ELSEVIER

Journal of Alloys and Compounds 275–277 (1998) 660–664

Journal of ALLOYS AND COMPOUNDS

Orientation of samarium–cobalt compounds by solidification in a magnetic field

B.A. Legrand[a,*], D. Chateigner[b], R. Perrier de la Bathie[a], R. Tournier[a]

[a]*Laboratoire EPM-MatForMag, CNRS, 25 Avenue des Martyrs, 38042 Grenoble, France*
[b]*Laboratoire de Physique de l'état condensé, Univ. du Maine, BP 535, 72085 Le Mans, France*

Abstract

The solidification from the liquid state in a magnetic field produces oriented polycrystalline materials. A high degree of orientation is obtained with Sm–Co compounds solidified in several Tesla. The samples are crystallographically oriented with their easy-magnetization axes lying along the direction of the magnetic field applied during solidification. The process can be applied to the production of bulk anisotropic permanent magnets, without using the powder metallurgy. A model, validated by experimental results in the case of Sm–Co alloys, is proposed to explain the orientation mechanism. © 1998 Elsevier Science S.A.

Keywords: Orientation; Anisotropy; Solidification in a magnetic field; SmCo; Permanent magnet

1. Introduction

The application of a static magnetic field of several Tesla during the solidification of some alloys can favour their crystallographic orientation. This is the case of the paramagnetic $YBa_2Cu_3O_{7-\delta}$ ceramic which can be oriented by cooling from the liquid state in a magnetic field of 5 T, at a rate of 20°C h^{-1} to allow the peritectic reaction of the compound [1].

The aim of this paper is to show that solidification in a magnetic field of the intermetallic compounds $SmCo_5$ and Sm_2Co_{17} produces oriented polycrystals, even in extreme solidification conditions such as high cooling rate or strong and uncontrolled thermal gradients. The resulting high degree of orientation is used in two ways. First, the process is applied to the production of bulk oriented Sm–Co permanent magnets. Secondly, the results validate a model which explains the physical orientation mechanism which occurs during the solidification process.

2. Experimental details

2.1. Materials

Due to the association of a rare earth and a transition metal, the ferromagnetic phases $SmCo_5$ (1:5) and Sm_2Co_{17} (2:17) are combining high saturation magnetization ($J_{s_{1:5}} = 0.95$ T and $J_{s_{2:17}} = 1.4$ T at room temperature), high Curie temperature ($T_{c_{1:5}} = 710$°C and $T_{c_{2:17}} = 917$°C), with a large uni-axial magnetocrystalline anisotropy along the crystallographic *c*-axis. The crystal structure of the $SmCo_5$ phase is hexagonal ($CaCu_5$-type). The structure of the Sm_2Co_{17} phase can be generated from that of $SmCo_5$ by an ordered substitution of Co dumb-bells into some of the Sm sites. Consequently, these two phases are crystallographically coherent and particularly have the same easy-magnetization axis (the *c*-axis) [2]. The study of the binary Sm–Co phase diagram [3] shows that $SmCo_5$ forms from the liquid and Sm_2Co_{17} ($T_{\text{melting}_{1:5}} = 1290$°C and $T_{\text{melting}_{2:17}} = 1340$°C).

The Sm–Co type permanent magnets are based on these two ferromagnetic phases. In particular, the fine-scale microstructure of the '2:17' industrial magnets consists of a network of 2:17-type phase cells (with a size of 100–200 nm) separated by a coherent 1:5-type boundary phase (5 to 20 nm) [4]. These '2:17' magnets are not binary compounds but also contain copper (5 to 8 at. %), iron (17 to 28 at. %) and zirconium (1 to 3 at. %) substituting cobalt atoms. Their composition is $Sm(Co, Cu, Fe, Zr)_{z=7 \text{ to } 8.5}$. The value of *z* determines the relative amount of the 2:17 and 1:5 phases. Fortunately, these substitutions do not radically affect the crystal structure and do not change the *c*-axis anisotropy. The magnetic properties of these '2:17' substituted compounds are adapted to permanent magnet

*Corresponding author. Tel.: +33 047 6887428; fax: +33 047 6881191; e-mail: legrandb@labs.polycnrs-gre.fr

0925-8388/98/$19.00
PII: S0925-8388(98)00414-9

production (J_s ranges from 1 to 1.2 T, T_c from 800 to 850°C and the anisotropy field $\mu_o H_a$ from 7 to 10 T).

