An Investigation of Structural and Magnetic Properties of the $Nd_{16}Co_{72-x}Ru_xC_{11}B$ Coro-Carbides

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$Nd_{16}Co_{72-x}Ru_xC_{11}B$ boro-carbides have been prepared by arc melting and studied by X-ray diffraction and magnetization measurements. X-ray diffraction results confirm that all the prepared alloys possess the tetragonal 2:14:1 ($P4_2$/mmm) hard magnetic phase. The observed decrease of the magnetization and Curie temperature indicate the development of antiferromagnetic spin correlations with the increase of the Ru content. The combined addition of B and C is favorable to the formation and stabilization of the tetragonal phase in these compounds. At lower Ru contents the Curie temperature is higher than in the corresponding Co-based boride in spite of larger cell volumes.

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

I. INTRODUCTION

Few decades ago the discovery of a new class of high energy magnets based on the rare earth-transition metal (R-T) compounds has stimulated the search for new ternary intermetallics as promising candidates for applications as permanent magnets[1–6]. Experimental findings have shown that the intrinsic magnetic properties of $Nd_2Fe_{14}B$-based magnets can be improved with the addition of transition metals[7–16]. The R_2Fe_14B compounds crystallize in a tetragonal structure belonging to the space group P42/mnm. The Fe atoms occupy six different sites, the Nd atoms occupy two different crystallographic sites and B occupies one type of position. Among the six nonequivalent crystallographic Fe sites, namely, $16k_1$, $16k_2$, $8j_1$, $8j_2$, 4e and 4c, the k-sites are preferred by the substituent for transition metals, while a preference of Fe for the j-sites has been found[1, 7–9, 16]. As Co atoms substitute for Fe atoms a deviation from random occupation has already been reported [3, 17]. An increase of the Curie temperature is observed as well as a decrease in the saturation magnetization and in the anisotropy field. The effect of the addition of cobalt on the magnetic properties of Nd-Fe-C ingot magnets has also been investigated. The Co substitution can lead to a significant decrease in the annealing time required to magnetically harden the ingots[23].

The role of boron is believed to be of that of stabilizing the tetragonal compound, and a deficiency of boron leads to the formation of Nd_2Fe_{17} as a second phase. By substituting B for C in this system a new family which crystallizes with the same tetragonal crystal structure has been found. The common structure of the tetragonal R-Fe borides and carbides suggests that they should form solid solutions over a wide range. The lattice parameter *c* of the borides and carbides differs sufficiently to enable easily phase separation[6, 16, 21, 24]. The coercivity mechanism in the carbides must differ from that in the sintered borides because high coercivities are not attainable in pure borides.

According to the results of Sui *et al.*[22], in order to make $Nd_2Fe_{14}C$ the main phase the Nd:C ratio must be kept within a certain range, because too little C leads to the formation of $Nd_2Fe_14C_x$ as the main phase, and too much C increases the α-Fe content inhibiting the formation of $Nd_2Fe_{14}C$. The tetragonal $Nd_2Fe_{14}C$ phase is formed at comparatively low temperatures (800 °C) contrarily to the tetragonal $Nd_2Fe_{14}B$ phase which forms at a comparatively high temperature directly from the melt. Primary cristallization products α-Fe and R_2Fe_{17} or a derivative of it[23, 24]. The upper limit of the temperature stability range of the tetragonal phase in the $Nd_2Fe_{14}C_{1-x}B_x$ increases very steeply with the B content in the range $0 < x < 0.05$[23]. Experimental results have shown that $Nd_2Fe_{14}C$ does forms but only under the proviso that the annealing treatment following the casting be performed in a fairly narrow temperature range[24]. One of the most interesting features of the R-Fe-C alloys is the development of high coercivities in bulk samples after an appropriate thermal treatment. No losses in coercivity occurs when the ingots are crushed and finely pulverized. The substitution of C for B in the 2:14:1 boron-based compounds was first reported by Bolzoni et al.[2]. An increase in the anisotropy field and a decrease of T_C and of the saturation magnetization were detected. As compared to the borides, the pure carbides exhibit higher coercivities and are less stable.

