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Coercivity of titanium-substituted high-temperature permanent magnets

Jian Zhou
University of Nebraska - Lincoln

Ralph Skomski
University of Nebraska-Lincoln, rskomski2@unl.edu

David J. Sellmyer
University of Nebraska-Lincoln, dsellmyer@unl.edu

Coercivity of Titanium-Substituted High-Temperature Permanent Magnets

Jian Zhou, Ralph Skomski, and David J. Sellmyer

***Abstract*—The temperature dependence of the coercivity of Sm–Co based magnets is investigated by magnetization measurements and model calculations. The Zr-free titanium-substituted Sm–Co material exhibits a positive temperature coefficient dH_c/dT of the coercivity (TCC) above room temperature, a reasonable hysteresis-loop shape, and an appreciable coercivity of 12.3 kOe at 500 °C for the nominal composition $Sm(Co_{6.2}Cu_{0.8}Ti_{0.3})$. The samples were produced by heat-treating the disordered 1 : 5 alloy commonly referred to as the $TbCu_7$ (or 1 : 7) phase. X-ray diffraction analysis shows that, upon annealing at 1165 °C, the starting material segregates into more-or-less stoichiometric 1 : 5 and 2 : 17 phases. The TCC is explained by taking into account that two-phase Sm–Co magnets are of the pinning type, that is the coercivity is realized by capturing (or repelling) domain walls at 1 : 5/2 : 17 phase boundaries. Starting from a planar-defect approach, the TCC is modeled as a function of the anisotropy constants of the involved phases. The present approach yields a fair agreement between theory and experiment, and explains the existence of a coercivity maximum in terms of the Cu concentration.**

***Index Terms*—Domain wall pinning, high-temperature permanent magnets, Sm–Co based permanent magnets, temperature dependence of coercivity.**

I. INTRODUCTION

VERY recently, permanent magnets with operating temperatures above 450 °C have become an area of worldwide scientific and industrial interest. Sm–Co based magnets are the most promising candidates for the high-temperature applications because of their high Curie temperature and good magnetic properties. Conventional Sm_2(Co,Fe,Cu,Zr)$_{17}$ permanent magnets provide large coercivity and energy product at room temperature, but the negative temperature coefficient of coercivity (TCC) makes the 2 : 17 magnets unsuitable for the high temperature usage since the H_c drops sharply to less than 5 kOe at 450 °C. Efforts on improving the high temperature coercivities of the 2 : 17 magnets have been made by adjusting the composition and the heat treatment conditions and some good results have been obtained. In this context an abnormal temperature dependence of intrinsic coercivity has been found in the Sm_2(Co,Fe,Cu,Zr)$_{17}$ magnets by several groups [1]–[3]. Recently, we reported a Sm–Co–Cu–Ti high-temperature permanent magnet with the positive temperature coefficient of coercivity [4]. In this paper we will present further improvements of the magnets performance of the material and give an explanation of the positive TCC behavior.

II. SAMPLE PREPARATION

A series of $Sm(Co_{7.05-x}Cu_xTi_{0.25})$ ($x = 0.4$, 0.5, 0.6, 0.65, 0.7, 0.8, 0.9) samples were prepared by arc-melting the starting elements materials with purity of at least 99.9% under flowing argon. The samples were sealed in a quartz tube filled with argon and heat-treated in the following way: solutionized at 1165 °C for 3 hrs, then cooled to 825 °C and annealed for 8 hrs, followed by slowly cooling with a rate of 1 °C/min down to 550 °C for another 8 hrs. X-ray diffraction was used to determine the crystal structure. Hysteresis-loop measurements at room temperature and at elevated temperatures (up to 600 °C) were performed by VSM and SQUID.

III. STRUCTURAL AND MAGNETIC PROPERTIES

The x-ray diffraction pattern show that the as-melted samples have the disordered $CaCu_5$ (1 : 5) structure which is commonly referred to as $TbCu_7$ (1 : 7) structure. After heat-treatment, the samples segregate into two phases: a nearly stoichiometric 1 : 5 grain-boundary phase and a main Th_2Zn_{17} (2 : 17) phase. Transmission electron microscopy shows that the microstructure is cellular and reminiscent of that of industrial 2 : 17 magnets. Details about the crystal structure and the microstructure can be found in our previous work [4]. The thermal-magnetic analysis confirmed the existence of this two-phase mixture.

