Characterization of the Structural and Magnetic Properties of $Nd_{16}Co_{76-x}Ru_xC_7B$ Alloys

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The $Nd_{16}Co_{76-x}Ru_xC_7B$ system has been investigated to assess the effect of boron-carbon combined addition on the ferromagnetic behavior of these intermetallic compounds. The results indicate that the addition of 1 at.% B favors the formation of the tetragonal magnetic phase 2:14:1 in these alloys. With the increase of the Ru concentration is observed an expansion of the lattice in the basal plane as well as a contraction along the *c* direction of the tetragonal unit cell. The Curie temperature decreases from 432 K at x = 6 to 421 K for x = 27, whereas the saturation magnetization has a steep decrease. The highest T_C value has been verified for the alloy with the largest *c* parameter, despite its *a* parameter is the smallest one. In comparison to isotypic borides and pure carbides, a loss of coercivity and remanence is observed.

Keywords: Carbides; Borides; Rare-earths; Permanent magnets; Ferromagnetism

I. INTRODUCTION

With the advent of the family of the rare-earth-transition metal (R-T) intermetallic compounds an extensive effort has been dispensed to improve their magnetic properties in technological applications[1–29]. High energy magnets were developed on the basis of these materials which are able to meet various needs in high technological industries where high performance has been long sought. Ever since the first reports the $Nd_2Fe_{14}B$ compound has been on the focus of attention as a promising permanent magnetic material. The crystal structure of $Nd_2Fe_{14}B$ is tetragonal with Fe ions on six sites, $16k_1$, $16k_2$, $8j_1$, $8j_2$, 4e and 4c, Nd ions on two sites, 4f and 4g, and B ions also on 4g. The Curie temperature is 585 K, the saturation magnetization is 37.3 μ_B/fu at 4.2 K and a energy product of $\approx$ 50.5 MGOe has been attained[17]. Intensive research has been devoted to investigate whether other elements combined can stabilize a structure similar to 2:14:1. In general Cu, Nb, Ti and Ga substitutions are very destructive to the formation of the 2:14:1 hard magnetic phase. The substitution of C for B in the 2:14:1 boron-based compounds was first reported by Bolzoni et al. in the $Nd_2Fe_{14}B_{1-y}C_y$ system[18]. Boron and copper addition can accelerate the formation of $Nd_2Fe_{14}C$; an increase of the anisotropy field as well as a decrease of T_C and the saturation magnetization has been observed. The role of boron is believed to be of that of stabilizing the tetragonal compound, whereas a deficiency of boron leads to the formation of Nd_2Fe_{17} as a second phase. However, the carbides are known to be less stable than the borides. The lattice is contracted in comparison with the isomorphous borides and their T_C values are also slightly lower. As compared to the borides, the carbides exhibit higher coercivities. $Nd_2Fe_{14}C$ possess a higher anisotropy field than that of $Nd_2Fe_{14}B$.

The carbides are magnetically hard, like the borides, but unlike them they usually do not crystallize directly from the melt, which allow to achieve high coercivities in cast materials. The coercivity mechanism in the carbides must differ from that in the sintered borides because really high coercivities are not attainable in bulk alloys with boron alone. However, a large coercivity can be developed from an appropriate microstructure. The common structure of the tetragonal R-Fe borides and carbides suggests that they should form solid solutions over a wide range. This can be checked readily because the lattice parameter *c* of borides and carbides differs sufficiently that phase separation would not escape detection. Co substitution enhances the Curie temperature, whereas decreases both the coercivity and the remanence of Nd-Fe-Co-C-based alloys[19]. Si substituted Nd-Fe-C present enhanced magnetic properties whereas Al substitution increases the coercivity slightly. Mn substitution increases the temperature limit for the formation of the tetragonal phase. However, the magnetic properties are relatively poor. Nb substitution increases the amount of both α-Fe and the Nd-rich phase besides the formation of $Nd_2(Fe,Nb)_{1-x}C_x$.

