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## Structural and magnetic properties of $R_2Fe_{17-x}Al_xC$ compounds ( $R \equiv Ho, Y$ or $Sm$ )

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**Abstract.** The single-phase compounds of  $R_2Fe_{17-x}Al_xC$  ( $x = 0-8$ ;  $R \equiv Ho, Y$  or  $Sm$ ) were fabricated by arc melting. Their structural and magnetic properties have been investigated by means of x-ray diffraction and magnetization measurements. X-ray diffraction patterns demonstrate that all compounds have a single phase with a hexagonal  $Th_2Ni_{17}$ -type or a rhombohedral  $Th_2Zn_{17}$ -type structure. The substitution of Al atoms leads to increase in the lattice constants and the unit-cell volume. The Curie temperature is found to change slightly when  $x \leq 3$  and then to decrease rapidly with increasing Al concentration. An approximately linear decrease in the saturation magnetization with increasing  $x$  is observed by the substitution of non-magnetic Al atoms. The compensation points are observed for the  $Ho_2Fe_{17-x}Al_xC$  samples with  $x \geq 5$ . Samples of  $Sm_2Fe_{17-x}Al_xC$  with  $x \leq 6$  exhibit an easy  $c$ -axis anisotropy at room temperature. The room-temperature anisotropy field increases to about 110 kOe when  $x = 2$  and then decreases with increasing Al concentration. The substitution of Al for Fe in a small concentration will increase the anisotropy field of  $Sm_2Fe_{17}$  carbides. This behaviour is the same as that of Ga and Si.

### 1. Introduction

Intermetallic compounds of the type  $R_2Fe_{17}$  have attracted much attention lately as possible high-performance permanent magnets. The large Fe concentration yields a high saturation magnetization while maintaining a low cost. However, the relatively low values of Curie temperature and the fact that none of them exhibits an easy-axis anisotropy at room temperature restrict the possible application of these materials as permanent magnets. In order to improve their magnetic properties, much work has been done by either substituting other elements into the  $R_2Fe_{17}$  structure or preparing materials with additional atoms located interstitially. It was found that introducing interstitial atoms, such as C or N, into  $R_2Fe_{17}$  intermetallics enhances their hard magnetic properties considerably [1, 2]. Unfortunately, the major drawback of nitrides or carbides prepared by gas–solid reaction is their high-temperature instability, which limits the application of these materials as sintered permanent magnets. Recently, we discovered that highly stable  $R_2Fe_{17}C_x$  compounds with a carbon concentration up to  $x \simeq 3$  could be formed by substitution of Ga, Si or Al for Fe [3–5]. In this work, we investigated the structural and magnetic properties of  $R_2Fe_{17-x}Al_xC$  compounds ( $R \equiv Ho, Y$  or  $Sm$ ).

## 2. Experimental details

Compounds of this type  $R_2Fe_{17-x}Al_xC$  ( $x \leq 8$ ,  $R \equiv Ho, Y$  or  $Sm$ ) have been prepared by arc melting from raw materials of Ho, Y, Sm, Fe, Al and Fe-C alloy. The ingots were annealed under an argon atmosphere at 1400 K for 5 days, followed by quenching into water. X-ray diffraction (XRD) experiments were performed on powder samples using  $Co K\alpha$  radiation to study the Al concentration dependences of the crystal structure and the unit-cell volume. The Curie temperatures and compensation temperatures were derived from the temperature dependence of magnetization  $\sigma(T)$  curves measured with an extracting-sample magnetometer in a field of 500 Oe. The saturation magnetization at 1.5 K was measured by means of a SQUID magnetometer in an applied field of 70 kOe. The anisotropy fields were obtained from the magnetization curves measured along and perpendicular to the aligned direction using the extracting-sample magnetometer with a magnetic field up to 70 kOe.

