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On the new $RFe_{11.35}Nb_{0.65}$ (R = rare earth metals) alloys and their related hydrides and carbides

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Abstract. New interstitial hydrides $RFe_{11.35}Nb_{0.65}H_y$ and carbides $RFe_{11.35}Nb_{0.65}C_y$ (R = rare earth metal) have been synthesized. Structural characteristics and preliminary magnetic properties (T_C and m_{Fe}), together with those of the starting alloys, are presented and compared to the previously studied nitrides. Large increases of the Curie temperature and of the iron moment, particularly large in the carbides, are obtained. The evolutions of the deduced Fe–Fe and R–Fe exchange interactions are discussed. The large Curie temperature obtained with the carbides makes this series particularly attractive for permanent magnet applications, owing to the easy route proposed for the synthesis.

1. Introduction

It is well established that the pure RFe_{12} alloys (R = rare earth metal) do not exist; however, the tetragonal $ThMn_{12}$ type structure can be stabilized in the pseudo-ternary $RFe_{12-x}M_x$ compounds when a M element, with M = Al, Si, Ti, V, Mo, W, Re,. . ., is partly substituted for iron [1–3]. Among the stabilizing elements there are either sp- or d-valence electron metals. It was argued that in the R_2Fe_{17} parent series the substitution scheme of such different elements was Fe site selective owing to the relative heat of formation for a binary R–M or Fe–M system, i.e. the most negative heat of formation, the largest number of R (or Fe) neighbours in the $R_2(Fe, M)_{17}$ [4]. This is effectively realized in $RFe_{12-x}Al_x$ ($x \leqslant 4$), but it is reversed for the parent RFe_4Al_8. Besides relative electron filling and transfer considerations, the atomic radius value plays a determining role in the formation of the ternary $ThMn_{12}$ structure type of compound. The largest accommodated metal is titanium ($r_{Ti} = 1.47$ Å), whereas the isoelectronic zirconium does not stabilize the $ThMn_{12}$ type of structure ($r_{Zr} = 1.58$ Å).

For a given M element, the smaller x is, the larger the Curie temperature. Therefore in the search for new materials for permanent magnet applications, the elements M which allow the smallest x values are of particular interest. This is the case of the series of $RFe_{11.35}Nb_{0.65}$ compounds which have been recently obtained, with R = Y, Sm, Gd to Er and Lu [5]. The niobium's ability to form the 1–12 compounds can be explained because its radius is similar to that of titanium ($r_{Nb} = 1.47$ Å). Furthermore the authors of the above referenced paper have synthesized the corresponding $RFe_{11.35}Nb_{0.65}N_y$ nitrides using a gas–solid reaction. An

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extended investigation of the magnetic properties of the nitrides was also reported, appearing strongly modified in comparison with the starting alloy characteristics.

This present paper is devoted to the new interstitial hydrides $RFe_{11.35}Nb_{0.65}H_y$ and carbides $RFe_{11.35}Nb_{0.65}C_y$ that we have synthesized by hydrogen gas reaction for the first series and carbonation using anthracene for the second one. Structural characteristics and preliminary magnet measurements are presented.

2. Experimental details

The $RFe_{11.35}Nb_{0.65}$ compounds were prepared by melting the constituents (purity better than 99.9%) in a cold crucible induction furnace under argon gas atmosphere of high purity (99.995%). The samples were annealed at 800 °C for 1 month. The alloy homogeneity was checked using conventional x-ray powder diffraction technique. (Fe $K\alpha_1$ radiation). For the preparation of the hydrides, a high purity hydrogen atmosphere (99.9995%) was applied at 2.5 MPa pressure in a special steel autoclave. The hydrogen uptake was achieved within 48 hours when the sample was thermally activated at 230 °C. For the preparation of carbides, the alloys were finally crushed (mean size less than 50 μm) and then carefully mixed with a determined amount of anthracene so that the carbon amount exceeds slightly the expected final stoichiometry. The mixed powder was compacted into tablets of about 2–3 g and then sealed under vacuum in quartz tubes. Since the anthracene decomposition brings a corresponding amount of hydrogen gas, care must be paid to avoid either the absorption of hydrogen by the samples or reaching an over-pressure level so that the ampoule explodes. We have solved this problem by introducing into the ampoule a few magnesium chips that enable us to completely absorb hydrogen at 300 °C and above. Hence, the ampoule was divided in two parts by a narrow neck, the lower part containing the compressed tablets and Mg occupying the upper part. The synthesis of the ternary carbide via the decomposition reaction of $C_{14}H_{10}$ and then diffusion of elemental carbon was optimized by reacting at 420 °C for up to 150 hours.