$Nd_2Fe_{14}B$ resembles $Nd_2Fe_{14}C$ in many respects, including Nd moments close to the free-ion values. The largest Fe moment is at the $8j_2$ site and there is an analogous thermal-expansion anomaly generated by the spontaneous volume magnetostriction of the Fe sublattice. Ti addition decreases the magnetic properties drastically due to the formation of large amounts of $Nd_2(Fe,Ti)_{1-x}C_x$. All substituted Nd-Fe-C alloys contain at least three phases. A Nd-rich phase, Nd-carbides and small amount of α-Fe still exist in the substituted alloys. Cu, Nb, Ti and Ga substitution inhibit the for-

TABLE I: Composition, lattice parameters, c/a ratio, unit cell volume and Curie temperature of the $Nd_{16}Co_{76-x}Ru_xC_7B$ alloys.

x	a ($\AA$)	c ($\AA$)	c/a	V_o ($\AA$)^3	T_C (K)
6	7.650	12.252	1.601	717.02	432
27	7.822	11.425	1.461	699.02	421

mation of the 2:14:1 phase seriously. Both the formation of the hard magnetic phase and the evolution of the microstructure are responsible for the changes of magnetic properties. In the $Nd_2(Fe,Ni)_{14}B$ system the Ni atoms preferentially replace Fe on the 16 k_2 and 8j_2 sites. Besides, the changes in the hyperfine parameters suggested that the Ni interactions are localized, that is, confined to the nearest neighbors. The Curie temperature is mainly determined by the interatomic distances between Fe-Fe pairs. In $Nd_2Fe_{14}B$ the exchange interactions of 8j_1-16k_2 and 8j_1-8j_1 Fe pairs are negative; all others are positive. Partial substitution of B by C produces a small decrease in the saturation magnetization and in the Curie temperature. It has been seen that Co, Si and Al substitution does not affect the formation of the hard magnetic phase in the carbides. T_C is lowered with C addition while a appreciable increase has been verified when Fe is partially substituted by Co. In this contribution we investigate the effect of the carbon substitution for boron on the magnetic properties of these borides. The experimental techniques of X-ray diffraction, calorimetric and magnetization measurements have been used in this study.

II. EXPERIMENTAL DETAILS

$Nd_{16}Co_{76-x}Ru_xC_7B$ alloys with nominal compositions x = 6 and 27 were prepared from the starting materials (all with 99.9% purity) by melting several times the mixtures of the elements to obtain a homogeneous alloy in a vacuum arc furnace with argon atmosphere. The weight loss after melting and heat treatment was evaluated as $< 1\%$, and thus the nominal composition has been accepted as accurate. The ingots were sealed in an evacuated quartz tube and annealed for 3 days at 1000°C and then quenched rapidly to room temperature in water. The X-ray diffraction analysis was carried out on powdered polycrystalline samples by using Cu-K_α radiation. The Curie temperatures were determined by scanning magnetization versus temperature curves with a magnetobalance above room temperature (300 K). Hysteresis loops were registered at 300 K in a field up to 15 kOe by using a vibrating sample magnetometer.

III. RESULTS AND DISCUSSION

The analysis of the results of the X-ray diffraction revealed that, with the substitution of Ru for Co, these compounds possess the tetragonal 2:14:1 ($P4_2/mmm$) hard magnetic phase up to x = 27. It is formed mixed with secondary phases, which are probably a mixture of a Nd-rich phase with Nd_2C_3, α- and ε-type structures, as has been observed in earlier investigations in similar systems[20, 24, 26]. The diffractograms are shown in Fig. 1 and the corresponding lattice parameters of the main phase are listed in Table 1. With the increase of the Ru concentration, in Fig. 1 one can see a broadening of the Bragg peaks thus indicating smaller grain sizes as well as a tendency for amorphization.

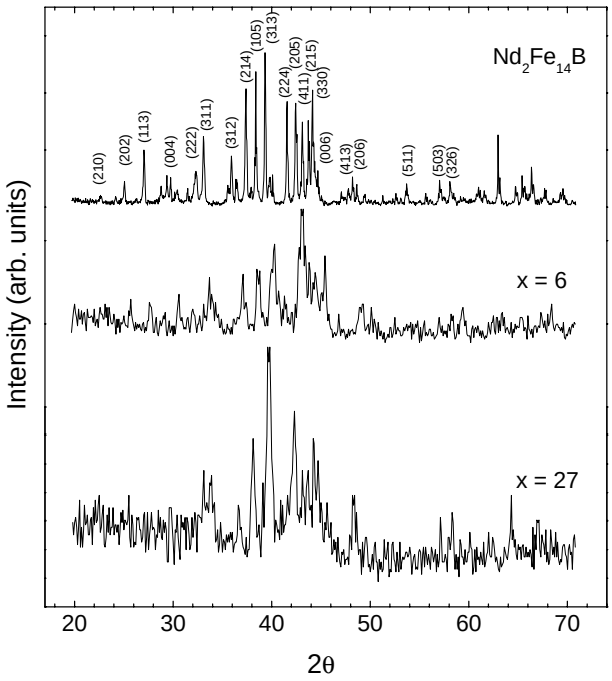

FIG. 1: X-ray diffraction patterns of $Nd_{16}Co_{76-x}Ru_xC_7B$ alloys. The marked reflections refer to the 2:14:1 tetragonal phase of $Nd_2Fe_{14}B$ which is shown at the top for the sake of comparison.

