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Magnetic properties of $Er_2Fe_{16}SiC_x$ ($x=0$–2.5) compounds prepared by arc melting

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Abstract

The formation, structure and magnetic properties of arc-cast $Er_2Fe_{16}SiC_x$ compounds with $x=0$, 0.5, 1.0, 1.5, 2.0 and 2.5 were studied. X-Ray diffraction indicates that these carbides are single phase with Th_2Zn_{17}-type or Th_2Ni_{17}-type structure, except for $Er_2Fe_{16}SiC_{2.5}$ which contains a few per cent of α-Fe. Our result shows that the substitution of Si for Fe in the $Er_2Fe_{17}C_x$ compounds helps the formation of high carbon rare earth–iron compounds with 2:17-type structure. A structural transition from Th_2Ni_{17} type to Th_2Zn_{17} type is observed as x increases. The Curie temperatures are found to increase monotonically with increasing x from 413 K for $x=0$ to 588 K for $x=2.5$. The saturation magnetization of these compounds is essentially constant at about 63 e.m.u. g^{-1}. Spin reorientation transitions are observed in the $Er_2Fe_{16}SiC_x$ compounds. The spin reorientation temperature is found to increase with carbon concentration for $x \leqslant 1.5$ and remains at a constant value of about 160 K for $x > 1.5$.

Keywords: Magnetic properties; Arc melting

1. Introduction

The rare earth–iron-rich $Sm_2Fe_{17}N_x$ and $Sm_2Fe_{17}C_x$ intermetallic compounds with the rhombohedral Th_2Zn_{17}-type or hexagonal Th_2Ni_{17}-type structure have been extensively studied [1–6]. It has been found that the interstitial atoms have a strong effect on the intrinsic magnetic properties of the 2:17 compounds. However, it is difficult to obtain the rare earth–iron compounds $R_2Fe_{17}C_x$ with high carbon concentration by means of arc melting [7–9]. Coey et al. [10,11] have succeeded in increasing the concentration of carbon in $R_2Fe_{17}C_x$ up to $x=2.2$ by means of gas phase interstitial modification using hydrocarbon gases. Unfortunately, the nitrides and carbides prepared by the gas–solid reaction method have poor thermal stability. The aim of our work is to search for highly stable hard magnetic materials based on these nitrides or carbides. In previous work [12–14] we have shown that the interstitial carbides $R_2Fe_{17}C_x$ with higher carbon concentration can be prepared by melt spinning and they are highly stable at high temperatures, at least up to 1000 °C. Recently, several investigations have shown that the substitution of Ga, Si or Al for Fe in $R_2Fe_{17}C_x$ is able to stabilize the structure of the 2:17-type rare earth–iron compounds with high carbon concentration [15–18].

Spin reorientation phenomena are observed in $Er_2Fe_{17}C_x$ compounds [2,13,19,20]. In our present work we discovered that the substitution of Si in the $Er_2Fe_{17}C_x$ compounds not only helps the formation of high carbon rare earth–iron compounds but also results in an increase in the spin reorientation temperature in these compounds. In this paper we report the formation, structure and magnetic properties of $Er_2Fe_{16}SiC_x$ compounds with $x=0$, 0.5, 1.0, 1.5, 2.0 and 2.5.

2. Experimental

Fe and C were first melted into Fe–C alloys in an induction furnace, then Fe, Si, Er and Fe–C alloys were arc melted under a high purity argon atmosphere into homogeneous buttons with the compositions $Er_2Fe_{16}SiC_x$ ($x=0$–2.5). The elements used were at least 99.9% pure. The ingots were melted at least four times to ensure their homogeneity, then annealed under an

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argon atmosphere at 1450 K for 48 h, followed by quenching into water. X-Ray diffraction measurements on powder samples were performed using Co Kα radiation to determine the crystallographic structure. Besides the X-ray patterns, thermomagnetic analysis was used to identify single-phase samples. The Curie temperature and spin reorientation temperature were determined from the temperature dependence of the magnetization measured by a vibrating sample magnetometer in a field of 700 Oe and an extracting sample magnetometer in a field of 1 kOe respectively. The saturation magnetizations at 1.5 K were derived from magnetization curves measured in a field up to 70 kOe by an extracting sample magnetometer.

