Effect of Pre-Aging Treatment on the Microstructure and Magnetic Properties of Sm(Co,Fe,Cu,Zr)\textsubscript{7.8} Sintered Magnets

Yosuke Horiuchi\textsuperscript{*}, Masaya Hagiwara, Keiko Okamoto, Tsuyoshi Kobayashi, Masaki Endo, Tadahiko Kobayashi, Naoyuki Sanada and Shinya Sakurada

Functional Materials Laboratory, Corporate R&D Center, Toshiba Corporation, Kawasaki 212-8582, Japan

The effects of pre-aging treatment on the microstructure and magnetic properties of Sm(Co\textsubscript{0.63}Fe\textsubscript{0.37}Cu\textsubscript{0.06}Zr\textsubscript{0.02})\textsubscript{7.8} were investigated. The main phase of both solution-treated magnet and pre-aged magnet was the 1 : 7 phase, and there were no distinct differences between the X-ray diffraction profiles of these magnets. Fine Cu-rich precipitates a few tens of nanometers in size were observed in pre-aged magnet by scanning transmission electron microscopy-energy-dispersive X-ray spectroscopy mapping, but such precipitates were not observed in solution-treated magnet. As for fully aged magnets, the cell size was smaller in pre-aged magnet than in non-pre-aged magnet. Thus, the pre-aging treatment gave a fine cellular structure. \(M_r\) and \(H_C\) of pre-aged magnet were almost same as those of non-pre-aged magnet. Squareness of the demagnetization curve for fully aged magnet was increased by pre-aging treatment. As a result, \((BH)_{\text{max}}\) of magnet subjected to pre-aging treatment was greater than that of magnet not subjected to pre-aging treatment. The fine cellular structure seemed to result in higher squareness. The following magnetic properties were obtained for Sm(Co\textsubscript{0.63}Fe\textsubscript{0.37}Cu\textsubscript{0.06}Zr\textsubscript{0.02})\textsubscript{7.8} by pre-aging treatment: \(M_r = 1.24\ T, H_C = 1490\ kA/m\), and \((BH)_{\text{max}} = 266\ kJ/m^3\). [doi:10.2320/matertrans.MBW201325]

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1. Introduction

Highly heat-resistant permanent magnets are needed for high-efficiency motors, such as traction motors in hybrid and electric vehicles, railroad cars, and industrial equipment that operates at relatively high temperatures. Samarium–cobalt (Sm\textsubscript{2}Co\textsubscript{17}) sintered magnet is a candidate material for these applications because it has high heat resistance due to its high Curie point and its low temperature-dependent remanence. A high maximum energy product \((BH)_{\text{max}}\) is needed for miniaturization and high efficiency in motors, and iron enrichment is effective for satisfying this requirement. In the 1970s and 1980s, many studies investigated Sm\textsubscript{2}Co\textsubscript{17} magnets.\textsuperscript{1–7} Magnetic properties have been reported for Sm(Co\textsubscript{0.63}Fe\textsubscript{0.37}Cu\textsubscript{0.06}Zr\textsubscript{0.02})\textsubscript{7} sintered magnet containing relatively high Fe content, \(V < 0.28\) (\(= 24.5\) mol\% Fe), and \((BH)_{\text{max}}\) as high as \(264\) kJ/m\(^3\) has been obtained.\textsuperscript{8,9}

We focused on Sm\textsubscript{2}Co\textsubscript{17} sintered magnet containing a larger amount of Fe than in the magnets investigated previously. We have reported that high coercivity can be obtained for Sm(Co\textsubscript{0.63}Fe\textsubscript{0.37}Cu\textsubscript{0.06}Zr\textsubscript{0.02})\textsubscript{7} sintered magnets by selecting an appropriate solution-treatment temperature that does not form precipitates of Sm\textsubscript{2}Co\textsubscript{17} phase.\textsuperscript{10} However, those magnets lack sufficient squareness, and the high \((BH)_{\text{max}}\) expected from its \(M_r\) could not be obtained. Therefore, improved squareness is necessary to achieve high \((BH)_{\text{max}}\) for these magnets. The microstructure and coercivity mechanism of Sm(Co\textsubscript{0.63}Fe\textsubscript{0.37}Cu\textsubscript{0.06}Zr\textsubscript{0.02})\textsubscript{7} magnets have been the subject of many papers,\textsuperscript{11–16} and it is well known that aging treatment conditions are important factors in controlling the cellular structure of these magnets. However, the relationship between microstructure and squareness is not yet sufficiently clear. Therefore, the effect of pre-aging treatment on the microstructure and magnetic properties of Sm(Co\textsubscript{0.63}Fe\textsubscript{0.37}Cu\textsubscript{0.06}Zr\textsubscript{0.02})\textsubscript{7} sintered magnets was investigated in this study.