Fig. 1 shows the typical hysteresis loops of a $SmCo_{6.65}Cu_{0.4}Ti_{0.25}$ sample at different temperatures. The intrinsic coercivity of this sample increases as the temperature goes up, from 0.1 kOe at the temperatures below 300 °C to a maximum value of 3.8 kOe at 550 °C. This coercivity change is reversible, i.e., the coercivity drops back to almost zero when the temperature goes back to room temperature after high temperature measurement. The magnets exhibit a positive temperature coefficient of the coercivity. Fig. 2 shows the temperature dependence of coercivity of five $Sm(Co_{7.05-x}Cu_xTi_{0.25})$ bulk samples with $x = 0.4$, 0.5, 0.6, 0.65 and 0.8. It can be seen that with increasing Cu content, the intrinsic coercivity of the samples increase and the temperature coefficient of coercivity decreases gradually to almost zero ($x = 0.65$). When Cu content is higher ($x > 0.65$), the TCC goes to negative value ($x = 0.7$ and 0.9 are not shown in the figure). A maximum value of 10.0 kOe coercivity at 500 °C was obtained in the $Sm(Co_{6.25}Cu_{0.8}Ti_{0.25})$ sample. To reach a higher H_c, we changed the composition of above sample

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The authors are with Behlen Laboratory of Physics and Center for Materials Research and Analysis, University of Nebraska, Lincoln, NE 68588 (e-mail: {jzhou; rskomski}@unlserve.unl.edu; cmra@unl.edu).

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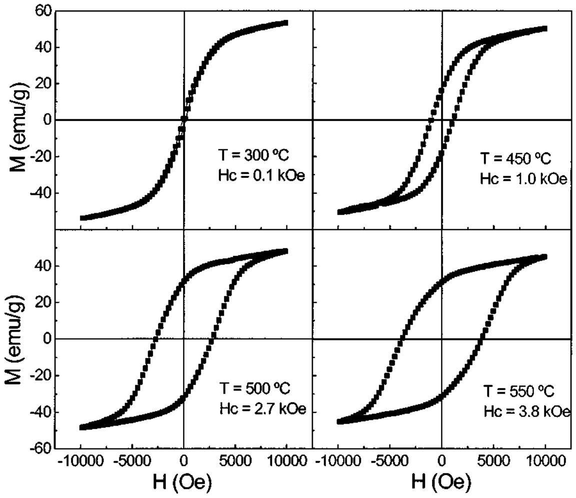

Fig. 1. Hysteresis loops of a $Sm(Co_{6.65}Cu_{0.4}Ti_{0.25})$ sample at different temperatures.

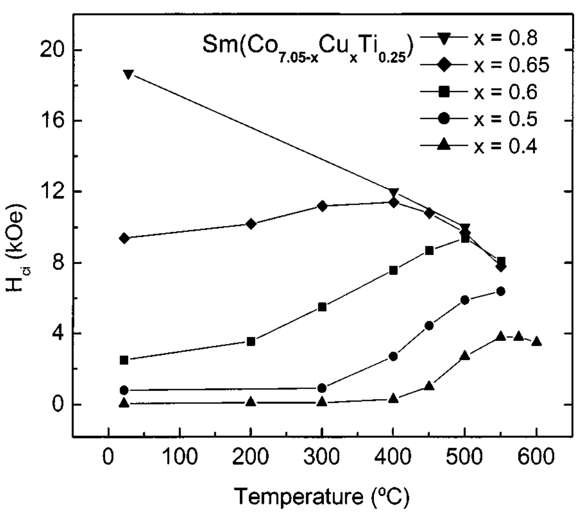

Fig. 2. Temperature dependence of intrinsic coercivities of $Sm(Co_{7.05-x}Cu_xTi_{0.25})$ bulk samples with $x = 0.4$–0.8.

slightly by adjusting the Ti amount to 0.3. After same heat treatment condition, this $Sm(Co_{6.2}Cu_{0.8}Ti_{0.3})$ sample showed a coercivity of 12.3 kOe at 500 °C (Fig. 3 shows a typical loop). Further investigations on the Ti content effect are under work.

