Evolution of Microstructure, Microchemistry and Coercivity in 2 : 17 Type Sm–Co Magnets with Heat Treatment

Y. Zhang, W. Tang, G. C. Hadjipanayis, C. Chen, C. Nelson, and K. Krishnan

***Abstract*—A systematic study has been undertaken to understand the evolution of microstructure, microchemistry, and coercivity of sintered $Sm(Co_{bal}Cu_{0.06}Fe_{0.015}Zr_{0.027})_{6.4}$ magnets with heat treatment using magnetometry, transmission electron microscopy, Lorentz microscopy, and nanoprobe chemical analysis. In general, the homogenized and quenched $Sm(Co_{bal}Cu_{0.06}Fe_{0.015}Zr_{0.027})_{6.4}$ magnets have a featureless microstructure with the 2 : 17 hexagonal structure. During isothermal aging at 700–850 °C, the 1 : 5 nuclei precipitate and then coalesce and start forming the cellular structure with 2 : 17 rhombohedral cells surrounded by 1 : 5 hexagonal cell boundaries. Uniform cellular and lamellar structures are formed after 2 hours of isothermal aging, and both the cell size and density of lamella phase slightly increase with longer aging. Nanoprobe chemical analysis shows that the Cu content in 1 : 5 cell boundaries increases during the slow cooling to lower temperatures, reaching a maximum value around 500 °C, which is consistent with the development of coercivity. Also the Cu content in the triple cell boundary junctions is twice as much as the amount at the regular cell boundaries regardless of cell size and boundary width. Lorentz microscopy indicates that the triple cell boundary junctions may play a major role in domain wall pinning.**

***Index Terms*—Coercivity, microchemistry, microstructure, Sm–Co.**

I. Introduction

THE MAGNETIC properties, especially the coercivity, of 2 : 17 type Sm (Co, Cu, Fe, Zr)$_z$ permanent magnets are known to be sensitive to their microstructure. Detailed microstructure studies on these magnets have been done in the past [1]–[8]. High coercivity is only obtained after a complex two-step heat treatment, which is accompanied by the formation of cellular structure (1 : 5 hexagonal +2 : 17 rhombohedral) superimposed on a lamella phase (1 : 3 rhombohedral or 2 : 17 hexagonal) [4], [7]–[10]. Previous results also showed that the 1 : 5 cell boundary phase is rich in Cu, the 2 : 17 cells in Fe, and the lamella phase in Zr [9]–[11]. Also it is not very clear why the coercivity is low, while the cellular morphology is fully developed after a long-time isothermal aging without the subsequent slow cooling [4], [7], [8], [10]. Obviously, besides the microstructure morphology, the microchemistry evolution during heat treatment plays an important role in the development of coercivity. It was found that the high temperature performance of precipitation hardened Sm(Co, Fe, Cu, Zr)$_z$ magnets is very sensitive to the Cu content, and a high coercivity and good temperature dependence of coercivity were obtained by controlling the Cu content in the magnets [12].

So far, few detailed microchemistry studies have been performed at the different heat treatment stages of Sm(Co, Fe, Cu, Zr)$_z$ magnets. In this article, a systematic study has been done to understand the evolution of microstructure and microchemistry upon heat treatment, and to determine their effect on the magnetic properties, especially on the coercivity.

II. Experimental

The sintered $Sm(Co_{bal}Cu_{0.06}Fe_{0.015}Zr_{0.027})_{6.4}$ permanent magnets have been subjected to a heat treatment consisting of homogenization at a high temperature in the range of 1160–1190°C, followed by aging at 700–850°C for 5 min to 24 h. After aging, the samples were subjected to either a quenching to room temperature or to a slow cooling down to 400 °C at 0.5–1 °C/min. Some samples were cooled to intermediate temperatures and then quenched to room temperature in order to retain the intermediate temperature state. Two sets of samples were prepared perpendicular and parallel to the alignment direction. The lamella phases as discussed below are parallel to the basal hexagonal plane and can only be observed in samples cut parallel to the alignment direction. All TEM samples were mechanically polished and thinned by ion milling. Conventional TEM was carried out on a JEOL JEM-2000FX at 200kV. Fresnel and Foucault mode Lorentz microscopy were perform on a JEOL JEM100-CX at 100kV. Nanoprobe was done with a Philips CM200 at 200kV. The magnetic properties were measured using a vibrating sample magnetometer (VSM) with a maximum applied field of 26 kOe.