## 3. Results and discussion

XRD diagrams demonstrate that the  $Ho_2Fe_{17-x}C$  samples with  $x \leq 3$  are a single phase of hexagonal  $Th_2Ni_{17}$ -type structure, while samples with  $4 \leq x \leq 8$  are a single phase of rhombohedral  $Th_2Zn_{17}$ -type structure. All samples of  $Y_2Fe_{17-x}Al_xC$  and  $Sm_2Fe_{17-x}Al_xC$  are single phases with rhombohedral  $Th_2Zn_{17}$ -type structure. It can be shown that Al atoms can substitute for Fe in  $Y_2Fe_{17}C$  and  $Sm_2Fe_{17}C$  up to a very high concentration without changing the crystal structure, except for volume changes. Figure 1 shows the x-ray patterns of  $R_2Fe_{17-x}Al_xC$  compounds. The lattice constants  $a$  and  $c$  and the unit-cell volume for  $Ho_2Fe_{17-x}Al_xC$ ,  $Y_2Fe_{17-x}Al_xC$  and  $Sm_2Fe_{17-x}Al_xC$  are summarized in tables 1, 2 and 3, respectively. An approximately linear increase in unit-cell volume with increasing Al concentration can be seen in figure 2. In order to compare the volumes of the hexagonal cells with the rhombohedral cells, we have multiplied the former by  $\frac{3}{2}$ . A linear relationship between the unit-cell volume and Al concentration was also observed for  $R_2Fe_{17-x}Al_x$  compounds with  $R \equiv Ho$  or  $Y$  [6] and  $R \equiv Sm$  [7]. The substitution of larger Al atoms for Fe in these materials results in an expansion of the unit-cell volumes.

Table 1. The structural and magnetic parameters for  $Ho_2Fe_{17-x}Al_xC$  compounds.

$x$	$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	$T_C$ (K)	$T_{comp}$ (K)	$\sigma_s$ (1.5 K) (emu g <sup>-1</sup> )	$M_s$ ( $\mu_B$ /formula unit)	$\bar{\mu}_R$ ( $\mu_B$ )
0	8.587	8.298	529.9	508		70.5	16.3	9.0
2	8.626	8.359	538.7	504		48.3	10.7	8.4
4	8.648	12.562	813.6	425		16.9	3.6	9.0
6	8.708	12.696	833.5	320	69	-24.1	-4.8	8.7
8	8.745	12.750	844.8	253	87	-38.9	-7.4	7.3

Figure 3 shows the Al concentration dependence of the Curie temperature of these samples. The Curie temperatures are found to change slightly up to  $x = 3$  and then to decrease rapidly with increasing  $x$ . It is commonly assumed that the Curie temperature in rare-earth-iron intermetallics is dominated by the exchange interactions between iron sublattices, which are strongly dependent on the iron-iron interatomic distance. The generally low values of Curie temperature in  $R_2Fe_{17}$  compounds result from the relatively small Fe-Fe distance in these materials. As Jacobs *et al* [6] have shown that the exchange