3. Results and discussion

X-Ray powder diffraction indicates that the $Er_2Fe_{17}SiC_x$ alloys are single phase with the rhombohedral Th_2Zn_{17}-type or hexagonal Th_2Ni_{17}-type structure, except for $Er_2Fe_{16}SiC_{2.5}$ which contains a small amount of α-Fe phase. However, it is difficult to obtain single-phase $Er_2Fe_{17}C_x$ with $x > 1.0$ by arc melting. Fig. 1 shows the X-ray diffraction pattern of arc-melted $Er_2Fe_{17}SiC_{2.0}$ in comparison with that of the Si-free

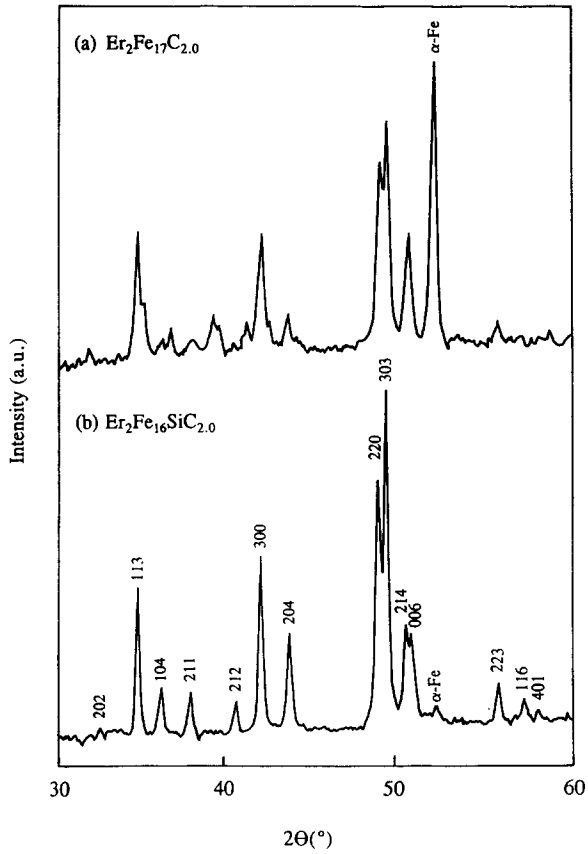

Fig. 1. Co Kα X-ray diffraction patterns of arc-melted $Er_2Fe_{17}C_{2.0}$ and $Er_2Fe_{16}SiC_{2.0}$.

ingot of $Er_2Fe_{17}C_{2.0}$. It can be seen that the arc-melted $Er_2Fe_{17}C_{2.0}$ contains a large amount of α-Fe. The present study has shown that the addition of Si, like that of Ga [15,16] or Al [17], to $R_2Fe_{17}C_x$ plays an important role in the formation of the high C rare earth–Fe intermetallics with 2:17-type structure.

The structural transformation from hexagonal Th_2Ni_{17}-type to rhombohedral Th_2Zn_{17}-type with increasing carbon concentration is observed in the arc-melted $Er_2Fe_{17}SiC_x$ ingots. $Er_2Fe_{16}Si$ is formed with the hexagonal Th_2Ni_{17}-type structure. $Er_2Fe_{16}SiC_{0.5}$ adopts both the hexagonal Th_2Ni_{17}-type structure and the rhombohedral Th_2Zn_{17}-type structure. The compounds $Er_2Fe_{17}SiC_x$ with $x = 1.0$, 1.5, 2.0 and 2.5 crystallize in the rhombohedral Th_2Zn_{17}-type structure.

