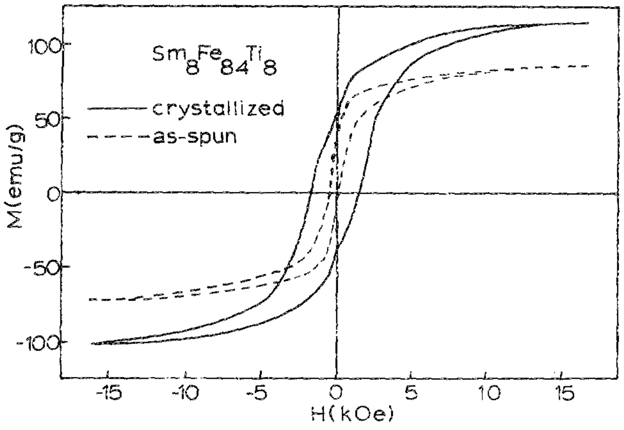

FIG. 5. Hysteresis loop for $Sm_8Fe_{84}Ti_8$ at room temperature.

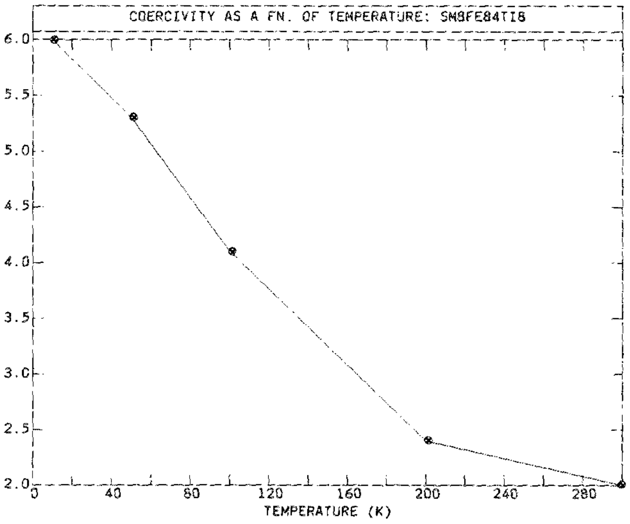

FIG. 6. $H_c(T)$ from 300 to 10 K for $Sm_8Fe_{84}Ti_8$ crystallized ribbons.

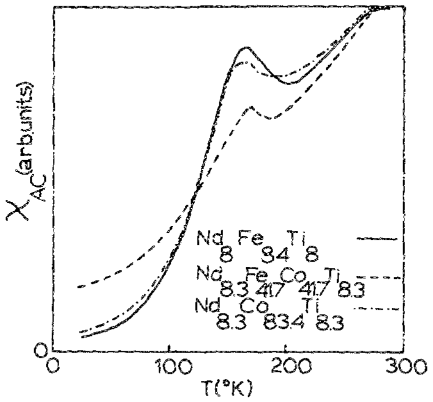

FIG. 7. ac susceptibility for as-spun Nd-Fe(Co)-Ti samples.

tained in these compounds are much lower than those obtained in $R_2Fe_{14}B$ alloys despite the fact that the anisotropy fields are comparable. The lower coercivities can be explained by the large amount of α-Fe which is found in all the samples after crystallization.

ac susceptibility data on crystallized ribbons showed no additional magnetic transitions below room temperature down to 77 K. However, in as-spun ribbons a small peak occurs just below room temperature and at about 170 K (Fig. 7 for samples with cobalt substitution). Thermomagnetic measurements using a SQUID magnetometer for a $Nd_{8.3}Fe_{41.7}Co_{41.7}Ti_{8.3}$ sample showed a large change in magnetization at 170 K with the magnetization increasing with increasing temperature. This magnetic transition may be related to spin reorientation. Preliminary hysteresis loop measurements for the same sample below and above the transition temperature (10 and 190 K) showed coercivities of 3 and 0.2 kOe, respectively. This large change in H_c is attributed to this transition. Further studies are currently being made to clarify these transitions.

IV. CONCLUSIONS

The 1:12 phase has been observed in all the melt-spun samples studied. The Curie temperature of this phase is found to be lower in the ribbon samples. The coercivity was found to be strongly dependent on the heat treatment and therefore on microstructure. The lower values of H_c have been attributed to the presence of α-Fe precipitates. We believe that further studies are needed to find the right heat treatment that will not induce α-Fe precipitation and therefore would lead to high H_c values.

ACKNOWLEDGMENTS

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