As it can be seen from Table 1, with the addition of Ru the lattice has an expansion along the a direction of the unit cell (basal plane), whereas along the c direction a shrink is observed. As a result, the unit cell volume decreases. The c/a ratio also decreases with the increase of the Ru concentration. $Nd_2Fe_{14}B_{1-x}C_x$ has been confirmed to form in the $Nd_2Fe_{14}B$ structure up to $x = 0.9$ after an appropriate annealing[17]. Lattice parameters show a linear dependence on x: a increase, c decreases and the cell volume decreases. The same behavior is observed for the studied alloys.

Results of an earlier investigation in the $Nd_2Fe_{14-x}Ru_xB$ system have shown that only one phase is formed for a Ru concentration up to 14 at. % Ru. In the $Nd_{16}Co_{76-x}Ru_xC_7B$ alloys, at higher Ru concentrations a decrease in the c/a ratio has been observed, with a slightly larger decrease in the c direction as compared to the basal plane. The Ru atom is larger than the Co atom, which occupies the six crystallographic sites 16k_1, 16k_2, 8j_1, 8j_2. The lattice expansion in the basal plane thus indicates that Ru preferentially occupies the Co sites, whereas the shrink of the lattice along the c direction indicates an enhanced cohesion. However, as compared

to the $Nd_2(Fe_{1-x}Co_x)_{14}B$ boride, the lattice contraction in the basal plane is lesser in this case[27].

The measurements of the temperature dependence of the total magnetization above room temperature were obtained with a magnetobalance and are shown in Fig. 2. Magnetic transitions showing the collapse of the magnetization can be seen in the registered traces. The corresponding Curie temperatures T_C are collected in Table 1. As one sees, T_C decreases steadly with the increase of the Ru concentration. The Curie temperatures of these alloys are lower than those of pure borides[24, 27] as well as those of $Nd_2Fe_{14-x}Ru_xB$ alloys[24, 29]. T_C is mainly determined by the direct exchange interaction of the 3d magnetic ions, and thus it is expected to change very sensitively with the increase of the Ru concentration. The monotonic decrease of the magnetization before the collapse as seen in Fig. 2 is thought to be due to a residual contribution from the minority phases. The formation of a broad hump in the scanning curve at x = 6 might be associated to the formation of ferromagnetic clusters in a solid state decomposition reaction which takes place with the increase of temperature.

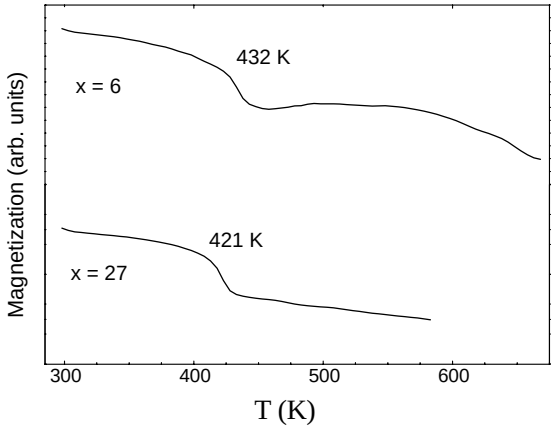

FIG. 2: Magnetization versus temperature for the $Nd_{16}Co_{76-x}Ru_xC_7B$ alloys.

The hysteresis loops recorded at room temperature (300) K are shown in Fig. 3. As it can be seen, neither remanence nor coercive field are observed. Although at x = 6 saturation is attained, for the alloy with x = 27 a paramagnetic (or antiferromagnetic) behavior is identified. However, a non negligible slope can be seen, which confirms that a ferromagnetic entity still is present in this alloy. This result corroborates the results of measurements with the magnetobalance, which detected a ferromagnetic contribution in this alloy with T_C = 421 K. However, a small contribution might also be expected from the secondary phases which are present in this alloy.

Somewhat surprisingly, the Curie temperature decreases smoothly with the increase of the Ru concentration, whereas the saturation magnetization has an abrupt decrease. Thus, the effect of variations in the composition on these quantities is much more harsh than that which could be expected from a simple dilution mechanism. From this behavior one is lead to think that a tendency to establish an antiferromagnetic ordering is taking place in these alloys, where Co-Ru antiferromagnetic interactions are competing with the Co-Co and Ru-Ru ferromagnetic couplings.