The lattice parameters a and c and the unit cell volumes V of the $Er_2Fe_{16}SiC_x$ compounds with $x = 0$–2.5 are listed in Table 1. In comparison with the experimental data for $Er_2Fe_{17}C_x$ reported by Shen et al. [21], it is found that the unit cell volume of $Er_2Fe_{16}SiC_x$ decreases when Fe is replaced by the smaller Si atom. The introduction of interstitial carbon atoms leads to an expansion of the unit cell volume, which is consistent with the results reported for melt-spun $Er_2Fe_{17}C_x$ [21]. The unit cell volume is found to increase monotonically with increasing carbon concentration. For $x = 2.5$ the unit cell volume has increased by 5.1% over that of the carbon-free compound $Er_2Fe_{16}Si$.

The saturation magnetizations M_s at 1.5 K and the Curie temperatures T_c of the $Er_2Fe_{16}SiC_x$ compounds are also summarized in Table 1. There is little change in the saturation magnetization of the $Er_2Fe_{16}SiC_x$ compounds as the carbon content increases, except for the value of $Er_2Fe_{16}SiC_{2.5}$ which is relatively large owing to some α-Fe as an impurity phase. The Curie temperature is found to increase monotonically with increasing carbon concentration x from 413 K for $x = 0$ to 588 K for $x = 2.5$ as shown in Fig. 2, in which T_c of $Er_2Fe_{17}C_x$ [21] is also presented for comparison. A large effect of the addition of Si on the Curie temperature is observed. The substitution of Si for Fe results in an increase in T_c of the $Er_2Fe_{17}C_x$ compounds with the lower carbon concentrations, $x < 1.5$, whereas in the case of the higher carbon carbides with $x > 1.5$ the addition of Si decreases T_c. Fig. 3 shows the Curie temperatures of $Er_2Fe_{16}SiC_x$ as a function of the unit cell volume V. An approximately linear dependence of T_c on the unit cell volume is observed. This shows that the exchange interaction in $Er_2Fe_{16}SiC_x$ depends strongly on the unit cell volume. The enhancement of T_c with x in $Er_2Fe_{16}SiC_x$ is mainly due to the increase in the Fe–Fe exchange interactions induced by the interstitial carbon atoms.

Spin reorientation transitions are observed in the $Er_2Fe_{16}SiC_x$ compounds as shown in Fig. 4. The spin reorientation temperatures T_{sr} are listed in Table 2.

Table 1
Lattice parameters a and c, unit cell volume V and magnetic data for $Er_2Fe_{16}SiC_x$ compounds with $x = 0$–2.5

Compound	Structure	a (Å)	c (Å)	V (Å^3)	T_c (K)	M_s(1.5 K) (e.m.u. g^{-1})
$Er_2Fe_{16}Si$	Th_2Ni_{17}	8.452	8.231	509.2	413	62.63
$Er_2Fe_{16}SiC_{0.5}$	Th_2Ni_{17}	8.509	8.245	517.0	475	62.44
	Th_2Zn_{17}	8.509	12.367	775.4		
$Er_2Fe_{16}SiC_{1.0}$	Th_2Zn_{17}	8.555	12.401	786.0	530	64.48
$Er_2Fe_{16}SiC_{1.5}$	Th_2Zn_{17}	8.597	12.415	794.6	559	63.00
$Er_2Fe_{16}SiC_{2.0}$	Th_2Zn_{17}	8.613	12.450	799.8	577	61.71
$Er_2Fe_{16}SiC_{2.5}$	Th_2Zn_{17}	8.623	12.464	802.6	588	80.83

