Effect of sintering in a hydrogen atmosphere on the density and coercivity of (Sm,Zr)(Co,Cu,Fe)Z permanent magnets

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Abstract. The effect of heat treatments in manufacturing (Sm,Zr)(Co,Cu,Fe)Z-based permanent magnets sintered in a hydrogen atmosphere on their properties has been studied. It was shown that the dynamics of the magnetic hardening of the studied magnets during heat treatments, in whole, corresponds to available concepts of phase transformations in five-component precipitation-hardened SmCo-based alloys. Peculiarities of the studied compositions consist in the fact that the coercive force magnitude of magnets quenched from the isothermal aging temperature is higher by an order of magnitude than those available in the literature. It was noted that, in using the selected manufacturing procedure, the increase in the density of samples does not finish at the sintering stage but continues in the course of solid-solution heat treatment.

Key words: rare-earth permanent magnets, coercivity, precipitation-hardening, heat treatment.

1. Introduction

Permanent magnets based on rare-earth intermetallic phases with transition metals attract the attention of specialists and are widely used in modern industry. The rare-earth permanent magnets (REPMs) exhibit the best characteristics as compared to those of previously known materials when operating in electric and hybrid drives, wind turbines, gyroscopes, contactless bearings and couplings, loudspeakers, MRI machinery, focusing systems of microwave tubes, etc. These advantages are associated primarily with outstanding hysteretic properties of NdFeB-type permanent magnets exhibiting record values of remanence \( B_r > 14 \) kG, and maximum energy product \((BH)_{max} > 50 \text{ MGOe}\). However, (Sm,Zr)(Co,Cu,Fe)Z-type magnets remain are highly relevant owing to the stability of their characteristics in the wide temperature range (0 – 800 °K), corrosion resistance, in particular, in hydrogen-containing atmosphere.

(Sm,Zr)(Co,Cu,Fe)Z alloys are complex metallurgical systems, and their hysteretic properties and structural state are closely related to their chemical composition and heat treatment parameters. Moreover, the magnets based on the alloys should be produced using fine micron-sized powders; otherwise, the energy potential of compositions cannot be realized completely. Despite a great number of works related to the study of the structure and properties of these alloys and magnets based on them, the nature of their high-coercivity state and processes of its formation are poor understood [1-6]. High-coercivity state of (Sm,Zr)(Co,Cu,Fe)Z alloys is achieved by four-stage heat treatment (HT). The purpose of this study is to determine the effect of sintering in a hydrogen atmosphere on the properties of (Sm,Zr)(Co,Cu,Fe)Z-type magnets.
2. Experimental

Samples were prepared by standard powder technology used for sintered magnets; final dimensions of magnets are Ø15×14 mm. The alignment of samples is along the axis rotation.

The Sm0.5Zr0.16(4Co0.70Cu0.09Fe0.25)6.25 composition was prepared by melting in a vacuum induction furnace in a high-purity argon atmosphere using individual components of more than 99.5 wt % purity. The chemical composition was controlled by atomic emission spectrometry with microwave plasma.

The alloy was crushed to a particle size of <500 µm using a mechanical crusher and a nitrogen atmosphere for prevent oxidation. A fine powder with an average particle size of 3.5-4 µm was prepared in a vibratory ball mill; pots were completely filled with absolute isopropyl alcohol used as the oxidation protector. The powders were dried in vacuum and compacted at a pressure of 75 kg/mm² in an aligning magnetic field of 16 kOe.

To obtain the high degree of powder particles alignment, the blank-samples were compacted using pseudo-isostatic pressing in a matrix with a polyurethane insert. This scheme ensures uniform compression of powder in all directions. The green blanks were subjected to four step-by-step heat treatments, which included sintering, solid solution heat treatment (SSHT), quenching, and two consecutive aging – isothermal aging (IA), and slow-cooling aging ('step aging' - SA). To clarify the effect of slow cooling aging on the formation of high-coercivity state, two additional heat treatments were performed, namely, heating to the isothermal aging temperature, 15 min holding, and quenching, and second step-aging. Conditions of experimental heat treatment are shown in Figure 1 (a) and Table 1.

