



SPECIAL FEATURES OF HYDROGEN AND RE-TM ALLOYS INTERACTION IN MAGNETS WHILE IN PRODUCTION AND OPERATION

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Abstract—The microstructure, domain structure and magnetic properties of the sintered RE-Co-Cu-Fe-Zr magnets produced by using hydrogen decrepitation (HD), sintering in hydrogen-containing atmosphere and hot isostatic pressing (HIP) processes have been investigated. The applications of these operations are shown to have a positive effect on the magnetic properties and magnet homogeneity. The following magnetic properties have been obtained for the $\text{Sm}_{0.7}\text{Gd}_{0.1}\text{Er}_{0.2}(\text{Co}_{0.683}\text{Cu}_{0.083}\text{Fe}_{0.210}\text{Zr}_{0.024})_{7.35}$ magnets: remanence (Br) = 1.07 T; intrinsic coercivity (iHc) = 1610 kA/m; maximum energy product (BHmax) = 215 kJ/m³. It is demonstrated that Gd- and Er- alloy magnets are less resistant to failure if operating in the hydrogen atmosphere. Copyright © 1997 International Association for Hydrogen Energy

INTRODUCTION

The results of investigations into the influence of hydrogen on the alloys based on rare-earth and ferrum group metals are published in [1]. However, they are mostly dedicated to Nd-Fe-B alloys. The employment of hydrogen in the Sm-Co-Cu-Fe-Zr magnet production, including grinding [1,2] and sintering [1] is recognized. However, the data on microstructure, domain structure, phase composition and hydrogen resistance for the magnets produced by HD, sintering in hydrogen atmosphere and HIP that provide high properties, are absent in the latest papers. These properties are of a specific interest because in actual practise, the magnets are occasionally used in hydrogen-containing atmosphere. For some applications, especially for electric generators and motors, such media are preferential due to low friction coefficient and high heat capacity. This makes it possible to improve the device performances. The influence of chemical composition and various process factors on the microstructure, domain structure and magnetic properties of the magnets and their hydrogen resistance are studied in the present work.

EXPERIMENTAL TECHNIQUE

The $\text{Sm}_{0.7}\text{Gd}_{0.1}\text{Er}_{0.2}(\text{Co}_{0.683}\text{Cu}_{0.083}\text{Fe}_{0.210}\text{Zr}_{0.024})_{7.35}$ and $\text{Sm}(\text{Co}_{0.642}\text{Cu}_{0.084}\text{Fe}_{0.251}\text{Zr}_{0.023})_{7.56}$ alloys were manufactured in an inductance furnace in the inert gas atmosphere. The ingots obtained were mechanically grounded or subjected to HD with subsequent fine milling in a ball mill. Then the powder was isostatically pressed under the

pressure of 750 MPa in the 1200 kA/m magnetic field. The compacts were consolidated by sintering in the argon (1490 K, 30 s) or hydrogen (1440 K, 30 s) atmospheres with subsequent HIP (1300–1425 K; $p = 100\text{--}180$ MPa; $3.6\text{--}7.2 \times 10^3$ s) after which the solution treatment (1430–1450 K; 10.8×10^3 s) followed by isothermal aging (1070–1120 K; $14.4\text{--}79.2 \times 10^3$ s) and cooling down to 670 K with the rate of 1–2 K/s. Microstructure and domain structure were studied in the D12 × 6 samples with the help of the Neofot-30 microscope; chemical etching-agent (1%-solution of HNO₃ in ethanol) was used. An analysis of structural components was performed by the use of the Comebax radiospectrum microanalyzer.

Magnet samples were tested in the hydrogen and helium atmospheres after holding for up to 31×10^5 s at the temperature of 380 K. The magnet samples were placed in quartz capsules that were evacuated, filled with hydrogen or helium up to the pressure of 0.1 MPa and sealed up. The capsules were then placed in a thermostat, and the temperature was kept within the accuracy of ± 2 K. Both machined and cadmium-plated samples were tested. The cadmium coating does not, practically, dissolve hydrogen and can provide a reliable protection against hydrogen permeation to the surface of the magnets. The steel shells employed in HIP were partly used as the protecting coatings as well.