IV. Origin of the Positive Temperature Coefficient

To explain the TCC we take into account that two-phase Sm–Co magnets are of pinning type [5], that is the coercivity is realized by capturing (or repelling) domain walls at 1 : 5/2 : 17 phase boundaries. There are two aspects: the interaction of a plane domain wall with the grain boundary [6] and the effect of the domain-wall curvature [7]. The pinning interaction of a plane wall is characterized by two effects. First, the domain-wall energy $g(x_0)$, where x_0 is the domain-wall position, acts as an attractive or repulsive potential which pins the wall. Second, the domain-wall fine structure of the wall changes on pinning. For example, if the grain-boundary region is soft-magnetic, then the domain-wall width increases.

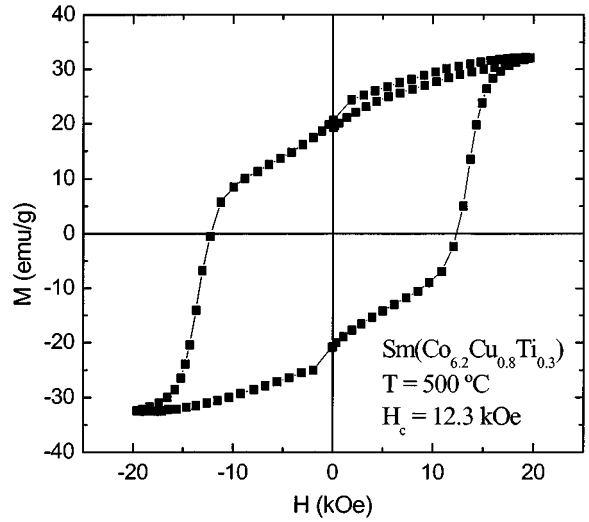

Fig. 3. Hysteresis loop of $Sm(Co_{6.2}Cu_{0.8}Ti_{0.3})$ at 500 °C.

A simple variational approach is to use a trial function for the magnetization $m = M_z/M_s$

$$m(x, x_0, \lambda) = \tanh\left(\frac{x - x_0}{\lambda}\right) \tag{1}$$

where λ is a wall-width parameter and x_0 is the position of the wall. After some calculation, we obtain the following expression for the pinning energy

$$\begin{aligned} Ep(\lambda, x_0) = {} & \eta(\lambda)\cdot\lambda\cdot\left(\tanh\left(\frac{b - x_0}{\lambda}\right) + \tanh\frac{x_0}{\lambda}\right) \\ & - \mu_0\cdot H\cdot(M_s - M_h)\cdot\lambda \\ & \cdot\ln\left(\cosh\left(\frac{b - x_0}{\lambda}\right)/\cosh\frac{x_0}{\lambda}\right) \end{aligned} \tag{2}$$

where

- h and s are the indices which refer to the main and boundary phases, respectively,
- b is the thickness of the boundary phase, and
- $\eta(\lambda)$ $= (A_s - A_h)/\lambda^2 + K_s - K_h$.

Minimizing the total energy with respect to x_o and λ yields two coupled nonlinear and field-dependent equations, and the coercivity is determined by the condition $\partial H/\partial x_0 = 0$. The solution of this problem goes beyond the scope of this work, but it can be shown that the coercivity can be approximated by the well-known equation

$$H_c = H_0\cdot\left(\frac{\pi\cdot b}{3\sqrt{3}\cdot\delta}\cdot\frac{|\Delta K|}{K_h}\right) \tag{3}$$

where H_o is the anisotropy field of the main phase. Essentially, the corrections to this equation, which is exact for thin boundaries $b \ll \delta$, amount to the replacement of the factor $\pi/(3\sqrt{3})$ by a weakly exchange and boundary-thickness dependent function.

