Effect of ingot cooling rate on Cu distribution and magnetic properties of Sm(\text{Co}_{\text{bal}}\text{Fe}_{0.28}\text{Cu}_{0.07}\text{Zr}_{0.03})_{7.6} magnets
Effect of ingot cooling rate on Cu distribution and magnetic properties of Sm(Co$_{1-x}$Fe$_{0.28}$Cu$_{0.07}$Zr$_{0.03}$)$_{7.6}$ magnets

ABSTRACT

The Sm(Co$_{1-x}$Fe$_{0.28}$Cu$_{0.07}$Zr$_{0.03}$)$_{7.6}$ magnets were made by a casting process with two different cooling rates. X-ray diffraction analysis shows that the main phase of the two as-cast alloys consist of 1:5, 1:7, and 2:17 (hexagonal) phase. While a few of rhombohedral 2:17 phases appear in the ingots with the lower cooling rate. The electron probe micro-analysis and corresponding wavelength dispersive x-ray results indicate that a higher cooling rate of the as-cast alloy is helpful to the uniformity of Cu element distribution in the ingots and magnets, especially for suppressing the formation of 2:17 R phase in ingots. The coercivity and squareness of magnet prepared from ingot with higher cooling rate increase by 72 and 48 percentage, respectively. The microstructure observation shows that some cell boundaries are destroyed in the magnet made by lower cooling rate, while the cell boundaries are well developed in the magnet made by higher cooling rate.

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I. INTRODUCTION

Sm$_2$Co$_{17}$-type magnets have high heat resistance due to their high Curie temperatures. Therefore, they are widely used in aerospace, defense industry, and other high-temperature applications.1–4 Although Sm$_2$Co$_{17}$-type magnets have been studied for decades, their energy density still needs to be improved for device miniaturization.5–7 The conventional method for preparing Sm$_2$Co$_{17}$-type sintered permanent magnets is by powder metallurgy. It is a complicated manufacturing process, including melting, casting, milling, orientational compression, sintering, solutionizing, isothermal aging, and slow cooling.8–11 The increase of the Cu concentration in the cell boundary phase is responsible for the enhancement of coercivity.12–14 The Cu enrichment at the cell boundary phase results in a higher domain wall energy gradient from the 2:17/1:5 interface to the cell boundary, thus a higher coercivity can be obtained.15 These previous studies mainly focus on the nanoscale Cu distribution in the cellular structure. However, the effect of the microscale Cu distribution in the grains on the magnetic properties also needs to be investigated in detail. Recently, Horiuchi et al. found the Cu-lean phenomenon in the grain boundary region of Sm$_2$Co$_{17}$-type magnets.16 These Cu-lean grain boundary regions have no cellular structure. The reduction of Cu-lean grain boundary regions can improve the squareness of the magnet.

In our previous studies,17,18 Cu-doped powders and increasing the sintering temperature can reduce the Cu-lean phenomenon in the grain boundary, which can improve the squareness to some extent. It indicates that the magnetic properties of the magnets can be further improved by modification the Cu distribution between the grains. However, a few researchers considered the impact of the melting process on the properties of Sm$_2$Co$_{17}$-type magnets. The ingots of sintered Sm$_2$Co$_{17}$-type permanent magnets are usually prepared by induction melting and casting technology.19–21
By changing the shape of the metal mold, the ingots with different cooling rates can be obtained. In this paper, the phase structure and microstructure of the magnets with different ingots cooling rate were studied. The evolution of Cu distribution from ingots to magnets is illustrated in detail.

II. EXPERIMENTAL

Cast alloys with a nominal composition of Sm(Fe_{0.28}Cu_{0.07}Zr_{0.03})_{7.6} were prepared by induction melting. The molten alloy was cast into a bullet type of copper mold (named as BM) and plate type of copper mold (named as PM) with water-cooling. The BM ingot is about 150 mm in diameter and the PM ingot is about 10 mm in thickness. The cooling rate of plate type mold and bullet type mold is about 110 K/min, and 30 K/min, respectively. The BM and PM magnets were prepared under the same process as described below. The powders were aligned and pressed under a magnetic field of 20 kOe, and then isostatically compacted under a pressure of 250 MPa for 120 s. All of the compacts were sintered at 1489 K for 1 h, and then solution treated at 1448 K for 5 h under an argon atmosphere and finally quenched to room temperature. The isothermal aging of the magnets was performed at 1083 K for 40 h, and slow cooling down to 693 K at a rate of 0.4 K/min, and were kept at 693 K for 10 h before cooling to room temperature.

Crystalline structures were determined using the X-ray diffraction with Cu Kα radiation. The composition and elements distribution analyzed by an electron probe micro-analyzer with a wavelength dispersive x-ray detector. The magnetic properties were tested using the NIM-500C ultrahigh temperature measurement system. The cellular structure and composition were examined using a transmission electron microscope with energy-dispersive spectroscopy.

III. RESULTS AND DISCUSSION

The XRD patterns of the BM and PM ingots are shown in Fig. 1(a). Both ingots mainly consist of hexagonal 2:17 H main phase, 1:5, and 1:7 minor phases. Besides, there is a small amount of rhombohedral 2:17 R phase in the BM ingot. With increasing cooling rate, the intensity of the (020) peak increases, while the intensity of (211) and (030) peaks decrease. The results indicate that the higher cooling rate can inhibit the development of the 2:17 R phase, and promotes the development of the 1:7 phase in the cast alloys.