Table 1. Conditions of experimental heat treatment (HT) of samples.

| HT   | Heat Treatment Details                      |
|------|--------------------------------------------|
| HT1  | Sintering (T=1190-1200°C, t=1 h)            |
| HT2  | HT1 + SSHT (T=1165-1170°C, t=5 h) + Quenching |
| HT3  | HT2 + Isothermal aging (T=760, 800, 840 and 880°C, t=4-20 h) + Quenching |
| HT4  | HT3 + Step aging (from T(IT) to 400°C, 90°/h) + Quenching |
| HT5  | HT4 + “Recovery” (T(IT), t=0,25 h) + Quenching |
| HT6  | HT5+ Isothermal aging (T=760, 800, 840 and 880°C, t=4 h) + Step aging (from T(IT) to 400°C, 90°/h), 90°/h) + Quenching |

All heat treatments were carried out in a vacuum resistance furnaces at an excess argon pressure of +0.1 bar and followed by quenching in a helium flow. The average particle size was monitored by measuring the specific surface area of powders. The density of blanks was determined by hydrostatic weighing method. Magnetic properties were investigated in fields of ± 30 kOe using a completely closed magnetic circuit of hysteresis-graph.

3. Results

The main results are presented in Figures 1 – 3. Figure 1(a) shows the general scheme of the experiments - four main steps of heat treatment and two additional pilot stages of heat treatment.

Figure 1 (b, c) shows the effect of the corresponding heat-treatment stages on the density (d) and coercive force (Hcj) of the samples.

The density of the sintered samples was in a range of 8.22-8.25 g/cm³ and increases to 8.32-8.35 g/cm³ during solid solution heat treatment (Figure 1(b)). The density of the samples was unchanged during agings.

Schematically, the dynamics of change in the coercive force during step-by-step heat treatments are shown in Figure 1 (c), and hysteretic properties of samples after different stages of heat treatments are presented in Figures 2 and 3. Figure 2(a) shows the magnetization-reversal portions of the major hysteresis loops for the samples subjected to complete heat treatment cycle – HT4 and to heat treatment HT6 (data are shown for isothermal aging at temperature T = 760°C). The samples had the same properties after both heat treatments (HT4 and HT6).
Figure 1. Scheme of heat treatment and experimental results: (a) four stages heat treatment during the manufacturing of magnet samples based on the Sm$_{0.84}$Zr$_{0.16}$(Co$_{0.70}$Cu$_{0.07}$Fe$_{0.23}$)$_6$ alloy and two additional experimental stages (see explanations in the text and Table 1), and (b) density (d) and coercive force ($H_{cj}$) of samples at different stages of heat treatment.

Figure 2 (b) presents the magnetization reversal portion of the major hysteresis loops for the samples subjected to HT3 and HT5; digits at the curves correspond to the isothermal aging time (h). In this case, the heat treatments (HT3 and HT5) lead to identical properties of the samples. The properties of samples heat-treated at other isothermal aging temperatures (T=800, 840 and 880°C) demonstrate qualitatively identical behavior.

Figure 2. Magnetization reversal portions of the major magnetic hysteresis loops for Sm$_{0.84}$Zr$_{0.16}$(Co$_{0.70}$Cu$_{0.07}$Fe$_{0.23}$)$_6$ permanent magnet samples (a) after complete heat-treatment cycle (HT4) and restore of high-coercivity state after a short-time heating to the isothermal aging temperature (HT6); (b) after quenching from the isothermal aging temperature (HT3) and after complete heat-treatment cycle and following short-time heating to the isothermal aging temperature; digits near the curves correspond to isothermal aging time (h) at isothermal aging temperature T = 760°C.

Summary results for all investigated temperatures are shown in Figure 3, where: a) and b) are the dependences of the coercive force ($H_d$) and the critical field ($H_c$) on the temperature and time of isothermal aging, respectively, as a result of HT3 and HT5 (hereinafter $I$) – parameters of the samples.
that were tempered at 760, 2) – 800, 3) – 840 and 4) – 880°C); c) – H_k of the high coercive state samples that were subjected to HT4 and HT6.

**Figure 3.** Summary results for heat treatments of Sm_{0.84}Zr_{0.16}(Co_{0.70}Cu_{0.07}Fe_{0.23})_{6.25}-based permanent magnet samples: (a) H_{cj} and (b) H_k after quenching from the isothermal aging temperature (HT3) and after complete heat-treatment cycle and following short-time heating to the isothermal aging temperature; and (c) H_k after complete heat-treatment cycle (HT4) and restore high-coercivity state after short heating to the isothermal aging temperature (HT6) (at isothermal aging temperature T = 760°C - 1, 800°C - 2, 840°C - 3 and 880°C - 4).

Since the majority of samples in the high-coercivity state had the H_{cj} values, which are higher than the limit of the used measurement method, the H_k parameter is adopted as a criterion of coercivity (H_k is the magnetization reversal field, which results in the 10-% reduction of the remanence (4πJ_k = 0.9×4πJ_r)).