2.2. Procedure

The intermetallic alloys are made by melting in a cold high frequency inductive crucible under argon atmosphere and by casting into a copper mould. Several alloys with different compositions have been prepared: binary $SmCo_5$ and substituted $Sm(Co, Cu, Fe, Zr)_z$ alloys. These alloys are next placed in a HF inductive furnace inserted into a room temperature vertical bore of a superconducting coil cryostat: the sample can be melted and solidified in a vertical applied magnetic field B_t of several Tesla. Several solidification conditions have been experimented with, depending on the nature of the crucible used for the treatment.

The produced samples are magnetically characterized by magnetization measurements carried out in a fluxmeter (in an open flux circuit). SEM observations are performed on polished surfaces of the samples, and combined with EDX analyses.

3. Experimental results

Two experiments have been carried out with about 20 g of alloy with 16.6 at. % Sm–83.4 at. % Co (samples 1A and 1B). In each case, the material was heated up to the fusion by HF induction in an alumina crucible. It was then solidified, within a few minutes, in a vertical thermal gradient. Sample 1A was solidified in a magnetic field $B_t = 2.5$ T, while no field was applied for sample 1B. The SEM analyses show that the two samples consist of two phases $SmCo_5$ and Sm_2Co_{17}. The presence of Sm_2Co_{17} is attributed to samarium losses occurring during the melting and associated with contamination by the alumina crucible (the two Sm–Co phases contain 2 or 3% of Al). A morphological phase texture can be observed on the SEM micrography of sample 1A (Fig. 1): the 2:17 phase is aligned parallel to the vertical direction in the 1:5 matrix phase. This morphological texture has not been observed on sample 1B and might be attributed to the combination of the vertical thermal gradient and the applied magnetic field. The magnetization measurements performed on the whole samples, in two perpendicular directions (vertical and radial) are presented in Fig. 2. Sample 1A exhibits easy-magnetization and hard-magnetization directions parallel and perpendicular to B_t, respectively. This is the volumic signature of a crystallographic orientation, the *c*-axes of the grains lying preferentially along the vertical direction. On the contrary, sample 1B is rather isotropic and does not reveal the *c*-axes orientation. The number of grains in the sample is probably too small to represent a perfect statistical isotropy, which explains the small difference observed between the two magnetization curves in the two perpendicular directions. It is interesting to note that sample 1A is both morphologically and crystallographically textured.

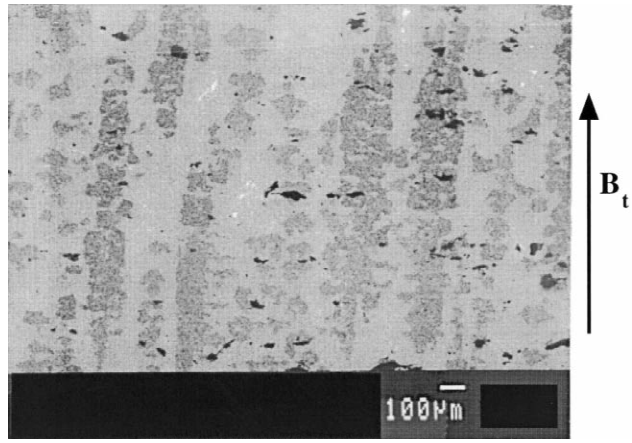

Fig. 1. SEM micrography of sample 1A: a morphological texture parallel to B_t is formed by the Sm_2Co_{17} phase (dark grey) in the $SmCo_5$ matrix (light grey). The black areas correspond to holes and cracks in the materials.

Because of the sample contamination produced by the fusion in the alumina crucible, subsequent experiments have been done directly in a cold inductive copper crucible. Solidification conditions are then radically changed. A 30-g sample of alloy (sample 2) with 16.6% Sm–83.4% Co has been melted by HF induction in a hemispherical crucible ($\phi = 33$ mm) and solidified in $B_t = 5$ T. Since the copper crucible was cooled by water circulation, the solidification occurred within a few seconds and the material was submitted to strong thermal gradients in several directions (perpendicular to the wall of the crucible). SEM analyses indicate that the sample consists of only the $SmCo_5$ phase which means that no significant samarium loss occurs during preparation. The grain size of the polycrystalline sample is about 100 to 200 µm.

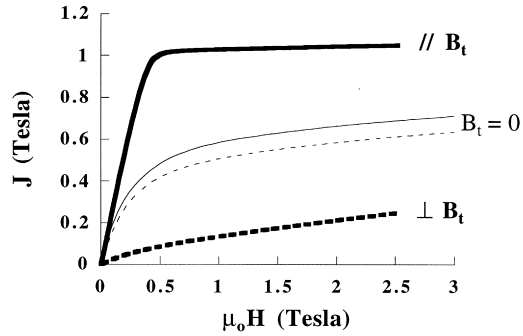

Fig. 2. Magnetization curves of two samples (mass = 20 g each) melted in an alumina crucible and solidified in a vertical magnetic field $B_t = 2.5$ T (sample 1A, bold lines) or in zero-field (sample 1B, fine lines). The full and the dotted curve correspond to vertical and radial measurements, respectively.

