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Abstract. The novel carbide Sm$_3$Fe$_{24}$Cr$_5$C$_y$ with the monoclinic Nd$_3$(Fe, Ti)$_{29}$ structure is synthesized by gas–solid reaction. Its hard magnetic properties, temperature stability, and corrosion resistance have been investigated by conventional methods. The hard magnetic properties were developed by the ball-milling technique. An intrinsic coercivity $\mu_{0i}H_c$ of 0.80 T at 293 K has been obtained. The temperature coefficient of the remanence is worse than that of Nd–Fe–B, while the temperature coefficient of the coercivity is better. The carbide powder has good corrosion resistance in comparison with Nd–Fe–B powder.

1. Introduction

New ternary rare-earth iron-rich intermetallic compounds are being widely investigated since the discovery of the R$_2$Fe$_{14}$B phase in 1984. In the past three years some new compounds, R$_2$(Fe$_{0.91}$V$_{0.09}$)$_{17}$ (R = Y, Nd, Sm, Gd) and Nd$_2$(Fe, Ti)$_{19}$ discovered by Shcherbakova *et al* [1] and Collocott *et al* [2] respectively, have been identified as having the monoclinic Nd$_3$(Fe, Ti)$_{29}$ (3:29) structure by Li *et al* [3] and Hu and Yelon [4]. The 3:29 structure is a structure intermediate between the well known rhombohedral Th$_2$Zn$_{17}$ (2:17R) and tetragonal ThMn$_{12}$ (1:12) structures, and consists of the alternate stacking of the 2:17R and 1:12 segments [3, 4]. The interstitial compounds with the 3:29 structure, R$_3$(Fe, M)$_{29}$X$_y$ (M = Ti, V, Cr, Mn, Mo and X = N, C), have a similar enhancement of their intrinsic magnetic properties to that observed for the 2:17-type compounds, and exhibit excellent intrinsic magnetic properties such as high magnetic ordering temperature, high magnetization and strong uniaxial anisotropy when R = Sm [5, 6]. This enhancement makes Sm$_3$(Fe, M)$_{29}$X$_y$ a potential candidate for use as a permanent magnet material. So far there have been many studies on 3:29-type nitrides [1, 2, 5, 7–12], but few studies on the 3:29-type carbides—especially on their hard magnetic properties—which may be due to the extremely difficulty of synthesizing the pure phase [13]. Recently, we have been successful in synthesizing the 3:29-type carbides Sm$_3$(Fe$_{0.933}$Ti$_{0.067}$)$_{29}$C$_y$ [6] and Sm$_3$Fe$_{24}$Cr$_5$C$_y$ [14], and have investigated their intrinsic magnetic properties. In this work, we report the results of our systematic study on the hard magnetic properties of Sm$_3$Fe$_{24}$Cr$_5$C$_y$ carbides, their thermostability, and their corrosion resistance.

2. Experimental procedure

Ingots with the composition $Sm_3Fe_{24}Cr_5$ were prepared by argon arc melting with starting elements of purity at least 99.9%. The starting compositions contained 10 wt% excess Sm in order to compensate the loss during the melting. The ingots were subsequently wrapped in molybdenum foil and sealed in quartz tubes, and annealed at 1273–1323 K under an argon atmosphere for 1–5 days. At the end of the annealing the ingots were quenched in water. The phases (3:29, 1:12, and α-Fe) present in the ingots have been examined by both x-ray diffraction (XRD) and thermomagnetic analysis (TMA). The ingots of single phase were pulverized into fine powders with a grain size of 20–35 μm. The carbonation was performed by heating the fine powders in acetylene (C_2H_2) at 1 atm and at a temperature of 773–873 K for 3–4 h. The carbide powders, which were identified as adding a small amount of α-Fe phase, were then ball-milled in petroleum ether using metal balls of 4–10 mm diameter with a sample-to-metal-ball weight ratio of 1:60. The magnetically aligned cylinder samples that were to be exposed to ball-milling, for various times t_{bm}, were made by mixing the powders with about 50 wt% epoxy resin, and then solidifying them in an applied field of 1.2 T at room temperature. The hysteresis loops were measured using a vibrating-sample magnetometer (VSM) in the temperature range 293–450 K. The magnetization indicated by the loops is that of the pure 3:29 carbide. The demagnetization factor was corrected according to the sample shape. The examinations of corrosion resistance were performed in environmental conditions with 87% relative humidity at 297.5 K for 70 days by exposing the carbonated powders.