4. Discussion

4.1. Thermal compaction of the samples

The remanence of the magnets is directly proportional to the density of the samples. Therefore, the maximum energy product is directly proportional to the squared density. Thus, the important task is to reach the maximum density of powder samples, which is solved in two sequential technological stages, namely, by mechanical and thermal compactions. We have not been analyzing the mechanical compaction stage in the present paper. The sintering solves the problem of reaching the maximum density by thermal compaction of green blanks. This is the most high-temperature stage among heat treatments. When determining the sintering temperature, we should consider several opposing trends.

The sintering of fine (activated) powders is accompanied by grain-growth processes and formation of a structure characterized by closed porosity at high temperature. A benefit, however, associated with the grain growth process is the improvement in alignment during sintering as compared to that of pressed compacted powder. The improved alignment occurs as a result of the incorporation of small poorly aligned particles into large well-aligned grains during the material compaction under thermally driven forces.

However, too high degree of recrystallization is the consequences of lowering the degree of crystallographic texture (alignment) and reduction of the remanence of the samples. Thus, the sintering conditions (temperature-time) are limited by normal recrystallization processes.

The thermal compaction of the samples ends after sintering when the sintering is performed in an inert gas. All other heat treatments are performed at the lower temperatures and do not result in an increase in the density of samples.

In this work, the density of samples after sintering in a hydrogen atmosphere was in a range of 8.22-8.25 g/cm³. As is shown in Figure 1 (b), the density continues to increase to 8.32-8.35 g/cm³ during the
solid solution heat treatment (HT2); in some cases, it was 8.45 g/cm³ (when the manufacturing method was used). Note that solid-solution heat treatment temperature was 30-35° below the sintering temperature of the samples. Thus, the densification of samples is not completed at the end of sintering and continues during the first stage of formation of high-coercivity state of samples, namely, during high-temperature supersaturated solid-solution heat treatment at a temperature that is lower than that of previous stage (Figure 1(a), stage II).

The most logical explanation of this fact was made by Kumar [1]. During sintering in an inert gas atmosphere, a pore is filled with an inert gas trapped at the pressure existed during sintering. An expected consequence of the sintering in a hydrogen atmosphere is a dosed pore structure; after subsequent pumping out hydrogen, pores will have a vacuum in them. The subsequent heat treatment (SSHT) completes the evacuation of hydrogen, following the densification to a closed porous structure at a temperature of 1170°C and an argon pressure above the atmospheric one.

Figure 4 shows the difference in the morphology of pores in samples sintered in hydrogen and argon.

![Figure 4. Pores in samples of permanent magnets Sm₀.₈₄Zr₀.₁₆(Co₀.₇₀Cu₀.₀₇Fe₀.₂₃)₀.₃₂₅, sintered in (a) argon and (b) hydrogen.](image)

This feature of the hydrogen sintering is especially attractive for manufacturing completely dense magnet with a high degree of magnetic crystallographic texture (alignment).

4.2. Magnetic hardening of the samples

As we noted above, (Sm,Zr)(Co,Cu,Fe)₂-type permanent magnet alloys are precipitation-hardened materials. The main purpose of heat treatment stages II – IV is the formation of crystal structure of alloy, which ensures the effective domain-wall pinning during magnetization reversal.

The structure of the (Sm,Zr)(Co,Cu,Fe)₂ alloys is constructed based on the main intermetallic phases SmₐCoₐ (hereinafter, A:B) of the Sm-Co equilibrium phase diagram. The structure results from the decomposition of the disordered supersaturated 1:7 solid solution into three structural components; these are the main cell R2:17-type phase (R = rhombohedral), the cell boundary structural components, and thin plates (lamellas) of Z-phase (1:3), penetrating cells and cell boundary phase strictly in the basal plane (perpendicular to the c-axis) of the samples [2-6]. Cell boundary is not a phase. This structural component is sequential alternating layers of the phases (2:7 + 5:19 + 1:5) in different volume proportions, which are formed at various stages of aging.

The formation of high-coercivity structural state in the studied samples mainly corresponds to known concepts.

The internal stresses in the structure are induced during quenching of supersaturated solid-solution samples. This initiates the decomposition of solid solution during quenching even at high cooling rates of the alloy [4]. As is shown in the Figure 2 (a, b), the isothermal aging for the first four hours of treatment (HT3) allows one to attain Hₐ of samples of more than 4.5 kOe, and, after slow cooling (step aging - HT4), – of more than 7.5 kOe.

The long time isothermal aging occurs in coarsening the cellular structure, which is accompanied by increase in Hₐ. The increase in the isothermal aging temperature causes the similar effect leading to the accelerated increase in the coercive force in the initial period of treatment. The coalescence of
precipitates occurs after more prolonged isothermal aging, which causes the statistical irregularity of the cell boundary thickness and, as a result, worsening the squareness of hysteresis loop of the samples (Figure 2 (curves 20) and Figure 3 (curves 4)).

