Effect of several heat treatments on the microstructure and coercivity of $SmCo_5$ magnets

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Abstract

$SmCo_5$ samples were investigated under the following conditions: 'as-sintered' at $1150\,^\circ C$ (low coercivity—0.1–0.5 T), heat-treated at 850–880 °C (coercivity ~2.5–3.0 T) and after heat treatment at 750 °C during 25 days (low coercivity—0.1–0.5 T). Transmission electron microscopy investigation showed that the increase of coercivity at 850–880 °C is not due to second phases precipitated at grain boundaries in the samples nor to the elimination of stacking faults or dislocations. After the heat treatment during 25 days at 750 °C, no clear evidence of eutectoid decomposition of $SmCo_5$ phase was found, but a slight change of lattice parameters was detected.
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1. Introduction

The coercivity of $SmCo_5$ magnets is strongly related to the temperature of heat treatment. In the 'as-sintered' condition (i.e. sample only heat treated at 1100–1150 °C), low coercivity (0.1–0.5 T) is often observed. High coercivity (>3.0 T) only develops after a heat treatment performed at 850–900 °C [1–4]. If the samples are submitted to heat treatment at 700–750 °C, the resulting coercivity is very low (<0.5 T), a fact that has been attributed to the eutectoid decomposition of $SmCo_5$ phase [5]. According to several authors [2,5], the $SmCo_5$ phase decomposes into Sm_2Co_{17} and Sm_2Co_7 phases below 800–820 °C. On the other hand, other authors [6,7] did not confirm that decomposition.

To clarify the origins of the wide variation of coercivity as function of temperature in $SmCo_5$ magnets, an extensive characterization of samples submitted to several heat treatment conditions was performed. The microstructure of samples was investigated by optical, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and by X-ray diffraction.

2. Experimental

The samples were prepared following the powder metallurgy route [8], including milling down to ~4 μm, orientation under pulsed magnetic field of 8 T, isostatic pressing, sintering and heat treatment (under an argon atmosphere of 1 atm; 101 325 Pa).

Sample A refers to the 'as-sintered' condition: this sample was submitted to 1150 °C during 30 min, followed by quenching. Sample B1 is a typical magnet: it was sintered at 1150 °C for 30 min followed by slow cooling (1150 to 1000 °C at 2 °C/min and from 1000 to 850 °C at 1 °C/min)

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down to 850 °C, held for 1.5 h at 850 °C and then cooled to room temperature at 200 °C/min. Sample B2 is also a typical magnet, with a slight processing change: it was sintered at 1150 °C for 30 min followed by cooling (5 °C min) down to 880 °C, held 4 h at 880 °C and then cooled to room temperature at 200 °C/min. It should be noted that sample A was processed as sample B2, and then was 'resintered' (at 1150 °C, during 30 min).

Samples C1 and C2 have slightly different samarium content, and followed the same processing of sample B2. After being sealed in quartz capsule, under an argon atmosphere, they were submitted to a heat treatment at 750 °C for 25 days, in an attempt to promote the eutectoid decomposition of the $SmCo_5$ phase.

The magnetic measurements were performed in a vibrating sample magnetometer with field up to 9 T. X-Ray diffraction patterns were acquired in a Philips PW1710 diffractometer, with Cu Kα radiation (40 kV, 50 mA). The precise measurement of lattice parameters was obtained by means of the Cohen method using the Nelson–Riley error function for correction.

The microstructure of the samples was examined by optical microscopy, SEM and TEM (JEOL JEM-2000 FX at 200 kV). The etching used for observation under optical microscope was chromic acid (8 g CrO_3 + 2 g Na_2SO_4 + 100 ml H_2O) [9].

3. Results and discussion

When comparing the microstrutures of all samples (for a large area of sample E see Fig. 1 and for sample A see Fig. 2) we note that the microstructures are very similar.