3. Results and discussion

3.1. Hard magnetic properties at 293 K

Figure 1 shows the dependence on the different ball-milling times of the coercivity $\mu_{0i}H_c$, remanence B_r, and energy product $(BH)_{max}$, which are deduced from the hysteresis loop measurements made by a VSM at 293 K on the $Sm_3Fe_{24}Cr_5C_y$ carbide samples magnetized using a pulsed field of $\sim$4 T before measurement. It can been seen that the values of $\mu_{0i}H_c$, B_r, and $(BH)_{max}$ increase initially with increasing ball-milling time, t_{bm}, and reach a maximum, and then decrease. The maximum $\mu_{0i}H_c = 0.722$ T appears for $t_{bm} = 12$ h, while the maxima $B_r = 0.795$ T and $(BH)_{max} = 87.4$ kJ m^{-3} occur for much shorter milling times: $t_{bm} = 4$ h. The gain in coercivity for 4 h $< t_{bm} < 12$ h corresponds to losses in the remanence and energy product. When $t_{bm} > 12$ h, $\mu_{0i}H_c$ decreases with increasing t_{bm}. This may be the result of oxidization due to the very small particle sizes at this stage. Such a change is similar to that observed in the nitrides $Sm_3Fe_{24}Cr_5N_y$ [15] and $Sm_3(Fe_{0.933}Ti_{0.067})_{29}N_y$ [8].

The coercivity $\mu_{0i}H_c$ also increases with increasing magnetizing field as seen for $Sm_3Fe_{24}Cr_5N_y$ nitride [15]. The coercivity $\mu_{0i}H_c$ of the sample for which $t_{bm} = 12$ h reaches 0.80 T after the sample is subjected to a magnetizing field up to 5.5 T.

Figure 2 shows typical room temperature hysteresis loops of a sample of the $Sm_3Fe_{24}Cr_5C_y$ carbide for which the ball-milling time was $t_{bm} = 4$ h after the samples were magnetized by a pulsed field of $\sim$4 T. The values of $\mu_{0i}H_c$, B_r and $(BH)_{max}$ of the sample for which $t_{bm} = 4$ h at 293 K are 0.507 T, 0.795 T and 87.4 kJ m^{-3}, respectively. The maximum energy product of $Sm_3Fe_{24}Cr_5C_y$ carbide is obviously lower than those of $Sm_3Fe_{24}Cr_5N_y$ [15] and $Sm_3(Fe_{0.933}Ti_{0.067})_{29}N_y$ nitrides [8]—about 105 kJ m^{-3}—due to its lower saturation magnetization compared with those of nitrides [14].

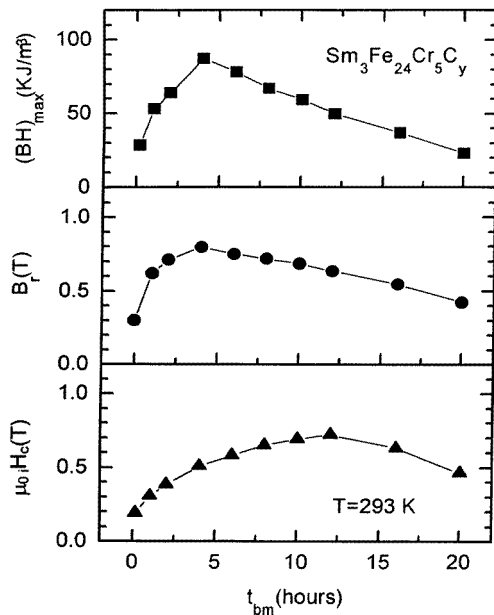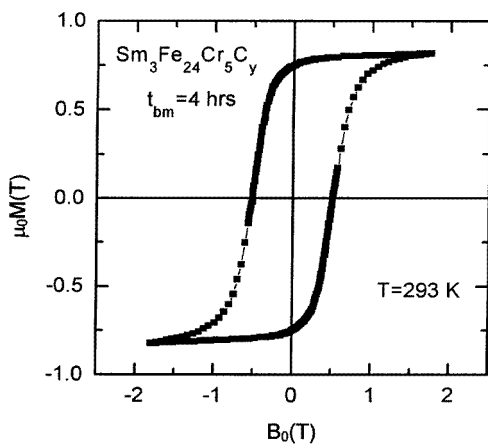**Figure 1.** The variation of B_r, $\mu_{0i}H_c$, and $(BH)_{max}$ for the $Sm_3Fe_{24}Cr_5C_y$ sample with t_{bm} at 293 K.