Many investigators have discussed the asymmetry results in a sequential rotation of step aging (HT4 and HT6) and quenching from the isothermal aging temperature (HT3 and HT5). The short-time (5-15 min) heating of high-coercivity samples to the isothermal aging temperature and subsequent quenching (HT5) lead to the drop of \( H_c \) by 18 times [3, 5] and even up to 30 times [2]. At the same time, to restore the level of \( H_c \) to the previous high-coercivity state of samples, the treatment for 5-15 min is insufficient. The complete step-aging in the course of very slow cooling (HT6) should be repeated, i.e. the heat treatment for about 5-10 h should be performed again. Properties are completely restored after repeated step-aging [2-5, 7, 8].

Unlike data of [2, 3, 5], according to which the “recovery” causes the catastrophic drop of the coercive force of the samples from 25-30 kOe to 1.4-1.6 kOe, in the present study, \( H_c \) reaches 11, 17.3, 22.9 and 17 kOe after quenching from an isothermal tempering temperature of 760, 800, 840 and 880°C, respectively (Figure 3(a)).

Differences in the behavior of \( H_c \) are likely to be related to the chosen working alloy. Studies [2, 3, 5] were made for magnets with narrow compositional interval: in Sm(Co,Cu,Fe,Zr)\(_Y\) alloys, \( Y = 7.19-7.5\); in (Sm,Zr)(Co,Cu,Fe)\(_Z\) alloys, \( Z = 5.48-5.54\). In the present work, the alloy is described by the corresponding coefficients equal to \( Y = 7.63\), and \( Z = 6.25\). The differences in the chemical composition of the alloys are likely to produce significant differences in the structural state of samples after isothermal aging and quenching.

It is known that the alloys with \( Z \) of more than certain values have the high values of the coercive force \( H_c \) immediately after isothermal aging before slow-cooling aging. As in this study, the slow cooling results in only one to a half to threefold increase in the coercive force of these alloys [7-9].

![Figure 5](image)

**Figure 5.** Magnetization reversal portions of the major magnetic hysteresis loops for Sm\(_{0.84}\)Zr\(_{0.16}\)(Co\(_{0.70}\)Cu\(_{0.07}\)Fe\(_{0.23}\))\(_6.25\) permanent magnet samples, sintered in (1) hydrogen and (2) argon after complete heat-treatment cycle.

| Sintering | Sintering | Density | \( B_r \) | \( H_{ch} \) | \( H_c \) | (BH)\(_{max}\) |
|-----------|-----------|---------|----------|----------|--------|-----------|
| \( \text{atmosphere} \) | \( T, ^\circ C \) | \( g/cm^3 \) | kG | kOe | kOe | MG*Oe |
| Ar | 1215 | 8.20 | 10.9 | 10.2 | 28.2 | 28.3 |
| \( H_2 \) | 1195 | 8.35 | 11.5 | 11.0 | 21.3 | 32.2 |

Table 2. The parameters of Sm\(_{0.84}\)Zr\(_{0.16}\)(Co\(_{0.70}\)Cu\(_{0.07}\)Fe\(_{0.23}\))\(_6.25\) samples sintered in argon and hydrogen.

The existence of samples (similar to those studied in the present work), the structural state of which ensures the high coercive force after isothermal aging followed by quenching, i.e., without the slow cooling to 400°C, even more sharpens the question about the mechanism of phase transformations upon
magnetic hardening of the (Sm,Zr)(Co,Cu,Fe)z alloys and the processes that generate “return” asymmetric effects during heat treatments.

The magnetization reversal portions of the major hysteresis loops of two samples sintered in hydrogen and argon are shown in Figure 5. Both samples were produce from the same alloy and subjected to optimal treatment for high-coercivity state. The starting and resulting data for the samples are presented in Table 2.

5. Conclusions
1. Four stages of heat treatment of (Sm,Zr)(Co,Cu,Fe)z alloys allow one, at the first stage (I, sintering in hydrogen), to produce dense samples, and after full heat treatment cycle (II, solid solution heat treatment, III, isothermal aging, IV, step aging), to ensure the development of high-coercivity structural state of the alloy with the effective domain-wall pinning.
2. The increase in the density of the samples is not completed at the first stage (I, sintering in hydrogen), and continues at the second stage (II, solid solution heat treatment).
3. Results obtained for the Sm0.8Zr0.16(Co0.70Cu0.07Fe0.23)6.25 alloy are rare consistent with available data on the formation of phase structure during the heat treatments.
4. The peculiarity of the investigated alloy is the high coercive force Hcj reached after isothermal aging, which is higher than that observed for other alloys of this system.

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