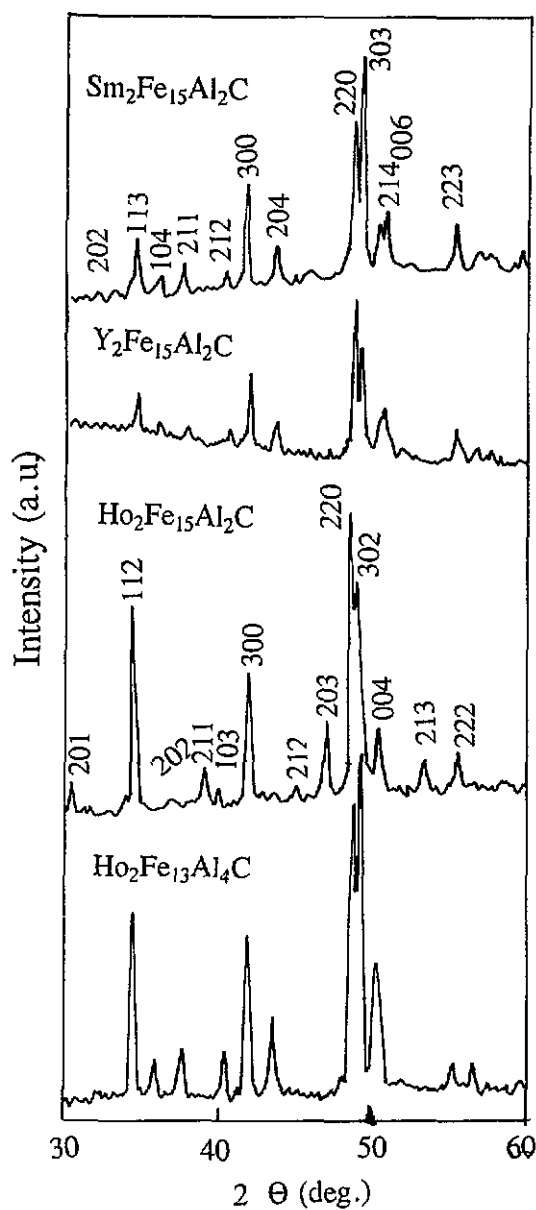


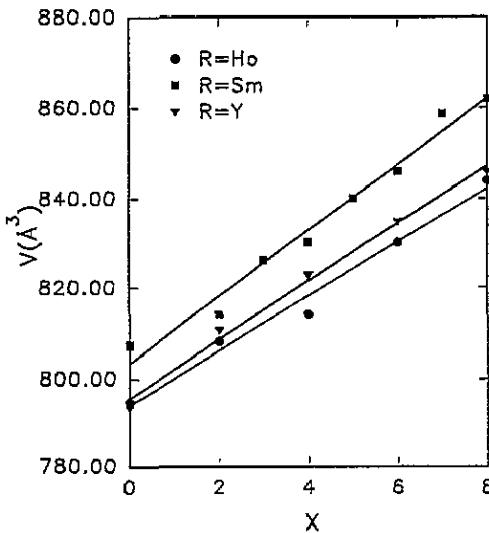
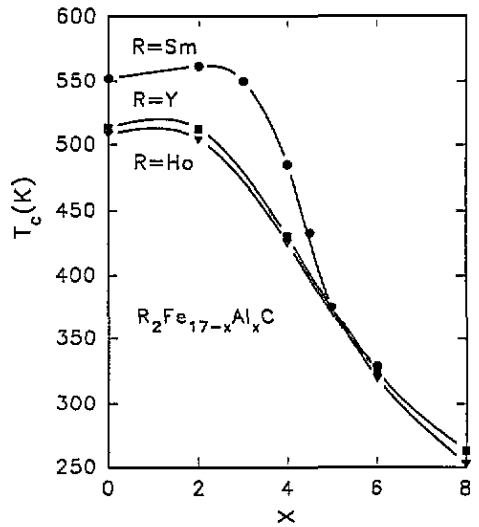
Figure 1. XRD patterns of  $R_2Fe_{17-x}Al_xC$  compounds (a.u., arbitrary units).

Table 2. The structural and magnetic parameters for  $Y_2Fe_{17-x}Al_xC$  compounds.

$x$	$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	$T_C$ (K)	$\sigma_s$ (1.5 K) (emu g <sup>-1</sup> )	$M_s$ ( $\mu_B$ /formula unit)	$\bar{\mu}_{Fe}$ ( $\mu_B$ )
0	8.589	12.421	793.5	513	168.4	34.4	2.02
2	8.657	12.487	810.5	512	143.4	27.4	1.83
4	8.689	12.587	822.8	430	117.8	21.6	1.66
6	8.728	12.652	834.7	325	73.6	12.7	1.15
8	8.753	12.756	845.9	263	14.4	7.2	0.80

**Table 3.** The structural and magnetic parameters for  $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x\text{C}$  compounds at room temperature.

$x$	$a$ (Å)	$c$ (Å)	$v$ (Å <sup>3</sup> )	$c/a$	$T_C$ (K)	$H_A$ (kOe)	$M_s$ (emu g <sup>-1</sup> )	Easy magnetization direction
0	8.644 <sup>2</sup>	12.476 <sup>2</sup>	807.3	1.443	552 <sup>2</sup>	53 <sup>12</sup>	—	$c$ axis
2	8.674	12.506	814.0	1.441	562	108	112.3	$c$ axis
3	8.709	12.575	826.0	1.444	550	98	103.2	$c$ axis
4	8.716	12.617	830.0	1.447	486	76	83.1	$c$ axis
5	8.753	12.664	840.2	1.447	375	65	58.0	$c$ axis
6	8.764	12.723	846.2	1.451	320	50	33.5	$c$ axis
7	8.806	12.787	858.7	1.452				
8	8.816	12.809	862.1	1.451				