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There is an increasing interest in the production of coercive and anisotropic $Nd_2Fe_{14}B$ powder for bonded magnets. The coercive forces are directly related to the microstructure. From experiments it has been found that a microstructure with favorable hard magnetic properties is already developed in the initial stage of the heat treatment and that extended annealing does not lead to improvements in the coercivity. In general the coercivity is very sensitive to variations in the composition, and the possibility of developing high coercivities in castings of R-Fe-C alloys, without resorting to powder metallurgy or rapid solidification, has been much sought since the earlier studies. Experiments have shown that the comminution of sintered Nd_2Fe_{14} permanent magnets to produce small particles suitable for practical application in bonded magnets leads to a severe loss of coercivity that is not found in the carbides. Besides, to avoid the propagation of the domain walls the size of the free particles must be controlled as well as the composition and the repartition of the minor intergranular Nd-rich phases. Research on solute replacements in $Nd_2Fe_{14}C$ compounds have indicated that $Nd_2Fe_{14-x}Ru_xB$ alloys with $0 < x < 2$ crystallize in a tetragonal P42/mnm structure isotypic with $Nd_2Fe_{14}B$. The phases which are formed formed in these alloys consist of $Nd_2(Fe,Ru)C$, α-Fe and $Nd_2(Fe,Ru)C_x$. T_C decreases when Fe is substituted by Ru [26]. This lowering is ascribed to the weakening of the overall exchange interactions which takes place with the lattice shrink and the increase of the Ru concentration as well as with the formation of antiferromagnetic Fe-Ru couplings. However, the magnetic properties obtained for the Nd-Fe-C-based alloys still are comparatively poor, partly due to the presence of very corrosive carbides. In this work we report an investigation of the structural and magnetic properties of the $Nd_{16}Co_{72-x}Ru_xC_{11}B$ system with a combined addition of B and C. We investigate the effect of using higher C contents at the expenses of a lowering in the Co concentration, as an extension of a previous study[32]. Results of x-ray diffraction analysis, calorimetric and magnetization measurements are discussed in this context.

II. EXPERIMENTAL PROCEDURES

$Nd_{16}Co_{72-x}Ru_xC_{11}B$ ingots of nominal compositions x = 6 and 11 were prepared by arc-melting the starting materials under argon atmosphere in a water-cooled copper crucible. In order to homogenize the structure and composition the cast ingots were vacuum sealed in quartz tubes and annealed at 1000 °C for 3 days, then quenched to room temperature in ice water. The X-ray diffraction analysis was carried out on powdered polycrystalline samples by using the Cu-K_α radiation. The temperature dependence of the magnetization was registered above room temperature with a magnetobalance. Hysteresis loops were registered at 300 K in a field up to 15 kOe by using a vibrating sample magnetometer.

III. RESULTS

The X-ray powder diffraction patterns are shown in Fig. 1. A diffractogram of $Nd_2Fe_{14}B$ is included for the sake of comparison. A profile analysis with the Rietveld technique indicated that all the studied alloys possess the tetragonal 2:14:1 ($P4_2$/mmm) phase. Traces of minority phases were also detected, which are probably a mixture of Nd-rich phases, Nd-carbides (such as Nd_2C_3) as well as a mixture α- and ε-type structures, as has been observed in this class of compounds[3, 5, 6, 16, 21, 24]. The relative proportion of the secondary phases seemingly diminishes with the Ru content, as can be observed by the decrease of the intensities of the Bragg reflections. The lattice parameters determined for the main tetragonal phase are listed in Table 1. As it can be seen, there is a lattice expansion in the basal plane, with the increase of the Ru concentration. Conversely, along the c direction a shrinkage has been verified. This leads to a decreasing c/a ratio as well as to a decreasing unit cell volume, with the Co substitution by Ru. This behavior differs from that observed in the Co-based borides, where the cell volume increases as Ru substitutes for Co[29].