RESULTS AND DISCUSSION

Table 1 gives the data on principle magnetic properties and optimal isothermal aging treatment times for $\text{Sm}_{0.7}\text{Gd}_{0.1}\text{Er}_{0.2}(\text{Co}_{0.683}\text{Cu}_{0.083}\text{Fe}_{0.210}\text{Zr}_{0.024})_{7.35}$ magnets that

Table 1. The data on the magnetic properties of the $\text{Sm}_{0.7}\text{Gd}_{0.1}\text{Er}_{0.2}(\text{Co}_{0.683}\text{Cu}_{0.083}\text{Fe}_{0.210}\text{Zr}_{0.024})_{7.35}$ magnets depending on the process conditions

No.	Br (T)	iHc (kA/m)	(BH) max (kJ/m ³)	T (s) × 10 ³
1	1.00	1315	176	72–79
2	1.02	1490	184	50–58
3	1.04	1580	200	29–43
4	1.07	1610	215	14–22

(1) Grinding and sintering in the argon atmosphere, (2) HD and sintering in argon atmosphere, (3) HD and sintering in the hydrogen atmosphere, (4) HD, pre-sintering in the hydrogen atmosphere and HIP.

were produced by grinding and consolidation under various conditions. As seen from Table 1, the highest magnetic properties and shortest heat-treatment time are observed when HD, hydrogen pre-sintering and HIP are used. If the surfaces of the microsections prepared to study microstructures are compared, it is apparent that there is no porosity for sample 4 as differentiated from samples 1–3. A comparison of microstructures reveals a significant fall in the contrast of magnet phase components as the magnetic properties of the magnets are improved from samples 1–4, suggesting that chemical compositions are equalized throughout a magnet. This finding is confirmed by the domain structure of the magnets which is homogeneous and regular in sample 4 over the whole surface normal to the magnet structure axis. This structure is typical for single-axle high-anisotropy magnets [1].

Surface oxidation was observed in magnet sample 4. It was most likely caused by the insufficiently pure argon used in HIP. So further experiments were made under the optimal conditions (i.e. by HIP) in protective steel shells.

The microstructure (a, c, e) and domain structure (b, d, f) of the magnets in the plane normal to the texture axis after all the above-mentioned heat treatments for the $\text{Sm}(\text{Co}_{0.642}\text{Cu}_{0.084}\text{Fe}_{0.251}\text{Zr}_{0.023})_{7.56}$ sample are shown in Fig. 1 for various HIP temperatures. A multiphase structure with a grain average size of about 30 μm is revealed after HIP, as viewed from Fig. 1a. The corresponding domain structure is relatively homogeneous and has domains of the isocoercive type (Fig. 1b). It has been found by radiospectrum analysis (Table 2) that about 96% of microsection surface are occupied by the grains

Table 2. The data on the chemical composition of the magnets based on the $\text{Sm}(\text{Co}_{0.642}\text{Cu}_{0.084}\text{Fe}_{0.251}\text{Zr}_{0.023})_{7.56}$ alloy at a HIP temperature of 1370 K

Type	Sm	Zr	Co	Cu	Fe
A	11.64	1.97	57.01	8.64	20.74
B	10.49	1.78	57.46	6.14	24.13
C	8.70	13.04	60.26	3.91	14.09
D	2.10	18.75	59.37	2.37	17.41
E	40.00	—	—	—	—

of two phases (A and B) that differ in structure. The A-phase (darker) is enriched with samarium and copper, the B-phase is enriched with iron. The contents of these phases are about the same. Besides the predominant phases, the C- and D-phases enriched in zirconium with the content of no more than 1% each and the E-phase (samarium oxide) with the content of about 2% are present.

The permanent magnets of this type have a very high intrinsic coercivity (up to 2400 kA/m) and high degree of rectangularity of hysteresis loop in its demagnetizing area. On magnetizing this magnet up to the saturation point with the subsequent application of a demagnetizing field, domains of the isocoercive type are developed. The shape and size of these domains are determined by the inhomogeneity of domain wall local coercivity distribution. As a rule, this is correlated with chemical composition inhomogeneity within a grain. The development of the domains occurs within the boundaries of a grain. As this takes place, grain boundaries present impenetrable barriers to domain wall propagation. These domains can vary in size. When the optimal heat treatment conditions are used the domain sizes correspond to the limiting level of the optical microscope resolution (less than 1 μm).

The growth of the B-phase grains with a simultaneous rise in their volume content is observed as the HIP temperature increases (1390–1420 K). In this case, the B-phase grains are enriched in iron and the B-phase grains are enriched in copper and samarium. The inhomogeneous distribution of copper and iron contents throughout the grain of the B-phase (the central area contains less copper and more iron). This results in the inhomogeneity of domain structure. The lower coercivity of domain walls is revealed in the central areas of grains. Iso-coercive domains are rather large there. They reduce in size as the domain wall coercivity grows from the central to the circumferential areas of grains. This domain structure was previously found for Sm–Zr–Co–Cu–Fe pseudo-single crystals [1]. Though the high intrinsic coercivity is retained for these crystals, the degree of hysteresis loop rectangularity becomes lower, especially, at HIP temperatures of 1420 K.