**Figure 2.** The unit-cell volumes of  $\text{R}_2\text{Fe}_{17-x}\text{Al}_x\text{C}$  as functions of Al concentration.**Figure 3.** The Curie temperatures of  $\text{R}_2\text{Fe}_{17-x}\text{Al}_x\text{C}$  as functions of Al concentration.

coupling between iron atoms increases with increasing Al content up to about  $x = 3$  for  $\text{Y}_2\text{Fe}_{17-x}\text{Al}_x$  and  $\text{Ho}_2\text{Fe}_{17-x}\text{Al}_x$  compounds. The value of the Curie temperature decreases with increasing  $x$  as a result of either the further dilution of the magnetic species or the further increase in Fe–Fe neighbour distances or both.

In contrast with earlier reports, which showed that Al atoms occupied randomly 18f, 18h, 9d and 6c sites [8] or occupied 9d and 6c sites [9], Gou *et al* [10] found that Al atoms occupied the three non-equivalent sites 6c, 18h and 18f with different occupancy fractions by means of neutron diffraction studies on  $\text{Ho}_2\text{Fe}_{17-x}\text{Al}_x\text{C}$  with  $x = 4$  and 7, which is similar to that reported by Yelon *et al* [11]. The difference between the iron magnetic moments of these four sites is not very large. Thus, we can approximately use an average iron magnetic moment  $\mu_{\text{Fe}}$  to replace the magnetic moments of iron atoms at different sites. Mössbauer experiments at low temperatures are currently being undertaken to obtain information on the site distribution on a microscopic scale and the magnetic moments of iron atoms at the four non-equivalent sites on the basis of the correlation between magnetic moments and hyperfine fields.

The saturation magnetizations of  $Ho_2Fe_{17-x}Al_xC$  and  $Y_2Fe_{17-x}Al_xC$  compounds at 1.5 K as functions of Al concentration are shown in figure 4. The Al concentration dependence of saturation magnetization is similar to that of carbon-free samples [6]. If we use the average iron magnetic moments of  $Y_2Fe_{17-x}Al_xC$  to replace those of  $Ho_2Fe_{17-x}Al_xC$ , the magnetic moments of Ho can be obtained. These data were summarized in table 1. The Ho magnetic moments are found to be slightly smaller than its free-ion value. This may be due to crystal-field effects which reduce  $\mu_R$  or which bring about a situation where  $\mu_R$  and  $\mu_{Fe}$  are non-collinear.

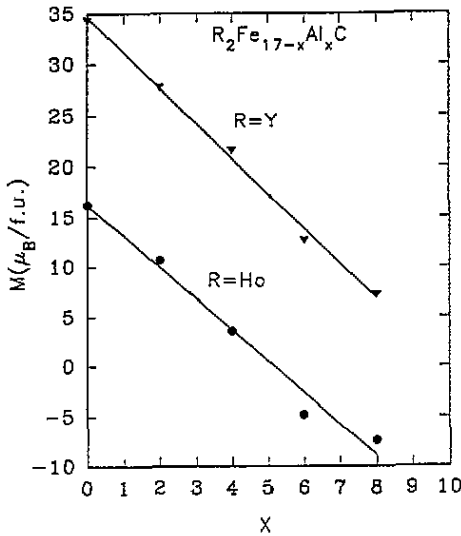


Figure 4. The magnetic moments of  $Y_2Fe_{17-x}Al_xC$  and  $Ho_2Fe_{17-x}Al_xC$  as functions of Al concentration.

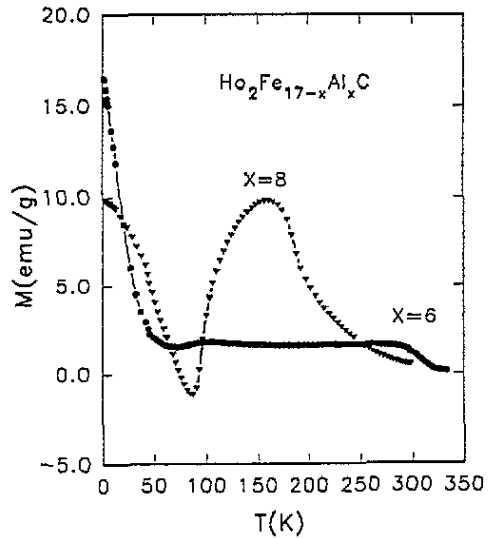


Figure 5. The temperature dependences of the magnetizations of  $Ho_2Fe_{11}Al_6C$  and  $Ho_2Fe_9Al_8C$  compounds in a field of 500 Oe.