TABLE I: Composition, lattice parameters, c/a ratio, unit cell volume and Curie temperature of $Nd_{16}Co_{72-x}Ru_xC_{11}B$ boro-carbides.

x	a ($\AA$)	c ($\AA$)	c/a	V_o ($\AA)^3$	T_C (K)
6	8.547	12.685	1.48	926.65	830
11	8.679	11.981	1.38	902.47	516

In Fig. 2 are displayed the hysteresis loops (M(H) isotherms) recorded at 300 K, where characteristics of a ferromagnetic behavior can be seen. Nevertheless, these alloys possess neither remanence nor coercive field, and besides saturation is not attained in applied fields up to 15 kOe at 300 K. The observed behavior indicates that the magnetization decreases with an increase in the Ru content. However, this effect is smaller than that which could be expected in the case of a simple dilution. The same behavior is expected for the magnetic moment per formula unit. Hence, a conclusion which is withdrawn from the observed trends is that a composition dependence of the Ru moment might be considered as well as the development of antiferromagnetic spin correlations at higher Ru contents, as has been observed in similar compounds[26, 27, 29–32].

Figure 3 shows the magnetization versus temperature curves of the $Nd_{16}Co_{72-x}Ru_xC_{11}B$ alloys registered with a magnetobalance above room temperature in a measuring field of ≈ 0.5 T. The so obtained T_C values are listed in Table 1. The steep increase with the formation of a hump as seen for the alloy with x = 6 was identified as an artifact of the apparatus, a signal characteristics of the furnace chamber which appears on heating. The first transition which is seen in Fig. 3 for x = 6 at 830 K is ascribed to the main tetragonal 2:14:1 phase. Nevertheless, a residual magnetization still is seen at higher temperatures, and the collapse of the total magnetiza-

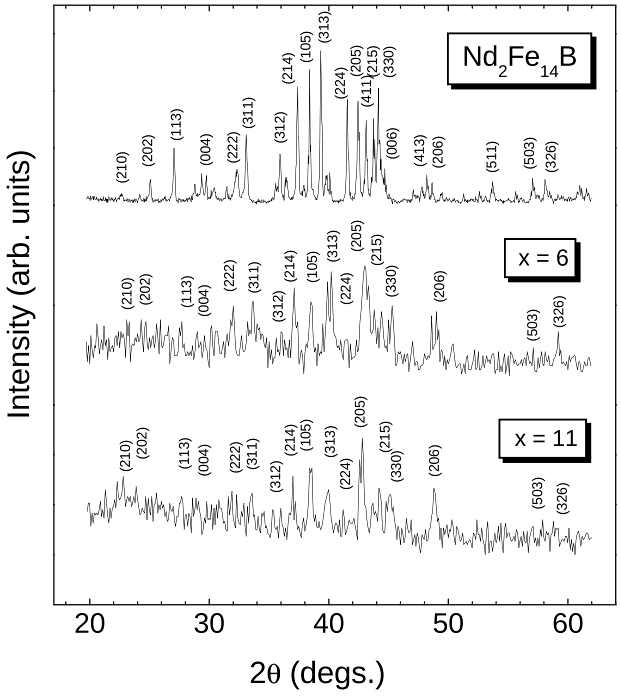

FIG. 1: X-ray diagrams of the $Nd_{16}Co_{72-x}Ru_xC_{11}B$alloys. Top: marked reflections of the 2:14:1 tetragonal phase for $Nd_2Fe_{14}B$.

tion takes place only at about 1068 K. This contribution is expected to be arising from the minority phases, as has been revealed from the X-ray diffraction studies. It is noteworthy that the Curie temperature T_C of $Nd_2Fe_{14}C$ is 535 K, while for the Co-based boride with x = 6, T_C = 789 K[29]. Despite the larger unit cell volume of the tetragonal phase for x = 6, as shown in Table 1, the Curie temperature is even higher than that of the carbide with the same amount of Ru and higher Co content. Furthermore, by increasing the Ru concentration the Curie temperature decreases down to 516 K, for x = 11.

