Effect of several heat treatments on the microstructure and coercivity of SmCo₅ magnets

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Abstract

SmCo₅ samples were investigated under the following conditions: 'as-sintered' at 1150 °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 SmCo₅ phase was found, but a slight change of lattice parameters was detected.

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Keywords: Rare earth compounds; Transition metal compounds; Permanent magnets; Microstructure; TEM

1. Introduction

The coercivity of SmCo₅ 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 (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 SmCo₅ phase was found, but a slight change of lattice parameters was detected.

To clarify the origins of the wide variation of coercivity as function of temperature in SmCo₅ 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.

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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 B 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)
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 SmCo5 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 microscopy was chromic acid (8 g CrO3 + 2 g Na2SO4 + 100 ml H2O) [9].

3. Results and discussion

When comparing the microstructures 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 SmCo5. The main ‘second phase’, often called Sm2Co7, was found to be more complex—a constituent formed by layers of phases belonging to the series Smn+2Co5+4 including Sm2Co7 and Sm5Co19—and it is here called the constituent V [3,4]. Minor phases are oxides (Sm3O7), pores and a carbide, SmCoC2 [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 SmCo5 phase decomposes at 750 °C, the phases Sm5Co19 and Sm2Co17 should appear. But the microstructures of the samples C (see Fig. 1) do not show any clear evidence of the formation of Sm2Co17, or a volume fraction increase of the Sm5Co19 phase.

After 25 days at 750 °C, SmCo5 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

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B1</th>
<th>B2</th>
<th>C1</th>
<th>C2</th>
</tr>
</thead>
<tbody>
<tr>
<td>c (Å)</td>
<td>3.962</td>
<td>3.967</td>
<td>3.968</td>
<td>3.961</td>
<td>3.960</td>
</tr>
<tr>
<td>a (Å)</td>
<td>5.004</td>
<td>5.001</td>
<td>5.002</td>
<td>5.007</td>
<td>5.006</td>
</tr>
<tr>
<td>ε/a</td>
<td>0.792</td>
<td>0.793</td>
<td>0.793</td>
<td>0.791</td>
<td>0.791</td>
</tr>
<tr>
<td>iHc (T)</td>
<td>0.17</td>
<td>2.90</td>
<td>2.54</td>
<td>0.48</td>
<td>0.05</td>
</tr>
</tbody>
</table>

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$$\rightarrow$Sm$_2$Co$_{17}$+Sm$_2$Co$_{17}$, however a reaction of the type SmCo$_5$$\rightarrow$SmCo$_{5-\alpha}$+xSmCo$_{5-\alpha}$ 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$_2$O$_3$ and Sm$_2$Co$_{17}$ 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$_2$Co$_7$ 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(FeCoCu)$_3$ 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(FeCoCu)$_3$ phase seems to be fundamental to understand the origin of coercivity in 2:17 type magnets.
4. Conclusions

After 25 days at 750 °C, no evidence was found of the eutectoid decomposition of SmCo5. However, a slight change of the lattice parameters of the matrix phase is observed.

The drastic increase of coercivity due to 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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