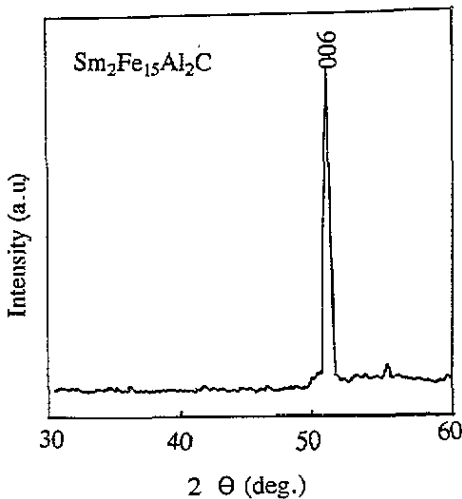


Figure 6. Room-temperature x-ray pattern of  $Sm_2Fe_{15}Al_2C$  aligned in an applied magnetic field of 20 kOe (a.u., arbitrary units).

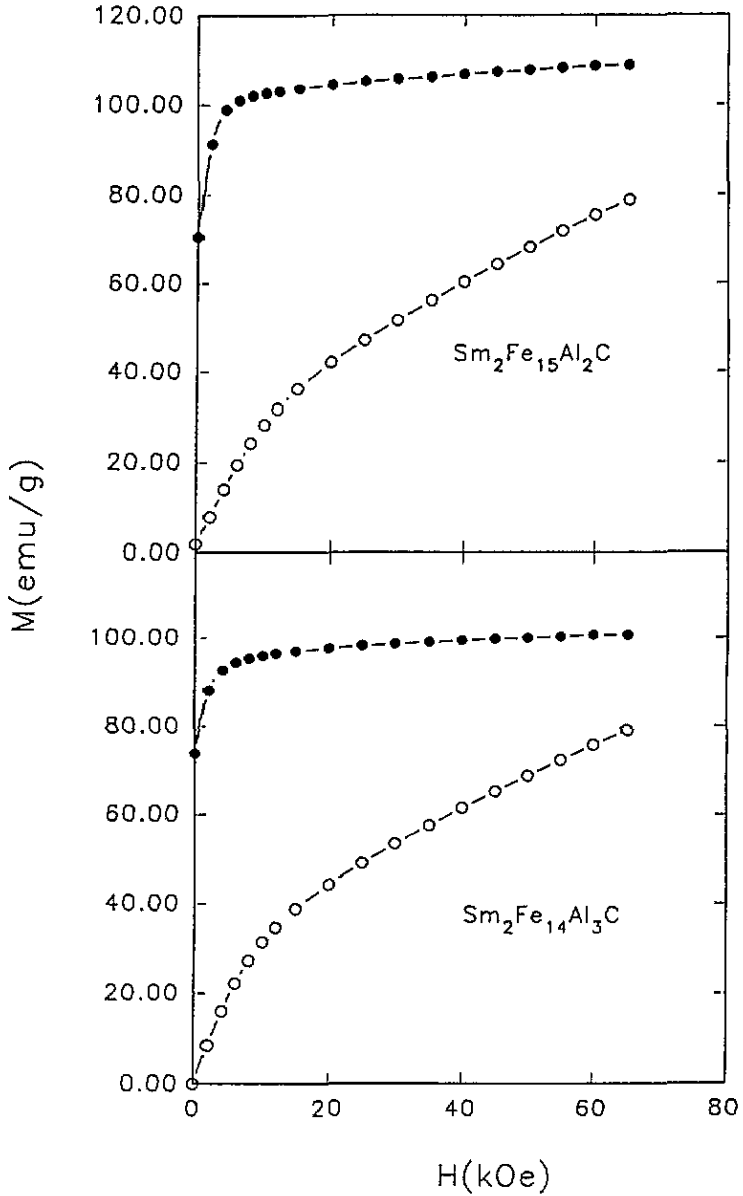


Figure 7. Magnetization curves of  $\text{Sm}_2\text{Fe}_{15}\text{Al}_2\text{C}$  and  $\text{Sm}_2\text{Fe}_{14}\text{Al}_3\text{C}$  at 300 K along (●) and perpendicular to (○) the aligned direction.