All the samples were also checked by x-rays for the starting alloys. The Curie temperatures were determined by using a high-sensitivity thermomagnetic balance, a few mg of powder being sealed in small silica sample holders. The very reduced dead volume allows us to maintain the hydrides close to their starting hydrogen stoichiometry when immediately creating a rather large over-pressure in the ampoule. Field dependences of magnetization were measured by the extraction technique.

3. Results and discussion

The x-ray analyses confirm that the dominating phase of the alloys has the $ThMn_{12}$ type structure. However the presence of small amounts of impurities was detected (Fe, R_2Fe_{17} (Th_2N_{17} type) RFe_2), the relative proportions depending on R. The purest compounds were the Ho and Er alloys. The characteristics of the crystal structure of these alloys are listed in table 1. The cell parameters a and c are very close to those obtained in the previous work [5]. The cell volume of the $RFe_{11.35}Nb_{0.65}$ compounds decreases with the increase of $Z(\mathrm{R})$ which results from the lanthanide contraction.

After hydrogenation and carbonation, the multiphase composition of the alloys changes. It is remarkable that both the amounts of the R_2Fe_{17} and the RFe_2 phases decrease and almost disappear. There are no Bragg peaks of R_2Fe_{17} type in the x-ray patterns for the compounds of Gd, Dy, Ho and e.g. Er (figure 1). The amount of the R_2Fe_{17} phases in less in the carbides of Y and Tb than in their starting alloys. This is well confirmed by the thermomagnetic analysis

Table 1. The crystal data and Curie temperature of the $ErFe_{11.35}Nb_{0.65}$ compounds.

Compound	a (Å)	c (Å)	c/a	V (Å^3)	T_C (K) This work	T_C (K) [5]
$YFe_{11.35}Nb_{0.65}$	8.530	4.800	0.563	349.25	522	526
$GdFe_{11.35}Nb_{0.65}$	8.550	4.818	0.563	352.20	600	597
$TbFe_{11.35}Nb_{0.65}$	8.518	4.807	0.564	348.78	553	556
$DyFe_{11.35}Nb_{0.65}$	8.512	4.802	0.564	344.92	534	536
$HoFe_{11.35}Nb_{0.65}$	8.503	4.805	0.566	347.40	523	520
$ErFe_{11.35}Nb_{0.65}$	8.485	4.801	0.566	345.64	509	507

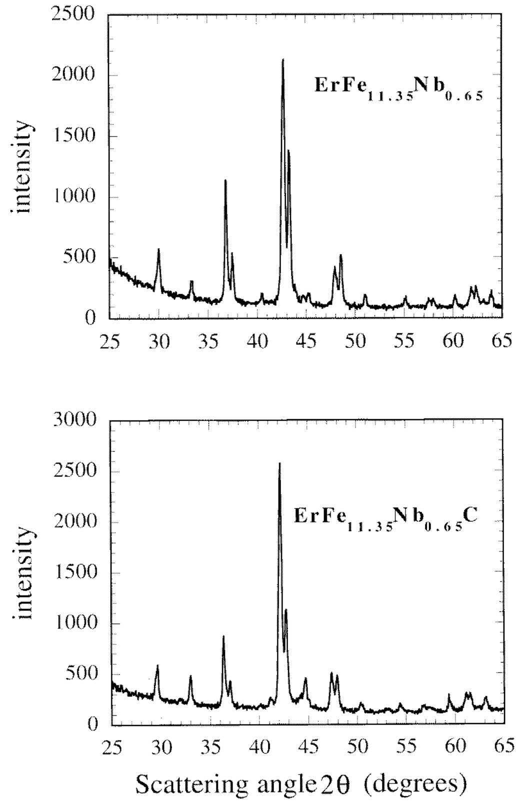

Figure 1. The x-ray patterns of $ErFe_{11.35}Nb_{0.65}$ (upper part) and $ErFe_{11.35}Nb_{0.65}C$ (lower part).