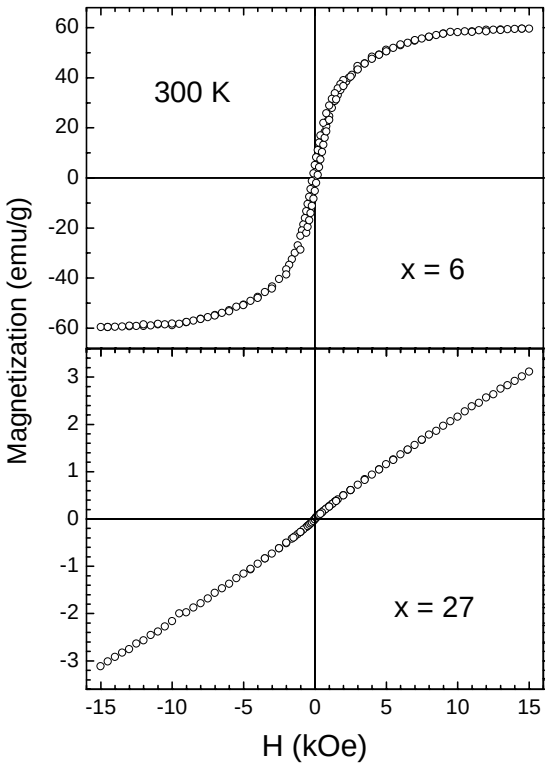

FIG. 3: Hysteresis loops at 300 K of the $Nd_{16}Co_{76-x}Ru_xC_7B$ alloys.

Like the borides the carbides are magnetically hard. The compound $Nd_2Fe_{14}C$ is ferromagnetic with a Curie temperature T_C = 535 K. The magnetic moments of the Fe atoms in this compound have been evaluated as 5% lower than in $Nd_2Fe_{14}B$. From the present investigation it may be concluded that the addition of boron favors the stabilization of the 2:1: tetragonal phase in these alloys. Furthermore, the substitution of Fe for Co is detrimental to the obtention of the 2:14:1 phase in these compounds, as we verified after few attempts. Earlier investigations have indicated that the addition of 1 at.% B increases the Curie temperature in the carbides, although it is detrimental to the coercivity[26]. In this case it may be pointed out that the same statement is valid for the $Nd_{16}Co_{76-x}Ru_xC_7B$ alloys.

The sites which are occupied by B and C atoms in the tetragonal structure are closer to those of Nd atoms. Thus, the effect of the interchange of B and C atoms is expected to cause a significant effect on the magnetocrystalline anisotropy. Therefore, in those systems with strong magnetocrystalline anisotropy, the critical field, which causes the reversal of the magnetization, is expected to increase as the grain size increases. In the studied alloys, it bas been observed from the X-ray studies that small grain sizes are formed with the increase of the Ru concentration, which is harmful to the development of the coercivity.

As a conclusion, in the Co-richer alloys the intrinsic magnetic properties are expected to be ruled by the Co subsystem, considering that the Co atom is carrying the largest magnetic moment. As a consequence, at lower Ru concentration, the behavior of the ferromagnetic Curie temperature is determined by the Co subsystem. However, with the increase of the Ru concentration, besides the lattice expansion in the basal plane, there is a tendency for the onset of Co-Ru and Ru-Ru antiferromagnetic exchanges in the matrix, which in turns makes increase the importance of the Ru subsystem on the behavior of T_C. The saturation magnetization is expected to undergo the same influence. It has been pointed out before that boron acts as an electron donor, and that carbon could donates even more electrons than boron[17], which could explain the maximum of the saturation magnetization of the Nd_2(Fe,Co)B compounds. In this case, for the $Nd_{16}Co_{76-x}Ru_xC_7B$ alloy with $x = 6$ the saturation magnetization measured at 300 K is higher than that observed in the $Nd_{16}Co_{76-x}Ru_xB$ boride at the same composition[27]. The combined addition of B,C is expected to be in the source of this result.

IV. SUMMARY

An investigation of the structural and magnetic properties of the $Nd_{16}Co_{76-x}Ru_xC_7B$ system has been performed. Results of the X-ray diffraction analysis confirm that the hard magnetic tetragonal phase 2:14:1 phase exists in the alloys. The addition of 1 at.% B favors the stabilization of the ordered phase in these compounds. With the increase of the Ru concentration the lattice parameter increases in the basal plane and decreases along the c direction of the tetragonal unit cell. As a consequence, the cell volume decreases. The Curie temperature decreases with the increase of the Ru concentration. The abrupt decrease of the magnetization at higher Ru concentrations lead us to conclude that the magnetic moment per formula unit drops more than would be expected in the case of a simple dilution, and that an antiferromagnetic ordering is being settled up as the Ru atoms substitute for Co atoms.

Acknowledgments

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