With increasing Al concentration, the T-sublattice moment will decrease. For the  $\text{Ho}_2\text{Fe}_{12}\text{Al}_5\text{C}$  sample, it is about equal to the Ho-sublattice moment. At higher Al concentrations, the T-sublattice moment is lower than the Ho-sublattice moment at 1.5 K. However, because the Ho-sublattice moment decreases more rapidly as a function of temperature than the T-sublattice moment does, they will be equal at a certain temperature.

In order to measure the values of Curie temperature and compensation temperature more precisely, the temperature dependences of the magnetizations of  $\text{Ho}_2\text{Fe}_{11}\text{Al}_6\text{C}$  and

$Ho_2Fe_9Al_8C$  were measured in a low magnetic field of 500 Oe, as shown in figure 5. In general, it proved to be necessary to cool the samples from room temperature to 1.5 K in a magnetic field of 20 kOe, since otherwise the net magnetization at low temperatures vanishes or is very low. The origin of this magnetohistory effect lies in the strongly temperature-dependent anisotropy. Because the initial susceptibility of  $Ho_2Fe_{11}Al_6C$  is very different from that of  $Ho_2Fe_9Al_8C$ , it is possible that magnetization at 500 Oe of  $Ho_2Fe_{11}Al_6C$  is larger than that of  $Ho_2Fe_9Al_8C$ . It can be seen that the temperature at which the two sublattice moments cancel is higher for higher Al concentrations, its upper limit being the Curie temperature. The compensation temperatures are also listed in table 1.

In order to investigate the magnetocrystalline anisotropy of  $Sm_2Fe_{17-x}Al_xC$  compounds, the samples were ground to very fine powders, mixed with epoxy resin and then aligned in a magnetic field of 20 kOe. XRD studies of magnetic-field-oriented powders can provide information concerning the magnetocrystalline anisotropy on the basis of the diffraction peaks present in each of the patterns. Uniaxial anisotropy occurs for all compounds as evidenced by the significant increase in the (0,0,6) reflection and the disappearance of ( $h, k, 0$ ). For example, figure 6 presents the room-temperature diffraction patterns of oriented  $Sm_2Fe_{17-x}Al_xC$  powders with  $x = 2$ . The rhombohedral  $c$  axis of  $Sm_2Fe_{17-x}Al_xC$  is readily aligned in the direction of the applied magnetic field. These data indicate that the easy axis of magnetization lies parallel to the  $c$  axis.

Figure 7 shows an example of the magnetization curves measured parallel and perpendicular to the aligned direction at room temperature for samples with  $x = 2$  and 3. The anisotropy field  $H_A$  estimated from the measurement curves, and the saturation magnetization  $M_s$  of  $Sm_2Fe_{17-x}Al_xC$  are summarized in table 3. The room-temperature saturation magnetization decreases monotonically with increasing Al content, while the room-temperature anisotropy field of  $Sm_2Fe_{17-x}Al_xC$  is found to increase from 53 kOe [12] for  $x = 0$  to 108 kOe for  $x = 2$ . Further substitution decreases the anisotropy field. This means that the addition of Al to  $Sm_2Fe_{17-x}Al_xC$  has a very significant influence on the magnetocrystalline anisotropy. Earlier reports indicated that the addition of Al to  $Sm_2Fe_{17}$  compounds can cause room-temperature uniaxial anisotropy to develop when  $x \geq 2$  [5, 7] without the need to introduce interstitial nitrogen or carbon atoms. For the sample with  $x = 2$ , the Curie temperature is about 560 K, the room-temperature saturation magnetization is about 110 emu  $g^{-1}$ , and the anisotropy field at room temperature is 108 kOe. The value of  $H_A$  is much higher than that for  $Sm_2Fe_{17}C$  and  $Nd_2Fe_{14}B$  (80 kOe), but the saturation magnetization is somewhat lower than that for the Al-free compound. In order to improve the hard magnetic properties, an effort to reduce the Al concentration is in progress. Thus, it is possible that these carbides can be used as the starting materials for producing high-performance 2:17-type sintered permanent magnets.

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