\textsuperscript{*}Corresponding author, E-mail: yosuke.horiuchi@toshiba.co.jp

2. Experimental Procedure

Sm(Co\textsubscript{0.63}Fe\textsubscript{0.37}Cu\textsubscript{0.06}Zr\textsubscript{0.02})\textsubscript{7.8} alloy powder was prepared by ball milling. The powder was then pressed at a pressure of 1.5 t/cm\(^2\) in a magnetic field of 1 T. The green bodies were sintered at 1463 K for 10.8 ks and then solution-treated at 1403–1433 K for 14.4 ks under argon atmosphere. Subsequent isothermal aging treatments were carried out at 1103 K for 14.4 or 144 ks, followed by quenching to room temperature (RT) or slow cooling to 673 K with subsequent furnace cooling to RT. Some samples were pre-aged at 1023 K for 3.6–36 ks before aging treatment. A schematic representation of the aging treatments is shown in Fig. 1. Magnets at various stages of aging, namely, a, b, c, and d in Fig. 1, were used for X-ray diffraction (XRD) analysis and scanning transmission electron microscopy (STEM) observation. A magnet aged to stage \(d\) in Fig. 1 is called a “fully aged magnet” in this study.
The crystal structures of specimens were characterized by XRD using Cu Kα radiation at RT. The microstructures of the specimens were examined by STEM and TEM. STEM was used to obtain the bright-field images and energy-dispersive X-ray spectroscopy (EDX) mappings of Cu, and TEM was used to obtain selected electron diffraction patterns. Magnetic measurements were done using an automatic recording flux meter (B-H tracer) with a maximum magnetic field of 2000 kA/m at RT. Ms, Hc1, squareness, and (BH)max were obtained from demagnetization curves. In this study, the squareness of the demagnetization curve was defined as the ratio of the measured value of (BH)max to the ideal value of (BH)max:

\[(BH)_{\text{max}} \text{(measured)}/(BH)_{\text{max}} \text{(ideal)} \times 100\% \quad (1)\]

Here, (BH)max (ideal) was determined by using Mt in the following formula:

\[(BH)_{\text{max}} \text{(ideal)} = M_t^2/4\mu_0 \quad (2)\]

3. Results

3.1 Phase constitution

Partial XRD profiles of magnets at each stage of aging for non-pre-aged magnets are shown in Fig. 2. At the initial stage (solution-treated magnet; Fig. 2(a)), there was no peak at around 38°. This indicates that the TbCu7-type phase (1 : 7 phase) was formed by solution treatment. After aging for 14.4 ks, a small diffraction peak from the TbCu7 phase (1 : 7 phase; cell boundary phase) was formed by solution treatment. After aging for 14.4 ks, a small diffraction peak from the phase (1 : 5 phase; cell boundary phase) was observed (Fig. 2(b)). The intensity of this peak was greater after aging for 144 ks than after for aging for 14.4 ks. This suggests that phase separation occurred, giving the Th2Zn17-type phase (2 : 17 phase; cell phase) and the CaCu5-type phase (1 : 5 phase; cell boundary phase). The intensity of the peak for a fully aged magnet was almost the same as that for a magnet after aging for 144 ks.

Figure 3 shows the partial XRD profiles at each stage of aging for magneto-terated magnets that were pre-aged. As shown in Fig. 3(a), a peak from (024)Th2Zn17 was not observed at the initial stage (pre-aged magnet). This means that the main phase of pre-aged magnet was still the 1 : 7 phase, as it is in solution-treated magnet. Thus, a distinct phase transition during pre-aging treatment was not observed by XRD. The change in the XRD profile upon subsequent aging treatment was almost the same as in the case of non-pre-aged magnet, and it can be assumed that pre-aging treatment does not influence the phase change process during the aging treatment.