indicating no trace of an R_2Fe_{17} signal either for $RFe_{11.35}Nb_{0.65}C_x$, with R = Gd, Dy, Ho and e.g. Er (figure 2), or for $RFe_{11.35}Nb_{0.65}H_x$ with R = Dy, Ho, Er. The thermomagnetic curves reveal a dramatic instability of both the hydrides and the carbides $RFe_{11.35}Nb_{0.65}C_x$ for temperatures higher than 820 K. The resulting increase of magnetization comes from the disproportionation of free iron particles.

The cell parameters and cell volumes of both the hydrides and the carbides are reported in table 2. The volume increases, with respect to those of the starting alloys, stand between 2.2 and 3.6% for the carbides; they are close to 1% for the hydrides (the small values for Y and Gd are probably related to the weak accuracy in the cell parameter determination of the hydrides arising from the very small amount of material used for the x-ray pattern). So,

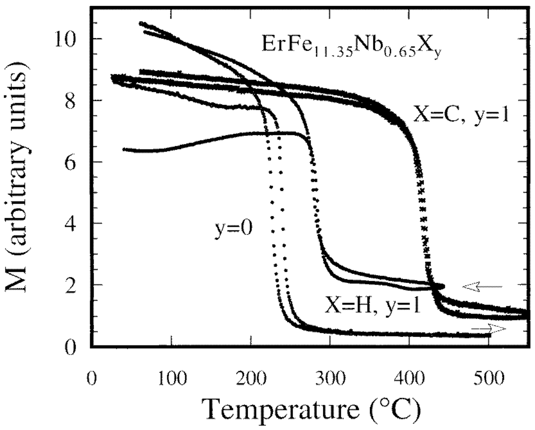

Figure 2. Magnetization versus temperature curves of $ErFe_{11.35}Nb_{0.65}$, $ErFe_{11.35}Nb_{0.65}H$ and $ErFe_{11.35}Nb_{0.65}C$. The three curves are expressed in relative arbitrary units.

reference to data obtained earlier for different values of carbon content in the $HoFe_{10.5}Mo_{1.5}C_x$ system ($x = 0.0, 0.22, 0.48, 0.67, 0.88, 0.99$) [6], we can quantify approximately the x value for the $RFe_{11.35}Nb_{0.65}C_x$ series from the $\Delta V/V_0$ ratio (table 2). For instances for the $TbFe_{11.35}Nb_{0.65}C_x$ and $ErFe_{11.35}Nb_{0.65}C_x$ x is equal to ~ 1. In the hydrides a precise determination is not possible due to the reduced volume expansion.

Table 2. The crystal data and Curie temperature of the $RFe_{11.35}Nb_{0.65}X_y$ ($X = H, C$) compounds.

Compound	a (Å)	c (Å)	c/a	V (Å^3)	$\Delta V/V_0$ (%)	T_C (K)
$YFe_{11.35}Nb_{0.65}C_y$ $x = 0.9$	8.609	4.856	0.564	359.90	3.05	703
$YFe_{11.35}Nb_{0.65}H$	8.53	4.79	0.561	348.53	−0.20	563
$GdFe_{11.35}Nb_{0.65}C_x$ $x = 0.5$	8.584	4.884	0.569	359.87	2.18	718
$GdFe_{11.35}Nb_{0.65}H$	8.57	4.80	0.560	352.54	0.10	663.90
$TbFe_{11.35}Nb_{0.65}C_x$ $x = 1$	8.588	4.882	0.568	360.6	3.24	708
$TbFe_{11.35}Nb_{0.65}H$	8.5530	4.810	0.562	351.90	0.89	603
$DyFe_{11.35}Nb_{0.65}C_x$ $x = 0.6$	8.562	4.886	0.568	356.71	2.53	696
$DyFe_{11.35}Nb_{0.65}H$	8.559	4.7930	0.560	351.10	0.91	588
$HoFe_{11.35}Nb_{0.65}C_x$ $x = 0.7$	8.562	4.864	0.568	356.57	2.64	706
$HoFe_{11.35}Nb_{0.65}H$	8.543	4.803	0.562	350.60	0.92	580
$ErFe_{11.35}Nb_{0.65}C_x$ $x = 1$	8.568	4.864	0.568	357.06	3.30	706
$ErFe_{11.35}Nb_{0.65}H$	8.520	4.791	0.562	347.90	0.65	549