III. Results and Discussion

In general, the homogenized and quenched $Sm(Co_{bal}Cu_{0.06}Fe_{0.015}Zr_{0.027})_{6.4}$ magnets have a featureless microstructure with the 2 : 17 hexagonal (2 : 17H) structure [Fig. 1(a)]. When the featureless homogenized samples are isothermally aged at 700–850 °C, the 1 : 5 precipitates nucleate and then coalesce and start forming the cellular structure in 5–30 min [Fig. 1(b)]. The lamella phase appears after the

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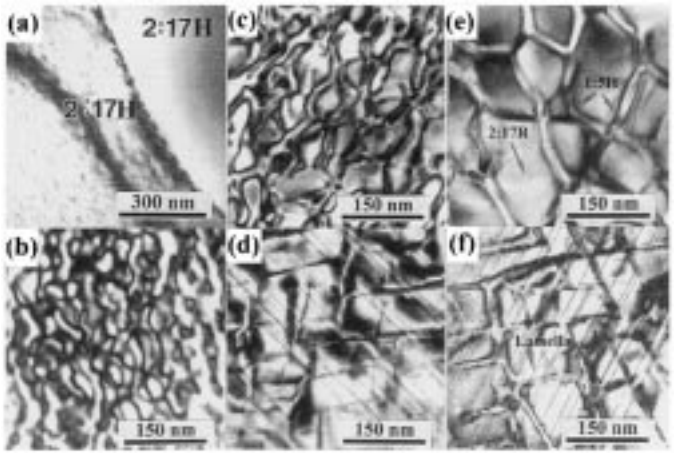

Fig. 1. Evolution of TEM microstructure in $Sm(Co_{bal}Cu_{0.06}Fe_{0.015}Zr_{0.027})_{6.4}$ magnets: (a) Homogenized at 1180 °C followed by quenching to room temperature; (b) Aged at 830 °C for 15 min followed by quenching to room temperature, showing cellular structure; (c), (d) Aged at 830 °C for 2h followed by quenching to room temperature, showing cellular structure and lamella phase superimposed on cellular structure, respectively; (e), (f) Aged at 830 °C for 24 h followed by quenching to room temperature, showing cellular structure and lamella phase superimposed on cellular structure, respectively.

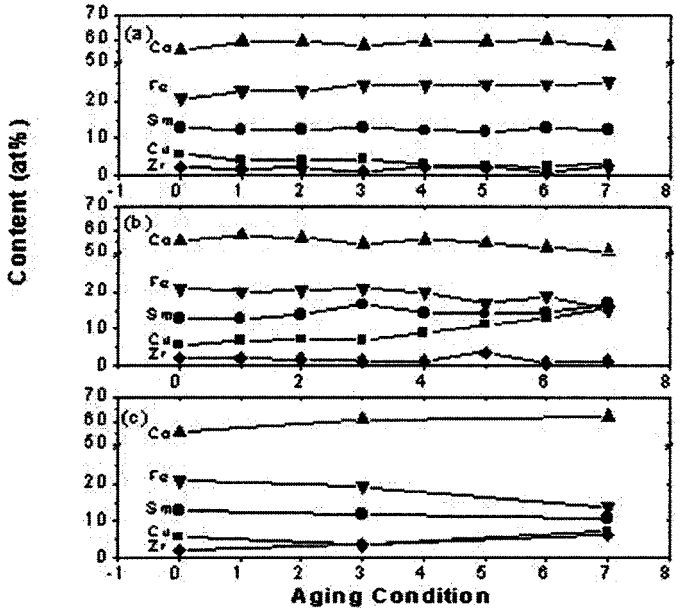

Fig. 2. Development of microchemistry in $Sm(Co_{bal}Cu_{0.06}Fe_{0.015}Zr_{0.027})_{6.4}$ magnets aged at 830 °C: (a) cell interior; (b) cell boundary; (c) lamella phase; 0, 1, 2 and 3 represent the initial state, 30 min, 2 h and 24 h aging followed by quenching to room temperature, respectively; 4, 5, 6 and 7 correspond to 24 h aging followed by a subsequent slow cooling to 700, 600, 500 and 400°C, respectively.

partial formation of cellular structure. Uniform cellular and lamellar structures are formed after 2 h of isothermal aging, and both the cell size and density of the lamella phase slightly increase with longer aging up to 24 h [Fig. 1(c)–(f)]. During subsequent cooling, after aging, both the cell size and lamella phase density are kept constant.