3.2 Microstructure

Figures 4 and 5 show the bright-field STEM images of magnets at each stage of the aging treatment. As shown in Fig. 4(a), fine, uneven contrast was observed as bands. In previous reports, twinning within the rhombohedral 2 : 17 cell is visible in micrographs as bands of alternating intensity running perpendicular to the c-axis. A similar twinning structure in the 1 : 7 phase might form in this type of magnet and the details are currently under investigation. Distinct precipitates were not observed in solution-treated magnet. It was found that fine contrast become more pronounced for pre-aged magnet, as shown in Fig. 5(a). This figure also shows that, small precipitates a few tens of nanometers in size were observed in pre-aged magnet (indicated by arrows). As for the 14.4 ks aged magnets, typical cellular structures were formed in both non-pre-aged and pre-aged magnets and cell boundary phase was observed (arrows in Figs. 4(b) and 5(b)). Figure 4(e) shows the TEM selected area electron diffraction pattern taken at the same area as the micrograph in Fig. 4(b). As shown in Figs. 4(f) and 4(g), the indexing results of this selected area electron diffraction pattern indicate that the orientation relationship between the rhombohedral 2 : 17 and hexagonal 1 : 5 phases is (001)2:17R // (001)1:5H and [010]2:17R // [110]1:5H. The orientation relationship and indexing results for these phases agree well with previous reports. The cellular structure became coarser upon further aging (Figs. 4(c) and 5(c)) and the cell size of fully aged magnet was almost the same as that of magnet aged for 144 ks. This trend was the same regardless of pre-
aging treatment. However, there were differences in cell size between magnet subjected to pre-aging treatment and magnet not subjected to pre-aging treatment. For 144 ks aged magnet and fully aged magnet, cell sizes of pre-aged magnets were smaller than those of non-pre-aged magnet. The approximate cell sizes of fully aged magnets subjected to pre-aging and not subjected to pre-aging were 160 and 220 nm, respectively. The thickness of the 1 : 5 phase was almost the same regardless of pre-aging treatment.

Figures 6 and 7 show STEM-EDX mappings of Cu obtained in the same observation areas as shown in Figs. 4 and 5, respectively. In solution-treated magnet, on the one hand, it was observed that Cu dissolved homogeneously (Fig. 6(a)). In pre-aged magnet, on the other hand, Cu contrast a few tens of nanometers in size was observed (Fig. 7(a)). This Cu contrast appears to correspond to the precipitates observed in the STEM image of Fig. 5(a). This Cu contrast appears to correspond to the precipitates observed in the STEM image of Fig. 5(a). Measured by EDX, the Cu concentration of the high contrast area in Fig. 5(a) was about 15 mol% and that of low contrast area was about 3 mol%. Distinct Cu-rich precipitates were observed in the 14.4 ks aged magnets (Figs. 6(b) and 7(b)).

These Cu-rich precipitates correspond to the 1 : 5 phase (cell boundary phase) in the STEM bright-field images. Comparing Fig. 6(b) to Fig. 7(b) shows that the spacing between Cu-rich precipitates was smaller for pre-aged magnets. Upon aging, this trend became more pronounced, in agreement with the STEM bright-field images. In the fully aged magnets, the spacing between Cu-rich precipitates in pre-aged magnet was also smaller than that in non-pre-aged magnet. Thus, it was found that the fine cellular structure was formed by introducing pre-aging treatment.

The Cu concentrations of the 2 : 17 phase (cell phase) and the 1 : 5 phase (cell boundary phase) for each magnet are shown in Table 1 and Fig. 8. The items (a), (b), (c), and (d) in the table and figure correspond to the aging conditions a, b, c, and d in Fig. 1, respectively. For condition (a), no data are shown because a distinct cellular structure was not observed in these magnets, although Cu-rich regions were detected in pre-aged magnet as shown in Fig. 5(a). The Cu concentration of the 2 : 17 phase decreased upon aging treatment (Fig. 8(A)). Furthermore, the Cu concentration in pre-aged magnets was less than that in non-pre-aged magnets for all
aging conditions. The Cu concentration of the 1 : 5 phase increased as aging treatment progressed (Fig. 8(B)). In particular, the increase from 14.4 ks aged magnet to fully aged magnet was substantial, and the amount of Cu exceeded 30 mol% in fully aged magnet. A comparison between non-pre-aged and pre-aged magnet shows that the Cu concentration of non-pre-aged magnet was less than that of pre-aged magnet. However, the Cu concentration of non-pre-aged magnet became greater than that of pre-aged magnet during aging.

3.3 Magnetic properties

The magnetic properties of fully aged magnet are summarized in Table 2. $M_r$ and $H_{cJ}$ of pre-aged magnet were almost the same as those of non-pre-aged magnet. However, the squareness was increased by pre-aging treatment. As a result, $(BH)_{\text{max}}$ of pre-aged magnet was greater than that of non-pre-aged magnet.