The Curie temperatures of the $RFe_{11.35}Nb_{0.65}$ compounds are close to those reported in [5] (table 1). The Curie temperatures of the hydrides increase from 7% (Y) to 11% (Gd). For the carbides the increases are much larger and range from 20% (Gd, $x = 0.5$) to 39% (Er,

$x = 1$). These increases are on the same order of magnitude as in the nitrides [5]. It can be speculated that the T_C increases markedly depends on $\Delta V/V_0$, i.e. on the carbon content. Such a dependence has been already studied in the $HoFe_{10.5}Nb_{0.65}C_x$ system [6] where T_C considerably increases up to $x = 0.5$, and then changes little for higher values. As the carbon contents of our compounds are larger or equal to 0.5, a comparison of the T_C of the different compounds can be valid.

We have performed magnetization measurements of the Gd based materials at 4 K in a field up to 10 T. The iron moments (m_{Fe}) have been determined from the spontaneous magnetization by assuming a moment (m_{Gd}) of 7 μ_B on the Gd atoms, where m_{Gd} are coupled antiparallel to m_{Fe}. These values are reported in table 3. In $GdFe_{11.35}Nb_{0.65}$ the saturation magnetization, obtained by extrapolating M against $1/H^2$ for $1/H^2 = 0$, reached 15.3 $\mu_B N$ fu^{-1}, a value very close to that (15.0 μ_B fu^{-1}) previously obtained [5]. For the nitrides, one can deduce an Fe moment of 1.96 μ_B when applying the result of [5] and assuming the same ratio between the spontaneous magnetization as that valid for the parent alloys. This value is close to that observed in the carbides (see table 3).

Table 3. $RFe_{11.35}Nb_{0.65}X_y$ compounds: average value of the Fe magnetic moments determined at 4 K for R = Gd; some characteristics of the exchange interactions obtained from the analysis (see text).

$RFe_{11.35}Nb_{0.65}C_y$	T_{Fe} (K)	C (K^2)	J_{FeFe} (K)	J_{RFe} (K)	m_{Fe} (μ_B)
$y = 0$	485	16 269	86	2.2	1.79
X = C	699	2783	102	0.8	2.03
X = H	529	17 783	84	2.2	1.93
X = N [5]	702	13 568	101	1.8	1.96

In this type of material, within the molecular field approximation and when neglecting the R–R interaction, it is usual to write the Curie temperature as [7–9]:

$$T_C = \tfrac{1}{2}\left(T_{Fe} + \sqrt{T_{Fe}^2 + 4T_{RFe}^2}\right) \tag{1}$$

where $T_{Fe} = AJ_{FeFe}S(S+1)$ and $4T_{RFe}^2 = BS(S+1)J_{RFe}^2G_J$. A and B are constants within a series of compounds; S and $G_J = (g_J - 1)^2J(J+1)$ are the iron spin an the de Gennes factor, respectively. J_{FeFe} and J_{RFe} are the exchange integrals between Fe–Fe and R–Fe nearest neighbours. With non-magnetic rare earth elements, $T_C = T_{Fe}$. Then T_{Fe} should be given by the Curie temperature of the Y compounds. However in in the former compounds the Curie temperatures are larger than those of the corresponding Er compounds which is in contradiction with equation (1). This has already been observed and generally one has a better estimate of T_{Fe} when R = La or Lu. Assuming that the exchange integral J_{RFe} is almost independent of R (which has been shown to be rather correct for heavy rare earth elements [9]) one expects that T_c depends only on G_J through