The microchemistry changes which occur during aging are shown in Fig. 2. The chemical composition of the 2 : 17 cells is given in Fig. 2(a), the 1 : 5 cell boundary is shown in Fig. 2(b),

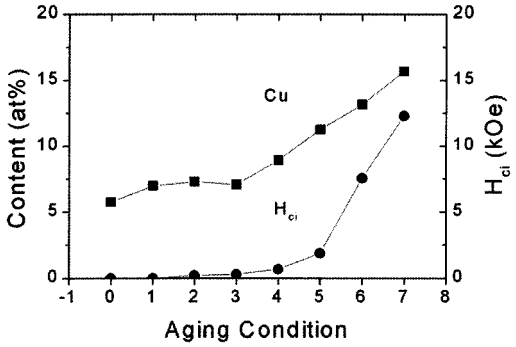

Fig. 3. Evolution of 1 : 5 Cu content and coercivity with aging in $Sm(Co_{bal}Cu_{0.06}Fe_{0.015}Zr_{0.027})_{6.4}$ magnets; 0, 1, 2 and 3 represent the initial state, 30 min, 2 h and 24 h aging followed by quenching to room temperature, respectively; 4, 5, 6 and 7 correspond to 24 h aging followed by a subsequent slow cooling to 700, 600, 500 and 400 °C, respectively.

and the lamella phase is shown in Fig. 2(c). Upon aging, the Fe atoms diffuse from the cell boundaries to the cell interiors, while Cu atoms migrate from cell interior to cell boundaries. It is remarkable that the Cu content in the cell boundary, which increases slightly during isothermal aging, is significantly increased during the subsequent slow cooling to 400 °C. After the full heat-treatment, the 2 : 17 cells are rich in Co and Fe and depleted in Cu and Zr; the 1 : 5 cell boundaries are rich in Cu and depleted in Fe and Zr; and the lamella phase is rich in Zr and depleted in Fe.

The evolution of Cu content and coercivity in the cell boundary phase with aging in the $Sm(Co_{bal}Cu_{0.06}Fe_{0.015}Zr_{0.027})_{6.4}$ magnets is shown in Fig. 3. The coercivity remains very low during isothermal aging, and develops only after the slow cooling to 400 °C. Obviously, the increase of Cu content in the cell boundary with slow cooling closely follows the increase in coercivity during cooling, while the microstructure morphology remains unchanged.

Table I shows the coercivity and microstructure data for the magnet aged at different temperatures. With increasing aging temperature, the cell size, boundary width, and lamella density increase leading to an increase in coercivity. The magnets with a smaller cell size also have a thinner boundary width, which leads to nearly the same volume fraction of cell boundary phase in both magnets. This is also consistent with the nanoprobe results which show that the Cu content in the cell boundaries of the magnets subjected to the 700 °C aging treatment is nearly the same with that of magnets subjected to the high temperature aging. Furthermore, the nanoprobe chemical analysis shows that the Cu content in the triple cell boundary junctions is much higher than the amount at the regular cell boundaries in all samples subjected to a full heat treatment regardless of aging temperature (Fig. 4).

For all the magnets studied, a strong domain wall pinning at the cell boundaries is observed only after the full heat treatment, irrespective of the aging temperature. The domain walls have a clear zigzag shape following some of the cell boundaries (Fig. 5).