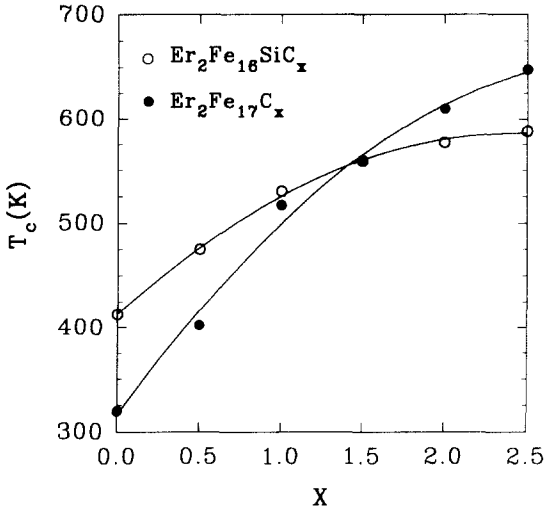

Fig. 2. Carbon concentration dependence of the Curie temperature T_c of $Er_2Fe_{16}SiC_x$ and $Er_2Fe_{17}C_x$ [21] compounds.

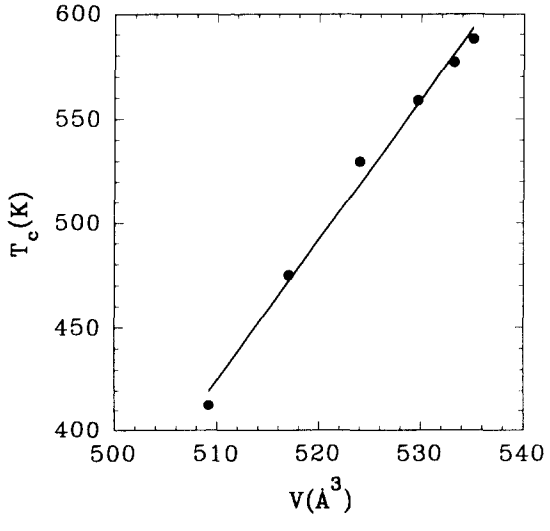

Fig. 3. Curie temperature T_c of $Er_2Fe_{16}SiC_x$ compounds as a function of unit cell volume V.

The carbon concentration dependence of T_{sr} of $Er_2Fe_{16}SiC_x$ is shown in Fig. 5 together with that of $Er_2Fe_{17}C_x$. T_{sr} is observed to first increase with increasing

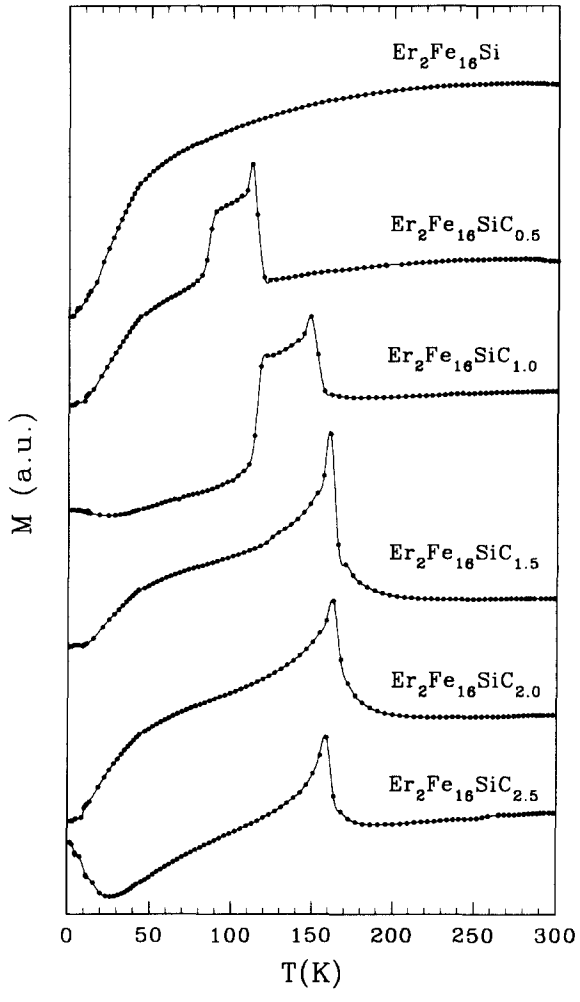

Fig. 4. Temperature dependence of the magnetization M of $Er_2Fe_{16}SiC_x$ compounds with $x = 0$, 0.5, 1.0, 1.5, 2.0 and 2.5.