The microstructure of the two ingots is shown in Fig. 1(b–e) and the corresponding WDX results are shown in Table I. There are three different regions in both of the ingots. The dark gray main phase, light gray minor phase and the white minor phase are 2:17 H phase (area 1, 4), 1:7 phase (area 2, 5) and 1:5 phase (area 3, 6), respectively. The 1:5 phase and 1:7 phase distribute like a network in the grain boundary of the 2:17 H matrix phase, as shown in Fig. 1(b) and (d), which is in agreement with previous work done by Wang et al.23 Moreover, with increasing of the cooling rate, the volume ratio of the white phases (1:5) in the PM ingot decrease, and that of the gray phases (2:17 H and 1:7) increases. Besides, the average grain size of the BM and PM ingots is about 39 and 21 μm, respectively, indicating that the higher cooling rate inhibits the formation of the 2:17 R phase and grain growth. The Cu element mainly enriches in the white phase for the BM and PM ingots, as indicated in Fig. 1(c) and Fig. 1(e). Furthermore, the difference value of the Cu content in the 2:17 H phase, 1:7 phase and 1:5 phase for the PM ingot is lower than that in the BM ingot.

The XRD patterns of the two final magnets are shown in Fig. 2(a). Both magnets contain the 1:5 phase and 2:17 R phase. However, there is a small amount of Zr_{6}(CoFe)_{23} phase with Th_{6}Mn_{23} structure in the BM magnet, while this phase is not observed in the BM ingots.24 EPMA was applied to analyze the composition and elements distribution, and the results are shown in Fig. 2(b–g). The white phase in Fig. 2(b) and (e) is the Sm_{2}O_{3} phase.24 A small amount of black phase appears in the BM magnet, while the content of the black phase in the PM magnet is very low, as shown in Fig. 2(b) and Fig. 2(e). According to the corresponding Zr mapping in Fig. 2(d) and (g), the Zr element enriches in the black phase, and correspond to the Zr_{6}(Co, Fe)_{23} phase.24 Fig. 2(b) and (c) show that

![FIG. 1. XRD patterns of the ingots (a), microstructure and Cu mapping of the ingots with different cooling rates, (b), (c) BM ingot, (d), (e) PM ingot.](image-url)
### TABLE I. The composition of different areas in Fig. 1(b) and (d).

| Ingot areas | Sm (at.%) | Co (at.%) | Cu (at.%) | Fe (at.%) | Zr (at.%) | phase | Volume |
|-------------|-----------|-----------|-----------|-----------|-----------|-------|--------|
| BM          | 1         | 9.5       | 58.9      | 2.6       | 28.1      | 1.0   | 2:17 H | 62%     |
|             | 2         | 13.0      | 53.2      | 9.1       | 23.6      | 1.1   | 1:7    | 11%     |
|             | 3         | 19.1      | 48.9      | 14.2      | 16.7      | 1.0   | 1:5    | 27%     |
| PM          | 4         | 9.3       | 57.4      | 3.7       | 28.5      | 1.1   | 2:17 H | 68%     |
|             | 5         | 12.3      | 56.1      | 5.8       | 24.8      | 1.1   | 1:7    | 22%     |
|             | 6         | 19.4      | 51.8      | 10.3      | 17.3      | 1.1   | 1:5    | 10%     |

the Cu element is enriched in the regions near to the Sm<sub>2</sub>O<sub>3</sub> phase and grain boundaries for the BM magnet, which is also observed by Horiuchi. It is clear that the Cu distribution in PM magnet is more uniform than BM magnet, as shown in Fig. 2(c) and (f). Due to the Cu element enrichment in the Cu-rich phase, the average Cu content in the matrix phase of the BM magnet is lower than that in the PM magnet.

Fig. 3(a) shows the demagnetization curves and their magnetic properties of the BM and PM magnets. It is seen that the coercivity, squareness, and energy density of the PM magnet are about 72%, 48%, and 55% higher than that of the BM magnet, respectively. To clarify the influence of the Cu distribution on the magnetic properties and microstructure, the two magnets were observed by TEM, as shown in Fig. 3(b) and (c). Some incomplete cells are observed...
TABLE II. EDS results of some areas at the cell boundary phase and cell phase in Fig. 3.

| magnets | Fe (at.%) | Co (at.%) | Cu (at.%) | Zr (at.%) | Sm (at.%) |
|---------|-----------|-----------|-----------|-----------|-----------|
| BM      | area 1    | 22.94     | 48.94     | 13.38     | 1.94      | 12.80     |
|         | area 2    | 23.39     | 55.30     | 6.27      | 2.11      | 12.93     |
| PM      | area 3    | 20.29     | 48.56     | 15.69     | 1.43      | 14.02     |
|         | area 4    | 25.48     | 55.98     | 4.49      | 1.24      | 12.80     |

**Fig. 4.** Schematic illustration of Cu distribution in different processing stages. (a) The BM cast alloy, compact and magnet. (b) The PM as-cast alloys, compacts, and magnets. Different colors denote different Cu contents in the samples, as shown in the arrow at right.

in the BM magnet, the average cell size is about 151 nm. However, clear and complete cellular structure is observed in the PM magnet and the average cell size is about 136 nm. Chemical composition in the cell boundary phase and cell phase are listed in Table II. The ratio value of the Cu concentration between the cell boundary phase and cell phase of the BM magnet and PM magnet is 2.1 and 3.5, respectively.

**IV. CONCLUSION**

The cast cooling rate of the BM and PM ingots has an important effect on the elemental Cu distribution and magnetic properties of the final Sm(Co_{0.28}Fe_{0.28}Cu_{0.07}Zr_{0.03})_{7.6} magnets. The high cooling rate can inhibit the development of the 2:17 R phase and promote the development of the 1:7 phase, and it is helpful for the uniformity of Cu distribution both in the ingots and in the final magnets. The homogeneous distribution of Cu element is helpful for the improvement of both squareness and coercivity.

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