4. Discussion

4.1 Effect of pre-aging treatment on microstructure

It is considered that the cellular structure of 1 : 5 phase and 2 : 17 phase was not formed by pre-aging treatment, because the diffraction peak from Th$_2$Zn$_{17}$ was not detected by XRD for pre-aged magnet (Fig. 3(a)). However, the fine contrast of Cu was observed for this magnet. The Cu contrast might be due to the modulated structure of the 1 : 7 phase, though the details of the crystal structure of the pre-aged magnet are not yet clear. Fine Cu-rich regions formed by pre-aging treatment might act as nuclei of Cu-rich 1 : 5 phase in subsequent aging treatment. These fine Cu-rich precipitates are considered to cause the finer cellular structure in fully aged magnet. The number of nuclei of Cu-rich phase is thus thought to be more greatly increased by pre-aging treatment at lower temperature than by subsequent aging treatment.

It was shown that the cellular structure become finer upon pre-aging treatment by contracting the morphology of the cellular structure. The formation of the finer cellular structure by pre-aging treatment was also observed from the Cu concentration in the each phase of the cellular structure. The Cu concentration of the 1 : 5 phase was lower in fully aged magnet subjected to pre-aging treatment than in fully aged magnet not subjected to pre-aging treatment. In contrast, the Cu concentration in the 2 : 17 phase of fully aged magnet subjected to pre-aging treatment was almost the same as that of fully aged magnet not subjected to pre-aging treatment. Therefore, the volume fraction of Cu-rich 1 : 5 phase must be larger for fully aged magnet subjected to pre-aging treatment because the total amount of Cu was the same regardless of pre-aging treatment, and furthermore, the thickness of the...
1:5 phase in fully aged magnet subjected to pre-aging treatment was also the same as that in magnet not subjected to pre-aging treatment. The increase in the volume fraction of Cu-rich 1:5 phase might cause the lower Cu concentration in the 1:5 phase of fully aged magnet subjected to pre-aging treatment. The fine cellular structure in fully aged magnet subjected to pre-aging treatment can be explained by the increased volume fraction of Cu-rich 1:5 phase.
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4.2 Effect of cell structure on squareness of fully aged magnet

An increase in the squareness of fully aged magnet by pre-aging was observed (Table 2). Many microstructural studies of SmCo-based alloys have shown that 1 : 5 phase acts as pinning sites of domain walls, though the coercivity mechanism is explained by several different models.11,19-21 Similarly to $H_{cj}$, squareness might also be related to the Cu-rich 1 : 5 phase as it is in solution-treated magnet. As mentioned above, pre-aging treatment appeared effective for obtaining a fine cellular structure. This means that the number of pinning sites for domain walls was greater in pre-aged magnet than in non-pre-aged magnet. Thus, the increase in squareness can be attributed to fine precipitates of the 1 : 5 phase.

5. Conclusion

Through observation of the phase constitution and microstructure of non-pre-aged and pre-aged Sm(Co$_{0.35}$Fe$_{0.06}$Cu$_{0.02}$Zr$_{0.02}$)$_{7.8}$ sintered magnets and measurement of their magnetic properties, the following has been shown.

1. The main phase in pre-aged magnet is the 1 : 7 phase, as it is in solution-treated magnet.
2. STEM-EDX mappings, Cu contrast a few tens of nanometers in size was observed in pre-aged magnet. In contrast, Cu dissolved homogeneously in solution-treated magnet.
3. The Cu-rich 1 : 5 phase precipitated in 14.4 ks aged magnets, regardless of pre-aging treatment. The cell size was smaller in pre-aged magnet than in non-pre-aged magnet.
4. The cell size becomes larger with aging. In fully aged magnet subjected to pre-aging treatment, the cell size was smaller than in fully aged magnet not subjected to pre-aging treatment and was also smaller than in 14.4 and 144 ks aged magnets.
5. $M_r$ and $H_{cj}$ of fully aged magnet subjected to pre-aging treatment were almost the same as those of magnet not subjected to pre-aging treatment. However, the squareness was increased by pre-aging treatment. As a result, $(BH)_{\text{max}}$ of fully aged magnet was higher for magnet subjected to pre-aging treatment.

Thus, it is concluded that pre-aging treatment was effective for obtaining a fine cellular structure, and for improving the squareness of Fe-rich Sm(Co,Fe,Cu,Zr)$_{7.8}$ sintered magnets.

The following typical magnetic properties were obtained for Sm(Co$_{0.35}$Fe$_{0.06}$Cu$_{0.02}$Zr$_{0.02}$)$_{7.8}$ by pre-aging treatment: $M_r = 1.24$ T, $H_{cj} = 1490$ kA/m, and $(BH)_{\text{max}} = 266$ kJ/m$^3$.

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