The matrix phase is $SmCo_5$. The main 'second phase', often called Sm_2Co_7, was found to be more complex—a constituent formed by layers of phases belonging to the se-
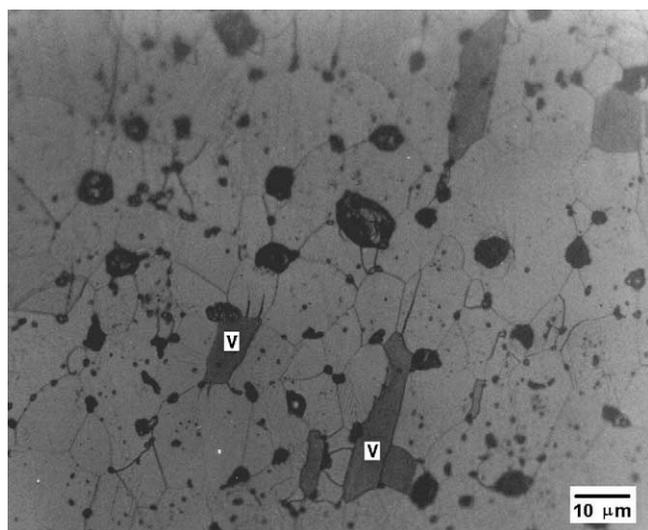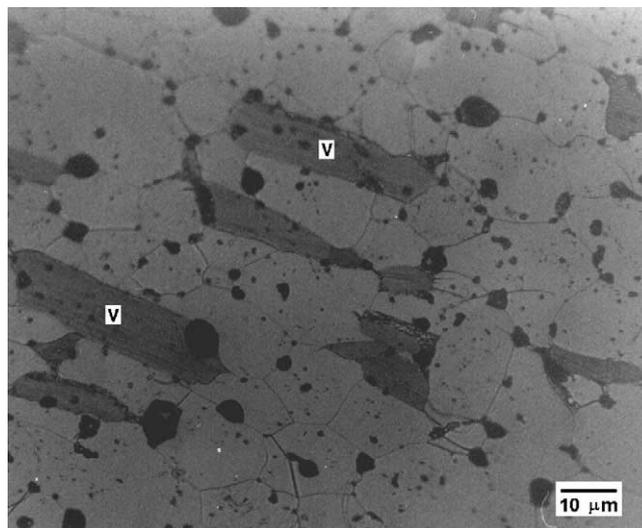

Fig. 2. Microstructure of sample A.

ries $Sm_{n+2}Co_{5n+4}$ including Sm_2Co_7 and Sm_5Co_{19}—and it is here called the constituent V [3,4]. Minor phases are oxides (Sm_2O_3), pores and a carbide, $SmCoC_2$ [10]. The volume fraction of constituent V is between 0.5 and 5% in the samples. Table 1 shows the lattice parameters of the matrix phase.

As stated above, samples A and C received the heat treatment of sample B2 and, thus, presented high coercivity (above 2.5 T, like samples B). After this, different heat treatments (25 days at 750 °C for samples C, or 30 min at 1150 °C for sample A) were applied, resulting in drastic reduction of the coercivity, as shown in Table 1.

If the $SmCo_5$ phase decomposes at 750 °C, the phases Sm_5Co_{19} and Sm_2Co_{17} should appear. But the microstructure of the samples C (see Fig. 1) do not show any clear evidence of the formation of Sm_2Co_{17}, or a volume fraction increase of the Sm_5Co_{19} phase.

After 25 days at 750 °C, $SmCo_5$ phase is still the main phase and, according to Table 1, its lattice parameters in samples C are similar, slightly different, when compared with the pair B. This can be evidence of a change in the lattice structure of the matrix phase after 25 days at 750 °C (samples C).

The microstructures of samples C are identical to those of samples B. It is possible to conclude that either eutectoid decomposition is very sluggish (maybe only beginning to occur after 25 days at 750 °C, in spite of the drastic drop in

Fig. 1. Microstructure of sample C2.

Table 1
Lattice parameters of the main phase and intrinsic coercivity of the samples

Sample	A	B1	B2	C1	C2
c (Å)	3.962	3.967	3.968	3.961	3.960
a (Å)	5.004	5.001	5.002	5.007	5.006
c/a	0.792	0.793	0.793	0.791	0.791
iHc (T)	0.17	2.90	2.54	0.48	0.05

Uncertainty = 0.002 Å.

coercivity) or $SmCo_5$ is a stable phase at this temperature. However, Table 1 points out a change in the lattice parameters.

After 25 days at 750 °C, it was not possible to confirm the existence of the eutectoid reaction $SmCo_5 \rightarrow Sm_5Co_{19} + Sm_2Co_{17}$, however a reaction of the type $SmCo_5 \rightarrow SmCo_{5+x} + SmCo_{5-x}$, may be occurring giving origin to Sm or Co rich clusters inside the crystalline structure. It is possible that the drastic fall of coercivity after heat treatments at 750 °C is related to a formation of those Sm or Co rich clusters. Other authors have suggested this could be attributed to a spinodal reaction [11].

Previous studies verified [2,5] that several days or weeks at 700–750 °C were necessary to begin the eutectoid precipitation, and they presented microstructures depicting the 2:17 phase. This could not be found in the present study. Oxidation due to oxygen inside the sealed containers, or sealing failures during the long heat treatments could transform $SmCo_5$ into Sm_2O_3 and Sm_2Co_{17} phases.

While no clear microstructural difference is found when comparing samples B with samples C, at least one clear difference is found when observing sample A: a change in the morphology of the carbide $SmCoC_2$, already previously reported [3].