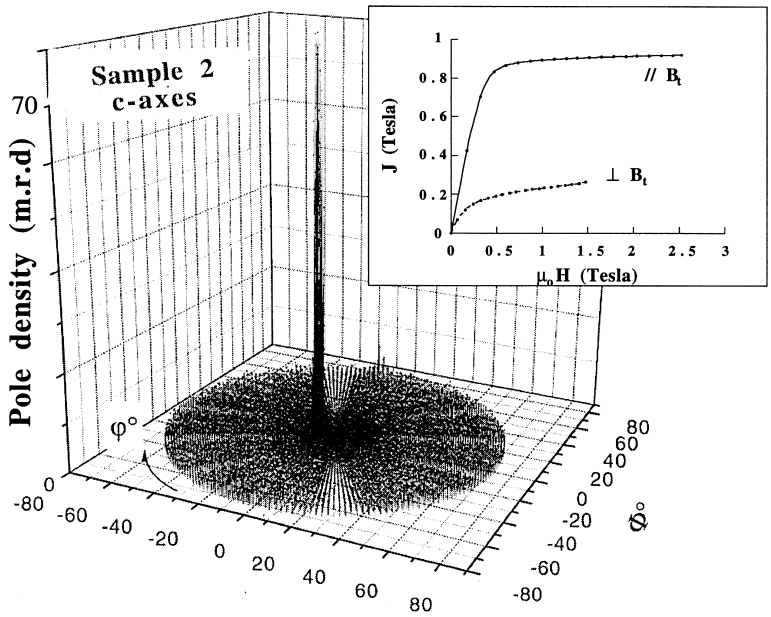

Fig. 3. *c*-axes pole figure measured on a face perpendicular to B_t of sample 2. The figure is the projection of the diffraction density (the unity is normalized to a multiple of a random distribution) of the {002}-$SmCo_5$ reflection as the sample is rotated. The poles are measured by scanning the tilt angle ϕ (between 0 and 72°) and the azimuthal angle j (between 0 and 360°). Insert: magnetization curves of sample 2 for two perpendicular directions.

Magnetization measurements performed on the whole sample have been completed by X-ray diffraction pole figures: Fig. 3 reveals that *c*-axes deviated by no more than 10° from the B_t direction. This figure is in good correlation with the volumic orientation shown by the magnetization curves (Fig. 3, insert).

Samples with substituted compositions have also been oriented in a cold crucible, this orientation being evidenced by magnetization measurements, but no phase-texture was shown by SEM (Fig. 4).

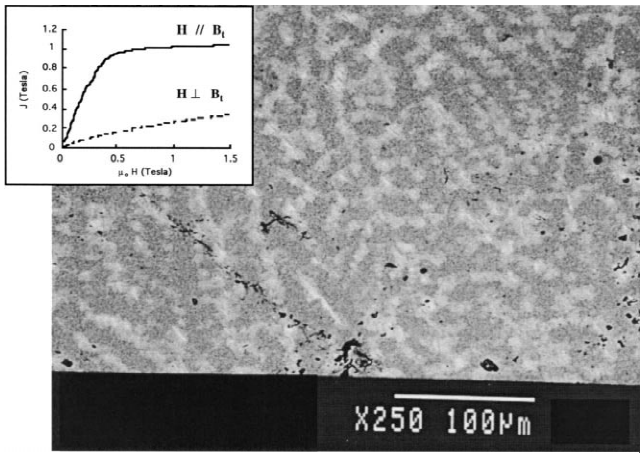

Fig. 4. SEM micrography of an alloy with the nominal composition $Sm(Co_{0.6}Cu_{0.08}Fe_{0.3}Zr_{0.02})_{8.35}$ melted in a cold inductive crucible and solidified in a magnetic field $B_t = 3$ T. Insert: magnetization curves of the sample for two perpendicular directions.