The domain-wall curvature, which reflects the geometry of the cellular structure of the magnet, has been outlined in [7] and is automatically contained in full-scale simulations [8]. Plane walls in complicated structures may exhibit a very low coercivity, because $K_1(\boldsymbol{r})$ is largely averaged inside the wall,

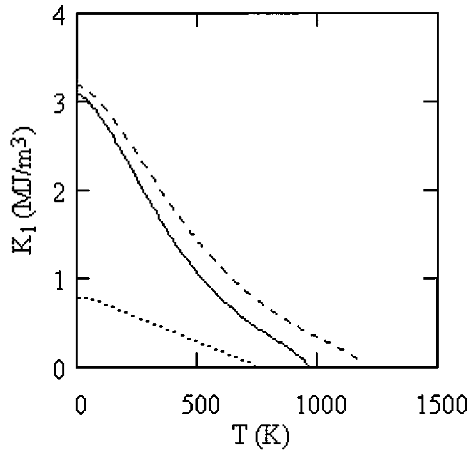

Fig. 4. Schematic temperature dependencies of anisotropy for a main phase (dashed line) and grain-boundary phases [9] having moderate Cu content (solid line) and high Cu content (dotted line).

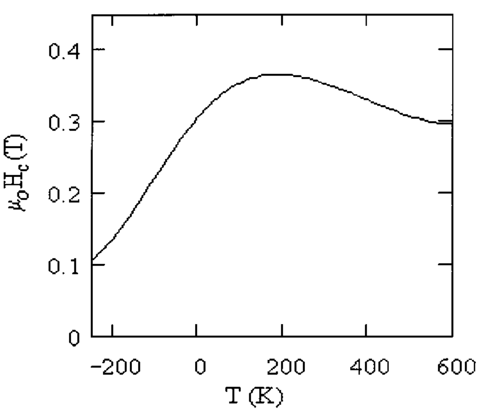

Fig. 5. Model calculation of the temperature dependence of the pinning coercivity.

so that some wall curvature is necessary to locally plane walls and to realize the coercivity (3). However, very high curvatures indicate magnetic softness and reduce the coercivity by suppressing H_o. Note that the plane-wall pinning and curvature effects are the main contributions to the pinning coercivity; magnetic viscosity is a small coercivity-reducing correction to these two effects [9].

Equation (3) shows that the pinning coercivity is essentially proportional to the anisotropy difference $\Delta K = |K_h - K_s|$ between the two involved phases. Fig. 4 shows typical temperature dependencies for a main phase (dashed line) and a grain-boundary phase (solid line), whereas the corresponding temperature dependence of the coercivity is shown in Fig. 5. It is important to note that $K_1(T)$ exhibits a pronounced dependence on the chemical composition. In particular, Cu strongly reduces the anisotropy of the 1 : 5 grain-boundary phase [3]. This is the origin of the composition dependence of the curves shown in Fig. 2: moderate amounts of Cu yield $K_1(T)$ dependencies similar to the solid line in Fig. 4 and give rise to a coercivity maximum, whereas a further increase of the Cu content suppresses the anisotropy at all temperatures (dotted curve in Fig. 4) and the coercivity becomes a monotonously decreasing function of the temperature. (Note that the low-temperature anisotropy of Cu-free $SmCo_5$ is much higher than that of Sm_2Co_{17}.) For intermediate Cu contents it follows from Fig. 4 that there are also temperatures at which $\Delta K = 0$. In this case, (3) predicts $H_c = 0$, but in reality there are chemical concentration fluctuations [10], so that the material is never truly homogeneous.

V. Conclusions

A Sm($Co_{7.05-x}Cu_xTi_{0.25}$) ($x = 0.4$–0.9) series of bulk samples were investigated and a positive temperature coefficient of coercivity was found in low Cu content samples ($x \leq 0.65$). When the Cu content is high ($x > 0.65$), the TCC changes to negative value. A Sm($Co_{6.4}Cu_{0.65}Ti_{0.25}$) sample with positive TCC reaches the maximum H_c of 9.7 kOe at 500 °C, while a Sm($Co_{6.2}Cu_{0.8}Ti_{0.3}$) sample with negative TCC gives an H_c of 12.3 kOe at 500 °C. This behavior is explained in terms of domain wall pinning mechanism in a two-phase magnet.

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