Figure 2. The typical room temperature hysteresis loops of the $Sm_3Fe_{24}Cr_5C_y$ sample with $t_{bm} = 4$ h.

3.2. The temperature dependence

Hysteresis loops of a sample with $t_{bm} = 10$ h in the temperature range of 293 K–450 K were measured by a VSM. The values of the remanence B_r and intrinsic coercivity $\mu_{0i}H_c$ at different temperatures were deduced from the hysteresis loop data obtained. The temperature dependences of B_r and $\mu_{0i}H_c$ for the sample with $t_{bm} = 10$ h of the $Sm_3Fe_{24}Cr_5C_y$ compound are shown in figure 3. Both B_r and $\mu_{0i}H_c$ decrease monotonically with increasing temperature. In order to investigate the temperature stability of the 3:29-type carbides, the
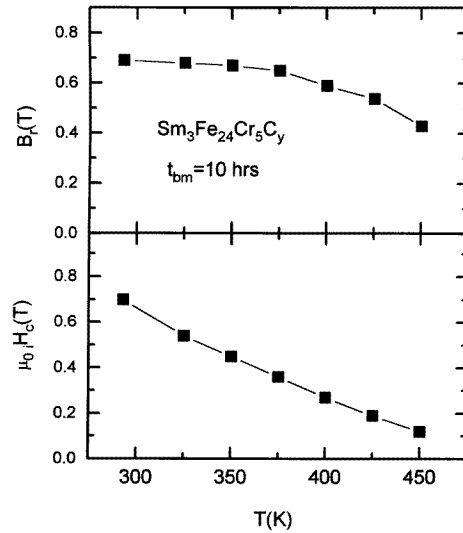
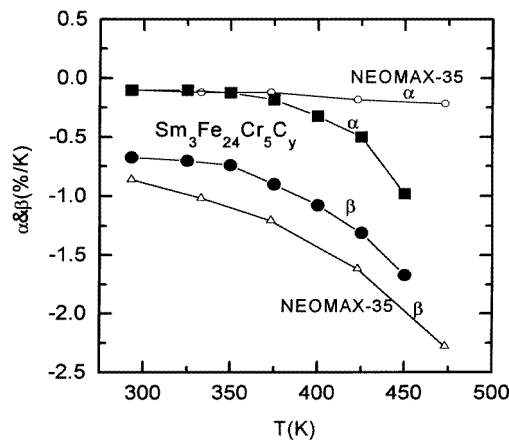**Figure 3.** The temperature dependence of B_r and $\mu_{0i}H_c$ for the $Sm_3Fe_{24}Cr_5C_y$ sample with $t_{bm} = 10$ h.

Figure 4. The temperature coefficient variation of the remanence and coercivity for $Sm_3Fe_{24}Cr_5C_y$ and NEOMAX-35 magnet [16] from 293 K to 450 K.

temperature coefficients for the remanence and the coercivity were calculated from the slopes of their temperature dependence curves. The temperature coefficient at temperature T is defined as follows [16]:

$$\alpha_T = \lim_{\Delta T \to 0} [\{[B_r(T + \Delta T) - B_r(T)]/B_r(T)\}/\Delta T] \times 100 \qquad (\% \ K^{-1})$$

and

$$\beta_T = \lim_{\Delta T \to 0} [\{[\mu_{0i}H_c(T + \Delta T) - \mu_{0i}H_c(T)]/\mu_{0i}H_c(T)\}/\Delta T] \times 100 \qquad (\% \ K^{-1}).$$