The above data are typical for the magnets subjected to vacuum degassing at a temperature of 1070 K during 7.2×10^3 s after hydrogen pre-sintering before HIP. The samples which are not subjected to vacuum degassing have special features that seem to be related to the residual hydrogen. A more intensive grain growth can be watched at HIP temperatures of 1390–1420 K and a drop in the intrinsic coercivity of up to 1650 kA/m.

In the course of the hydrogen action on permanent magnets at a temperature of 380 K during 31×10^5 s, the failure occurs but in the magnets alloyed with gadolinium and erbium in 5.5×10^5 s (it corresponds to an exposure of 86×10^5 s at an operation temperature of 340 K). In this case, laminations along magnet edges, scaly laminations over magnet planes and laminations throughout the magnets are observed in succession.

The magnets alloyed with gadolinium and erbium with

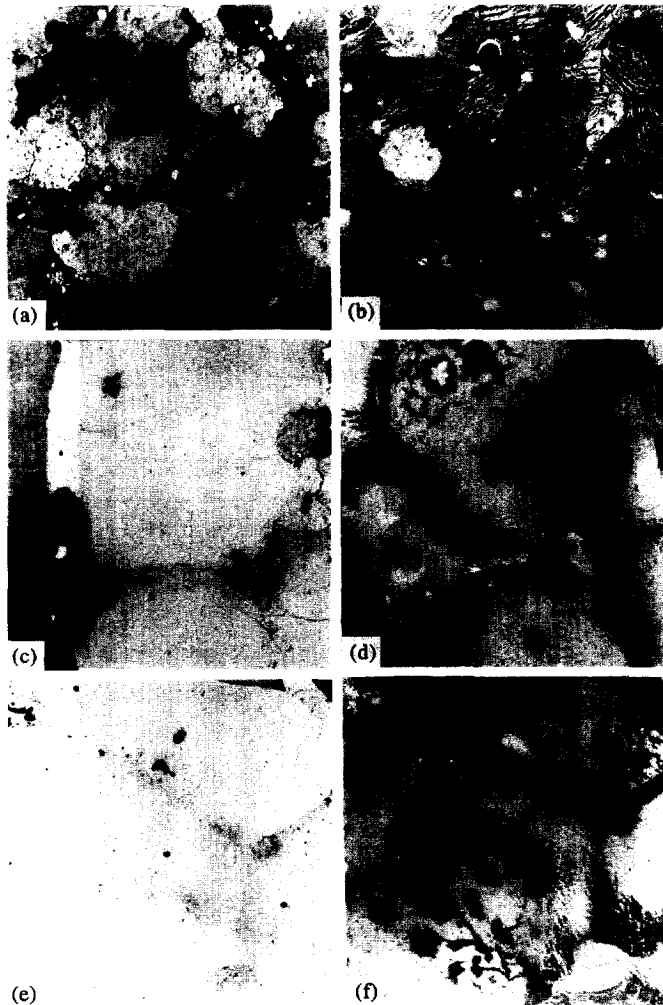


Fig. 1. A microstructure (a, c, e) and domain structure (b, d, f) for the $\text{Sm}(\text{Co}_{0.642}\text{Cu}_{0.084}\text{Fe}_{0.251}\text{Zr}_{0.023})_{7.56}$ at different HIP temperatures (a, b-1370 K; c, d-1390 K; e, f-1420 K) $\times 300$.

cadmium coating, as well as those unalloyed without coating, do not show susceptibility to failure when kept at a temperature of 380 K for 31×10^5 s. This corresponds to an exposure at a temperature of 340 K for 52×10^6 s.

CONCLUSIONS

(1) The hydrogen decrepitation and sintering technology in combination with HIP may be a factor of a significant improvement of magnetic properties, with the isothermal aging treatment time being shortened from 75.6×10^3 s to 14.4×10^3 s.

(2) The Sm-Co-Cu-Fe-Zr permanent magnets

alloyed with Gd and Er are more prone to hydrogen action than those of basic chemical composition. An application of cadmium coating significantly extends the service life of the magnets operating in the hydrogen atmosphere without failure.

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