$$T_C = \tfrac{1}{2}\left(T_{Fe} + \sqrt{T_{Fe}^2 + CG_J}\right) \tag{2}$$

In our case, in order to estimate T_{Fe} and $C = BS(S+1)J_{RFe}^2$ we proceeded as follows for each series; we plotted T_C as a function of G_J as shown in figure 3. Then we fitted the experimental data with the theoretical variations (in full lines in figure 3) and obtained for each series an estimate of T_{Fe} and C which are reported in table 3. Note that the full lines fit the experimental data rather well which shows that the properties of the compounds follow the model quite well. It is worth noting that the T_C of the carbides weakly depend on G_J (small value of C) in contrast to the other compounds which depend on G_J in approximately the same way (comparable values of C). This means that in the carbon compounds the R–Fe interactions are much smaller than in the three other series. Considering, as other authors, that S is half the low temperature value of the Fe moment m_{Fe} expressed in μ_B, from the values of T_{Fe} and C we have been able to estimate J_{FeFe} and J_{RFe} which are reported in table 3. From table 3 it appears that (i) for the hydrides the increase of T_C mainly results from the increase of the iron moment, whereas the exchange interactions are approximately the same as in the starting alloys; (ii) in the carbides and nitrides one observes approximately the same large increase of both the Fe–Fe exchange interaction and the iron moment; (iii) as mentioned above the insertion of carbon leads to a large decrease of the R–Fe exchange interaction. It is interesting to discuss the evolution of the magnetic properties in the light of the change of the lattice parameters. The volume expansion arising from the introduction of the interstitial elements leads, as expected, to the enhancement of both the Fe–Fe exchange interaction (in agreement with the Néel–Slater curve) and of the iron moment (associated with the localization of 3d electrons). The larger the volume expansion is the larger J_{FeFe} and m_{Fe}. For the hydrides, in which the volume expansion is small, the main effect occurs on m_{Fe}. Besides for nitrides [5] and hydrides one observes a decrease of the c/a ratio whereas this ratio increases for carbides. We conclude that the chemical bonds between the inserted elements and their next neighbour metal atoms (2R–4Fe) are not similar for all three series. This could be the origin of the difference in the evolution of the R–Fe exchange interaction. Neutron diffraction investigations are in progress in order to better understand these aspects.

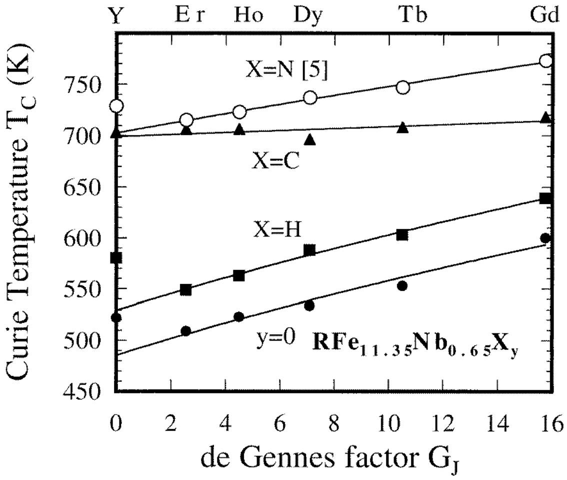

Figure 3. Curie temperature variation versus the 'de Gennes' factor $G_J = (g_J - 1)^2(J + 1)$ for the $RFe_{11.35}Nb_{0.65}X_y$ compounds ($y = 0$; full circles; X = H: full squares; X = C: full triangles; X = N: empty circles). Full lines are fits using equation (2) to the experimental points of each series except that of Y compounds ($G_J = 0$).

4. Conclusion

We have been able to synthesize new hybrides $RFe_{11.35}Nb_{0.65}H_x$ and carbides $RFe_{11.35}Nb_{0.65}C_x$. It appears that the atomic radius of the extra metal is one of the determining factors enabling the stabilization of such an iron rich 1–12 family. In the carbides we find particularly high Curie temperature since they alloy a minimum of non-magnetic elements. Whereas the increase of the Fe–Fe exchange interaction and of the iron moment is related to the cell volume expansion, the evolution of the R–Fe exchange interaction, especially small in the carbides, seems related to the evolution of the c/a ratio. The large Curie temperatures obtained in carbides make this series particularly attractive for permanent magnet applications.

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