IV. DISCUSSION

In Nd-Fe-C-based alloys the remanence and maximum energy product are improved by increasing both Nd and C contents[22]. An increase in the C content increases the amount of $Nd_2Fe_{14}C$. However, a high C content also increases the α-Fe content. In the present case, the addition of boron seemingly is favoring the formation of the tetragonal 2:14:1 phase. The Curie temperature T_C is strongly affected by variations in composition, which is reflecting the changes occurring in the interaction strengths and unit cell volume. Therefore, the relatively high T_C values obtained in these compounds, as compared to the carbides and borides, indicates that the B atoms also contribute to enhance the interaction strengths.

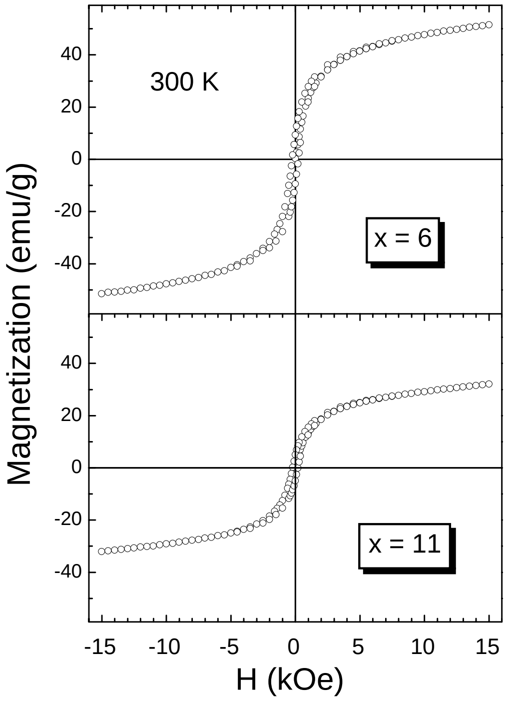

FIG. 2: M(H) isotherms (hysteresis loops) at 300 K of the $Nd_{16}Co_{72-x}Ru_xC_{11}B$ alloys.

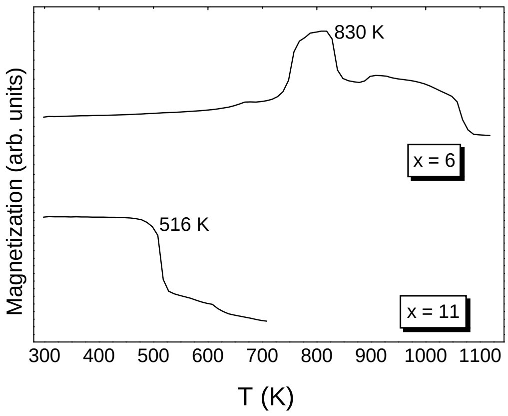

FIG. 3: Magnetization versus temperature scanning curves of the $Nd_{16}Co_{72-x}Ru_xC_{11}B$ alloys registered with a magnetobalance.

In the source of the strong composition dependence of the Curie temperature there is a volume effect: the lattice expansion in the basal plane weakens the Co-Co ferromagnetic interactions, whereas the lattice shrinkage along the *c* direction strengthens the Co-Ru and Ru-Ru antiferromagnetic exchanges, which are increasingly being formed at higher Ru contents at the expenses of the decrease in the number of ferromagnetic interactions. Positive interactions between Co-Co pairs impose the parallel alignment of the neighboring Ru moments, which is expected to be the dominant mechanism acting in the Co-richer alloys. The Ru substitution for Co therefore leads to a decrease of the lattice parameter *c* as well as the increase of *a*, which consequently shortens the distances between Ru sites, thus leading to an enhancement of the antiferromagnetic exchanges. The development of antiferromagnetic spin correlations inevitably leads to lower Curie points as more and more ferromagnetic interactions are disappearing with the increase of the Ru concentration. However, the dominant mechanism for such a sharp decrease of the Curie points seemingly is the decrease of the lattice parameter *c*. From Table 1 it can be seen that the Co-richer alloys have larger cell volumes and higher T_C.