4. Application

The orientation process can be exploited to produce bulk anisotropic Sm–Co magnets. In this case Sm(Co, Cu, Fe, Zr)$_z$-type substituted alloys are necessarily used. Indeed, due to copper, these alloys have a bulk coercivity, independent of the grain size, which is not the case with binary alloys [4]. We also used a cylindrical inductive cold crucible to obtain directly cylindrical ingots ($\Phi = 20$ mm, $L = 15$ mm) oriented with the easy-magnetization axis along their axial length. The orientation factor $\tau = M_r/M_s$ (where M_s is the saturation magnetization value and M_r is the remanence measured in the direction of B_t) reflects the grain alignment of the sample [5]. The factor τ has been measured for 20 samples, with different substituted compositions, solidified in $B_t = 5$ T. The results (Fig. 5) show the high success of the process since more than 80% of the samples are well-oriented with an orientation factor larger than 0.8. We did not observe any significant relationship between the chemical composition of the sample and its orientation factor. The relatively low values of τ measured for a few samples can be explained by their incomplete melting due to the experimental conditions. Indeed, during heating, the material is submitted to radial magnetic forces (due to a radial gradient of the static magnetic field) and is pushed against the cold walls of the crucible. This effect leads to an incomplete melting of the edge of the sample and therefore to an incomplete orientation. The factor τ, being an average value of the whole sample orientation, is decreased by the misorientated grains towards the edge of the sample.

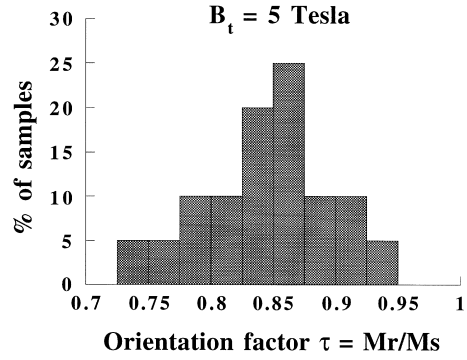

Fig. 5. Distribution of samples versus orientation factor $t=M_r/M_s$, for a fixed value of $B_t=5$ T. Twenty samples with substituted composition, melted in a cylindrical cold inductive crucible, have been analysed. (When the samples were not coercive, their remanent magnetization was given by the extrapolation of the slope of the demagnetization curve).

These orientated samples in the as-cast state are not coercive. They have to be magnetically hardened by appropriate annealings. In Fig. 6 the hysteresis loop of an oriented sample with composition $Sm(Co_{0.65}Cu_{0.08}Fe_{0.25}Zr_{0.02})_{8.34}$ which was heat treated for 5 h at 1150°C, is shown. Then, after quenching to room temperature, the sample was aged at 800°C for 10 h, followed by slow cooling to 400°C. The good magnetic properties obtained with this bulk magnet ($\mu_oH_c=2.8$ T, $J_r=1$ T, $(BH)_{max}=170$ kJ m^{-3}) show that solidification in a magnetic field can be a new process to produce bulk anisotropic permanent magnets. This process provides an alternative way to the currently used industrial technology based on powder metallurgy (i.e. orientation of ferromagnetic powdered material in a magnetic field, followed by a sintering step, and also by magnetic hardening heat treatments).

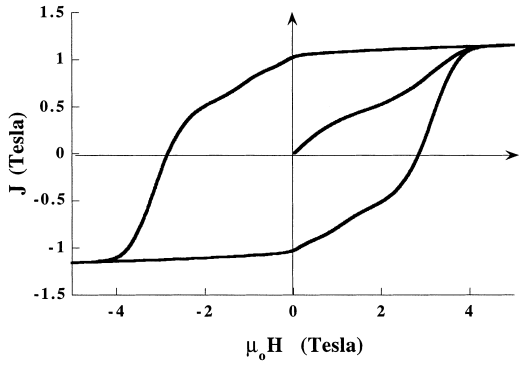

Fig. 6. Hysteresis loop of a bulk oriented permanent magnet produced with an initial composition $Sm(Co_{0.6}Cu_{0.08}Fe_{0.3}Zr_{0.02})_{8.35}$. The main magnetic properties of this magnet are: $\mu_oH_c=2.8$ T, $J_r=1$ T, $(BH)_{max}=170$ kJ m^{-3}.

5. Discussion

The experimental results have shown the relative facility to orient Sm–Co compounds by solidification in a magnetic field even in extreme cooling conditions.

The orientation mechanism is supposed to be linked to a residual paramagnetic anisotropy susceptibility $\Delta\chi$ (i.e. the difference between the susceptibility along two crystallographic axes) at solidification temperature. $\Delta\chi$ has been evaluated using a high temperature magnetometer developed in the laboratory [6], for a substituted alloy with composition $Sm(Co_{0.65}Cu_{0.06}Fe_{0.27}Zr_{0.02})_{8.1}$. At $T=$ 1175°C, immediately after the solidification, $\Delta\chi=3\times10^{-8}$ m^3 kg^{-1} [7].