The favorable effect of the heat treatment at 850 °C is approached when the samples A and B are compared. The lattice parameters of sample A (see Table 1) are different from those of samples B. The observation of samples by TEM (Figs. 3 and 4) permitted one to clarify some aspects. If samples A and B1 are compared, no clear differences are found. In both samples, the grains are strikingly free of defects like dislocations or stacking faults. There are no second phases precipitated at grain boundaries. The TEM data permit one to dismiss some hypotheses presented in the literature. For example, Narasimhan [12] claimed that the coercivity increase due to the heat treatment at 850–880 °C could be related to elimination of dislocations, but sample A has low density of dislocations. Liu et al. [13] suggested that the increase of coercivity at 850–880 °C is due to the formation of an epitaxial shell of Sm_2Co_7 that would surround the grains of $SmCo_5$ phase, but the TEM picture (see Fig. 4) shows that there are no second phases precipitated at grain boundaries.

The acquired data (lattice parameters and microstructural analysis) give support to the thesis [3] that the elimination of defects at the atomic level (for example vacancies) is responsible for the increase of coercivity due to heat treatment at 850–900 °C. The quantity of lattice defects decreases exponentially with the temperature.

It is worth making a few comments about the possible relevance of this study to understand the coercivity mechanisms in $Sm(CoCuFeZr)$ '2:17 type' magnets. Recent experimental results indicate that 2:17 type magnets are more correctly interpreted as nucleation controlled [14], and that the chemical composition of the $Sm(Co,Cu)_5$

(a)
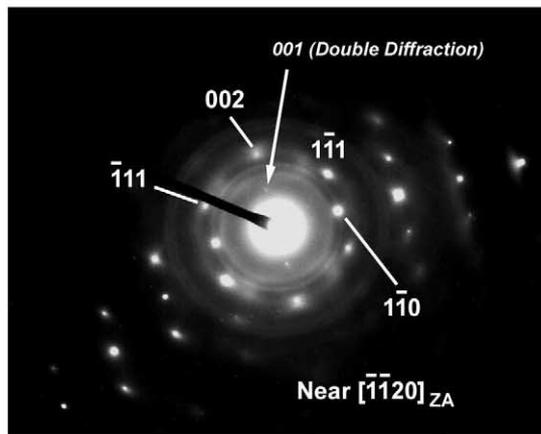
(b)

Fig. 3. (a) TEM microstructure of sample A. (b) Diffraction pattern for the region depicted in (a). The pattern is close to $[\bar{1}\,\bar{1}\,2\,0]_{ZA}$ for the 1:5 ($SmCo_5$) hexagonal structure.

phase has enormous influence on coercivity [14]. There are controversies about several features of the Sm–Co–Cu diagram [15–17]. The binary Sm–Co phase diagram has been subject of recent investigation [18]. Future study of Sm–Co–Cu phase diagram and of the eutectoid decomposition of $Sm(CoCu)_5$ phase seems to be fundamental to understand the origin of coercivity in 2:17 type magnets.
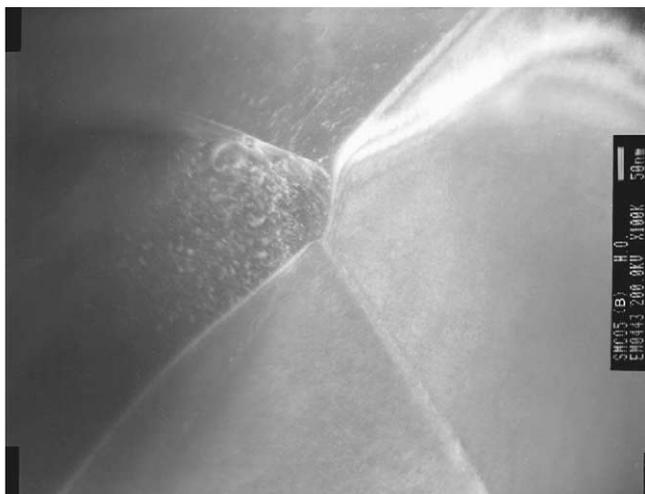
Fig. 4. TEM microstructure of sample B1.

4. Conclusions

After 25 days at 750 °C, no evidence was found of the eutectoid decomposition of SmCo$_5$. However, a slight change of the lattice parameters of the matrix phase is observed.

The drastic increase of coercivity due the heat treatment at 850 °C cannot be attributed to elimination of stacking faults or dislocations.

No evidence of the epitaxial shell suggested by Liu et al. [13] was found at grain boundaries.

The data obtained in this study support the thesis that the elimination of defects in atomic level (like vacancies) is the reason for coercivity increase after the heat treatment at 850–900 °C.

Acknowledgements

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