¿From Fig. 2 it may be inferred that the interaction strengths between the local moments, and consequently T_C, become less dependent on the rare earth ions. Moreover, owing to shorter Co-Co distances in the 2:14:1 structure, as compared to the Fe-bearing compounds, the 3d magnetic interactions are depleted, if one considers that these are strongly dependent on the interatomic distances. The magnitude of the Co moment depends on the local environment of the (six) crystallographic sites. Therefore, the 4f moment is determined by dominant 3d-4f interactions as well as by the crystalline electric field. It has been pointed out before that B itself does not seems to play a very important role in the magnetism of this type of compound. Nevertheless, the replacement of B by C is expected to affect the magnetocrystaline anisotropy of the Nd ions because these elements locate closer to the Nd ions. In $Nd_2Fe_{14}C$ the Nd moments are parallel to the Fe moments at 300 K, the easy magnetization direction being along the *c* axis. The average magnetic moment of the Nd atoms is 2.95 μ_B and for the Fe atoms it is 2.44 μ_B at 300 K. The R-R interactions are proceeded indirectly via the 4f-5d-5d-4f mechanism; the T-T are direct exchange interactions between the 3d spins, whereas the R-T are indirect interactions with a combination of the inter-atomic 4f-5d and interatomic 5d-3d.

The magnetic transition temperature of the R-T compounds is known to be mainly determined by the direct exchange interaction of 3d magnetic ions. The magnetic states of the Nd ions depend on the crystalline electric field, which is essentially created by the positive charge of the surrounding Nd ions, and on the 3d-4f magnetic interactions, which results in a large 4f anisotropy. A decrease in the magnetic anisotropy can thus be attributed to the combined effects of the decreasing of 3d-3d and 3d-4f interactions. The Co-Co distance and the filling up of the 3d sub-band can be slightly modified with the substitution of 3d transition metals which have a different metallic radius and a different number of 3d electrons, which results in a higher or lower T_C as compared to $Nd_2Fe_{14}B$, as a direct consequence of the dependence with distance of the exchange interactions. In the source of the high stability of the rare earth borides is the 3d-p hybridization as well as a decrease in the 3d-5d hybridization. Decreased T_C values are thus expected to lead also to a decrease of the anisotropy fields.

As a final remark, from the results above it may be concluded that, as compared to Co-based borides the addition of C is detrimental to the development of a coercivity mechanism in this class of compounds. Lower T_C values are also observed at higher Ru contents. The substitution of Ru for Co is also found to hinder the obtention of both remanence and coercivity in these compounds. Nevertheless, at lower Ru contents the Curie temperature in these alloys is noticeably higher than those verified in Co-based borides and Fe-based carbides. The B-C combined addition thus is expected to be favorable to the formation and stabilization of the tetragonal phase and leads to the development of stronger spin correlations at lower Ru contents.

V. SUMMARY

In this study has been performed an investigation of the structural and magnetic properties of the $Nd_{16}Co_{72-x}Ru_xC_{11}B$ boro-carbides. The unit cell volume of the tetragonal 2:14:1 phase undergoes a significant decrease at higher Ru contents, which leads to a decrease of the distance between Ru sites which in turn is expected to lead to an enhancement of the strength of antiferromagnetic spin correlations. Although the Curie temperature decreases when Co is replaced by Ru, for $x < 6$, T_C is higher than in Co-based borides with the same amount of Ru and higher Co concentration.

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