In an attempt to interpret the orientation mechanism during solidification, we assumed the existence of free and anisotropic crystallites of the compound in the melt.

The anisotropy energy of one crystallite can be written:

$$E_\theta = -\frac{1}{2\mu_o}\cdot V\cdot d\cdot\Delta\chi\cdot B_t^2\cdot\cos^2\theta$$

where d and V are the density and the volume of the particle, and θ is the angle between B_t and its c-axis. During solidification, the crystallites tend to minimize their anisotropy energy and orient their c-axis parallel to the applied magnetic field. In order to estimate the volume V of these crystallites, we have also supposed that this anisotropy energy is in competition with the thermal energy kT (k is the Boltzmann constant and T is the solidification temperature, about 1200°C for the substituted compounds). The average $\langle\cos\theta\rangle$, which corresponds to the orientation factor τ, can be calculated assuming a Boltzmann distribution $f(\theta)=e^{-(E_\theta/kT)}$ [7]:

$$\tau=\langle\cos\theta\rangle=F_a(B_t^2)\text{ where }a=\frac{\Delta\chi\cdot d\cdot V}{2\mu_o\cdot k\cdot T}$$

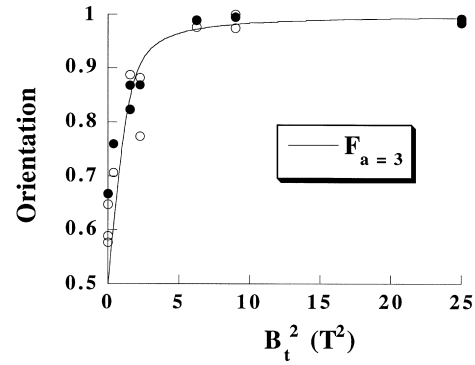

Fig. 7. Orientation factor as a function of B_t^2 for samples melted and solidified in cylindrical cold inductive crucible. The black and white points represent samples with compositions $Sm(Co_{0.6}Cu_{0.08}Fe_{0.3}Zr_{0.02})_{8.35}$ and $Sm(Co_{0.68}Cu_{0.08}Fe_{0.22}Zr_{0.02})_{7.6}$, respectively. τ was corrected for the edge effects by normalization to 1 for high field values. Note the good agreement between the experimental points and the function F_3.

The orientation factor of samples melted in a cylindrical cold crucible and solidified in different values of B_t have been experimentally measured and are plotted as a function of B_t^2 (Fig. 7). This curve has been fitted with different functions F_a, and is well represented by the function $F_{a=3}$. The individual volume of the anisotropic particles can then be evaluated: $V=7\times10^{-4}$ μm^3.

This small value is consistent with the idea of primary nuclei crystallizing at the beginning of the solidification process, and orienting in the magnetic field, during the solidification interval, before complete solidification occurs.

6. Summary

Solidification in a static magnetic field of several Tesla of Sm–Co alloys ($SmCo_5$ and Sm_2Co_{17}-type) produces oriented polycrystals. This orientation has been magnetically measured in the whole volume of the samples (ranging from 1 to 4 cm^3). The crystallographic orientation is obtained by solidifying at a relatively slow rate (in an alumina crucible) in a unidirectional thermal gradient, by quenching (in a cold crucible) in uncontrolled thermal gradients, and is due to the presence of the magnetic field. A morphological orientation completing the crystallographic orientation has been observed when solidification conditions combine a magnetic field and a thermal gradient in the same direction.

A direct application of the process is the production of high energy bulk Sm–Co permanent magnets. From a fundamental point of view, the experimental results of orientation in a cold crucible are consistent with a simple model of anisotropic crystallites which orient in the melt during the solidification process.

References

[1] P. de Rango, M.R. Lees, P. Lejay, A. Sulpice, R. Tournier, M. Ingold, P. Germi, M. Pernet, Nature 349 (1991) 770–772.
[2] K. Kumar, J. Appl. Phys. 63 (1988) R13.
[3] K.J.H. Buschow, J. Less-Common Metals 33 (1973) 311.
[4] K.J. Strnat, J. Magn. Magn. Mater. 100 (1991) 38–56.
[5] S. Liu, J. Appl. Phys. 76 (1994) 67576.
[6] B.A. Legrand, P. Courtois, E. Beaugnon, Proceedings of the International Congress of Electromagnetic Process of Materials-Paris, Centre Français de l'Electricité (Ed.), vol. 2, 1997, p. 283.
[7] B.A. Legrand, D. Chateigner, R. Perrier de la Bathie, R. Tournier, J. Magn. Magn. Mater. 173 (1997) 20–28.