The temperature coefficients of B_r and $\mu_{0i}H_c$ for the $Sm_3Fe_{24}Cr_5C_y$ sample with $t_{bm} = 10$ h compared with data for NEOMAX-35 (Nd–Fe–B) [16] are plotted in figure 4.   The

temperature coefficient of the coercivity for the $Sm_3Fe_{24}Cr_5C_y$ sample is better than that of NEOMAX-35 in the temperature range investigated, but the temperature coefficient of the remanence is not as good as that of NEOMAX-35. Although the Curie temperature ($T_c = 559$ K) of the $Sm_3Fe_{24}Cr_5C_y$ carbide is almost the same as that of NEOMAX-35 ($T_c = 558$ K), the coercivities of the $Sm_3Fe_{24}Cr_5C_y$ samples are obviously lower than that of the NEOMAX-35. The increase of absolute value of the temperature coefficients of the remanence for the $Sm_3Fe_{24}Cr_5C_y$ sample at high temperature results from the faster decrease of the remanence.

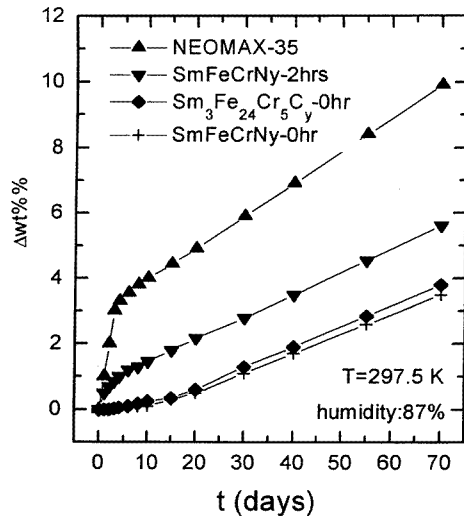**Figure 5.** Weight changes of $Sm_3Fe_{24}Cr_5C_y$ (0 h), $Sm_3Fe_{24}Cr_5N_y$ (0 and 2 h), and Nd–Fe–B powders with exposure time in a humid environment at 297.5 K.

3.3. Corrosion resistance

Powders of $Sm_3Fe_{24}Cr_5C_y$ carbide, $Sm_3Fe_{24}Cr_5N_y$ nitride, and sintered Nd–Fe–B magnet with average particle sizes of 20–35 μm were put together in a closed container with a constant relative humidity of 87%, which is created using a saturated aqueous solution of an excess of $Na_2CO_3 \cdot 10H_2O$, at 297.5 K for 70 days. The change of weight for the samples was obtained during the examination. In order to obtain the correct value, every type of powder was put in a glass container and all of the containers were dried in air for 20–30 minutes before weighing. Figure 5 shows the weight change of the powder samples of $Sm_3Fe_{24}Cr_5C_y$ carbide, $Sm_3Fe_{24}Cr_5N_y$ nitride, and sintered Nd–Fe–B magnet with the testing time. From figure 5 we can clearly see that the weight increase for nitride and carbide powders is obviously lower than that of Nd–Fe–B powder. This indicates that these nitrides and carbides have good corrosion resistance in comparison with Nd–Fe–B. We can also see that the weight increase tendency becomes almost the same for all of the powders after a certain time, but in the first few days the increase in weight of the Nd–Fe–B powder and $Sm_3Fe_{24}Cr_5N_y$ nitride with $t_{bm} = 2$ h is much faster than those of the other compounds, which shows that the big difference in corrosion resistance is caused at the initial stage of the oxidization.

In conclusion, the hard magnetic properties of the novel $Sm_3Fe_{24}Cr_5C_y$ carbide have

been investigated. The intrinsic coercivity $\mu_{0i}H_c$ for 0.80 T at 293 K has been developed. The temperature coefficient of the remanence for the carbide magnet is worse than that of NEOMAX-35, but the temperature coefficient of the coercivity is better. The $Sm_3Fe_{24}Cr_5C_y$ carbide powder has good corrosion resistance in comparison with the Nd–Fe–B powder.

Acknowledgments

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