When the Lorentz microscopy data are combined with the nanoprobe results, the conclusion is that the higher Cu content in the cell boundary phase, especially at the triple cell boundary

TABLE I
COERCIVITY AND TEM DATA FOR THE MAGNETS AGED AT DIFFERENT TEMPERATURES

Aging Temperature (°C)	Coercivity (kOe)	Cell Size (nm)	Boundary Width (nm)	Density of Lamella Phase (nm^{-1})	Cu in Cell Interior (at%)	Cu in Cell Boundary (at%)
700	6.5	50	6	0.046	2.1	14.4
850	13.0	105	11	0.061	3.1	15.7

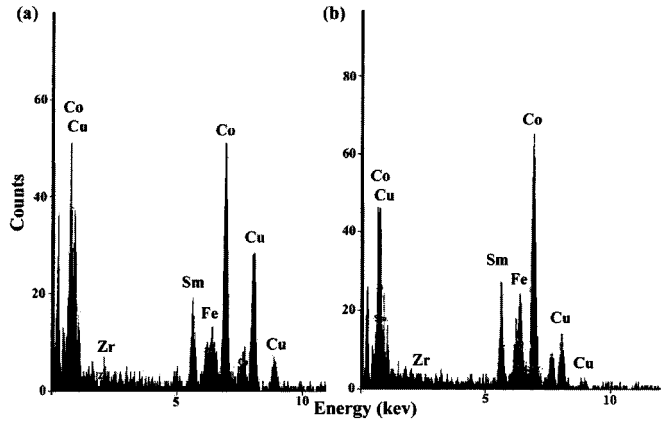

Fig. 4. Nanoprobe EDX patterns of $Sm(Co_{bal}Cu_{0.06}Fe_{0.015}Zr_{0.027})_{6.4}$ magnets homogenized at 1185 °C, aged at 700 °C for 24 h, and followed by a slow cooling down to 400 °C; (a) Triple cell boundary junctions, chemical composition (at%): Sm: 20.5, Cu: 29.4, Co: 37.7, Fe: 11.3, Zr: 1.1; (b) Regular cell boundaries, chemical composition (at%): Sm: 13.4, Cu: 14.4, Co: 53.1, Fe: 17.8, Zr: 1.3.

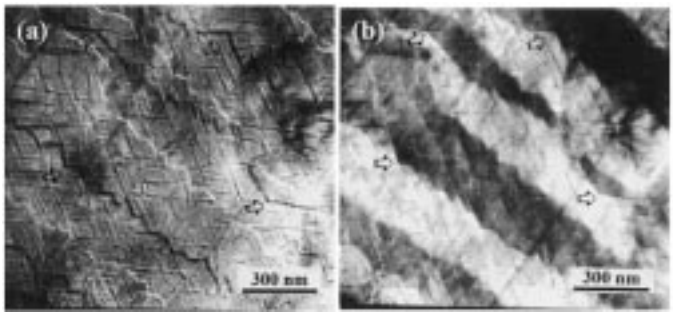

Fig. 5. Lorentz microscopy images showing domain walls pinned at the triple cell boundary junctions in fully aged $Sm(Co_{bal}Cu_{0.06}Fe_{0.015}Zr_{0.027})_{6.4}$ magnets: (a) Fresnel mode; (b) Foucault mode.

junctions, is responsible for the strong domain wall pinning. It is believed that this will be the key factor which controls the room temperature magnetic hardening behavior of these magnets. Cu dilutes the magnetic anisotropy and decreases the Curie temperature of 1 : 5 phase. The lower anisotropy leads to lower 1 : 5 domain wall energy and therefore to a large domain wall gradient at the 2 : 17/1 : 5 boundaries. This then leads to the high coercivity, since $H_c \propto (\Delta\gamma/\Delta x)_{\max}$($\Delta\gamma$: difference of domain wall energy between 1 : 5 and 2 : 17; Δx : domain wall width). For the lower cell size magnet with the same 1 : 5 Cu content, a lower coercivity is expected according to theoretical models [13].

IV. CONCLUSION

The homogenized sintered $Sm(Co_{bal}Cu_{0.06}Fe_{0.015}Zr_{0.027})_{6.4}$ permanent magnets have a featureless microstructure with the 2 : 17 hexagonal structure. The cellular and lamellar structures can be obtained by furnace cooling from the homogenized state. However, uniform cellular and lamellar structures are formed after 2 hours of aging at 700–850 °C. The increase of Cu content in the cell boundaries with slow cooling closely follows the increase in coercivity during cooling after isothermal aging, while the microstructure morphology remains unchanged. Triple cell boundary junctions containing high Cu play a significant role in domain wall pinning.

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