carbon concentration from 48 K for $x = 0$ to 162 K for $x = 1.5$, then it remains essentially constant at about 160 K for $x > 1.5$. This situation is similar to that observed in $Tm_2Fe_{17}C_x$ [22]. It is well known that the spin reorientation in rare earth–iron compounds generally results from competing anisotropies with different temperature dependences for the rare earth and iron sublattices. The anisotropy of the rare earth ion sub-

Table 2
Spin reorientation temperature T_{sr} of $Er_2Fe_{16}SiC_x$ and $Er_2Fe_{17}C_x$ compounds

Compound	T_{sr} (K)					
	$x=0$	0.5	1.0	1.5	2.0	2.5
$Er_2Fe_{16}SiC_x$	48	112	149	162	163	159
$Er_2Fe_{17}C_x$ [13]	–	–	91	133	141	136

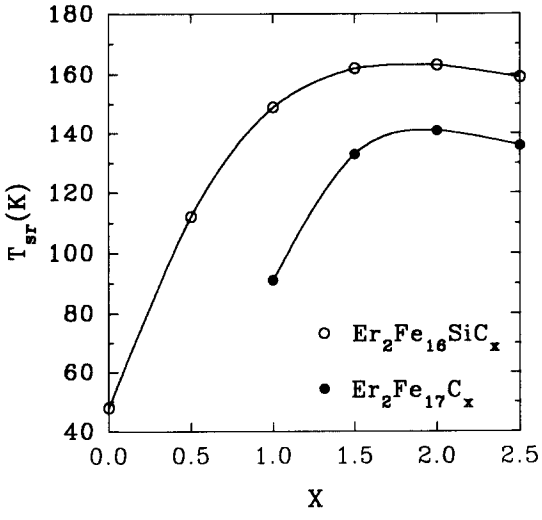

Fig. 5. Carbon concentration dependence of the spin reorientation temperature T_{sr} of $Er_2Fe_{16}SiC_x$ and $Er_2Fe_{17}C_x$ [13] compounds.

lattice is mainly determined by the product of the second-order Stevens coefficient α_J and the second-order crystal field parameter A_{20} on the basis of the crystal-field-induced single-ion model. In the case of the Er_2Fe_{17} compounds, $\alpha_J > 0$ and $A_{20} < 0$, hence the Er^{3+} sublattice exhibits a uniaxial anisotropy. However, the Er^{3+} sublattice anisotropy is too weak to overcome the iron sublattice anisotropy, so that Er_2Fe_{17} maintains an easy plane anisotropy. When carbon atoms enter interstitially into the Er_2Fe_{17} lattice, the A_{20} parameters are shifted towards more negative values with increasing carbon concentration, so the spin reorientation transformation moves to higher temperatures. Fig. 5 also illustrates that T_{sr} of $Er_2Fe_{16}SiC_x$ is markedly higher than that of $Er_2Fe_{17}C_x$. For $x=1.0$ and 1.5 the T_{sr} value has increased by 58 and 29 K respectively compared with the corresponding Si-free compounds. The present results are the same as those found by Gubbens et al. [23] on the basis of ^{169}Tm Mössbauer spectra of $Tm_2Fe_{15}M_2$, which indicated that silicon substitution led to a marked increase in the magnitude of the negative value of A_{20}, the corresponding increase in anisotropy of the rare earth ion sublattice explaining the shift of T_{sr} towards higher temperature. It can be seen from Fig. 4 that the temperature dependence of the magnetization of $Er_2Fe_{16}SiC_x$ with $x=0.5$ and 1.0 exhibits two turning points, indicating the changes in magnetic anisotropy first from easy plane to easy cone, then to easy axis.

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