Matrix effect in soft metal-bonded samarium–cobalt (SmCo_5) permanent magnets

A VERMA, P VERMA and R K SIDHU

Thapar Corporate Research and Development Centre, Patiala 147001, India

MS received 5 September 1994; revised 16 August 1995

Abstract. This paper discusses the preparation of samarium–cobalt (SmCo_5) alloy powders by reduction–diffusion process. These powders were blended with equal weight percentages of soft metal/alloy powders, such as indium, tin and solder alloy (Pb–17Sn), to prepare bonded magnets. Important magnetic properties such as remanence, coercivity and energy product of these magnets were measured. Effect of matrix metal/alloy on the magnetic properties of processed magnets is outlined.

Keywords. Samarium–cobalt permanent magnets; reduction–diffusion process; metal-bonded magnets.

1. Introduction

After the discovery of neodymium–iron–boron (Nd–Fe–B) permanent magnets (Hadjipanayis *et al* 1983; Croat *et al* 1984; Sagawa *et al* 1984) in 1983, the interest of researchers shifted from samarium–cobalt magnets to Nd–Fe–B magnets. Despite the superior properties of Nd–Fe–B , it has not replaced Sm–Co alloys in all applications due to the superior temperature characteristics of the latter. Further, for each ton of neodymium produced 125 kg of samarium gets generated (Sooner 1985). Thus, unless a suitable use of samarium, cerium, praseodymium, etc. is found out, the neodymium production will not be economically attractive.

It may be mentioned that after China and USA, India has the third largest reserves of rare earths, about 5% of the world total reserve (Luo 1990). However, the process of rare earth metal extraction from ores has not yet matured in India. Therefore, reduction–diffusion (R–D) process of rare earth magnets production holds greater promise. The R–D process involves reduction of cheaper samarium oxide (Sm_2O_3) by calcium and simultaneous diffusion of samarium in cobalt (Martin *et al* 1973; Mcfarland 1973; Cech 1974; Herget and Domazer 1975). The process is based on the relative thermodynamic stability of oxides. Since free energy of formation of CaO at 1273 K is 1013.1 kJ/g mol O_2 , which is lower than that of Sm_2O_3 , 970.4 kJ/g mol O_2 , it is possible to reduce samarium oxide by calcium metal. The process is, therefore, popularly known as calciothermic reduction also.

The process involves blending of raw materials, viz. samarium oxide, cobalt and calcium. The charge is heated at 1373–1423 K in argon or vacuum for sufficient time to obtain alloy powders. The unreacted Ca and CaO formed as a result of reduction reaction are leached out by water and mild acids. The process has yield of > 95% and the powder so produced contains residual calcium and oxygen 1000 ppm and 4000 ppm, respectively (Hsi *et al* 1987; Jones 1987). The disadvantage of this process is that the residual oxygen may form compounds with samarium resulting in depletion of samarium. This gives rise to an alloy composition containing higher percentage of cobalt than the stoichiometric ratio. The high percentage of cobalt adversely affects the magnetic properties.

The chemical composition, phase constituents, oxygen content and impurities of SmCo_5 powder are critical in further processing of sintered magnets and their final magnetic properties. Thus, a stricter composition and phase control is desirable for making good quality sintered magnets. However, the requirements are not very stringent for bonded magnets. Bonded magnets, based on rare earth-transition metal alloys, were initially proposed and prepared under laboratory conditions as far back as 1967 (Strnat 1967).

However, bonded Sm-Co products were first developed in the mid 1970s in Europe (Bachmann and Nagel 1976; Taylor and Wainwright 1976) and especially vigorously by Japanese companies (Kamino and Yamane 1976). Initially, the binder matrix was typically epoxy resin, nylon, ethylene vinyl acetate, etc. Later on, it was shown that soft metal binders can also be employed for making bonded magnets (Strnat 1976, 1987; Strnat *et al* 1976, 1981). They are beneficial when better mechanical integrity, high thermal conductivity and good long-term stability at elevated temperatures are required. The present paper examines the influence of matrix metal/alloy on the magnetic properties of bonded magnets.

2. Experimental

Samarium oxide powder (99.9% pure) and cobalt powder (99.9% purity) were characterized for their particle size and shape. These powders were weighed in the desired ratios. In view of the higher vapour pressure of samarium, it was added in quantities more than the desired stoichiometry. The excess quantity was optimized through experimentation. The powders were first mixed in agate-mortar and then ball milled in a planetary ball mill at 100 rpm for 15 min. The ball to charge ratio was kept at 2:1. The calcium granules of 1–2 mm size were added to the powder mixture. Calcium was added 40% in excess of the chemical formula. This mixture was compacted as a cylindrical pellet by applying a pressure of 270 MPa. The pellet was heated to 1473 K at the heating rate of 10 K/min under high purity argon gas. A soaking time of 3 h was found to be optimum for the formation of desired phase. This was ascertained by X-ray powder diffraction. The furnace was cooled at the rate of 20 K/min to room temperature.

The reduced pellet was granulated in a hammer mill. The pellet showed considerable brittleness at this stage and it was easy to disintegrate it into a powder form. The powder was repeatedly washed with distilled water to remove the unreacted calcium and calcium oxide. The residual calcium was leached out by washing with 5% v/v acetic acid. After acid leaching the powder was once again washed with distilled water. Finally, the powder was washed with acetone. This powder was dried at 333 K under a vacuum of 10^2 Pa. The X-ray diffraction pattern of dried powder *vis-a-vis* starting powder mix was recorded on a Rigaku X-ray diffractometer (Model: Rigaku D-Max III C) using copper target and graphite crystal monochromator.

The dried powder was ball milled in a planetary ball mill for 1 h at 160 rpm under hexane liquid to avoid oxidation of powder. The grinding bowl and balls of ball mill were made of cemented tungsten carbide. The diameter of the grinding ball was 1 cm. The selected ball to charge ratio was 5:1. The milled powder was vacuum dried under the vacuum of 10^2 Pa. The particle size distribution of the powder was determined with an image analyser (Model: Buehler).

The above powder was mixed with indium, tin and solder alloy powders to obtain powder mix containing 15 wt% non-magnetic phase. All the non-magnetic powders were of -400 mesh size. The mixed powders were compacted in the shape of 12 mm diameter cylindrical pellets under 1.59×10^3 kA/m pulsed magnetic field by an application of 860 MPa pressure. The compaction pressure was applied in the direction of magnetic field. These compacts were heated close to the melting point of non-magnetic phase under a vacuum of 10^2 Pa. These compacts were given a final magnetization in the pulsed magnetic field of 1.59×10^3 kA/m. Thus, the bonded magnets were axially magnetized. Samples measuring 2 mm diameter and 4 mm height were cut along the axial direction for magnetic measurement. The magnetic measurement was carried out with the help of PAR vibration sample magnetometer (Model: 150 A). The direction of magnetization was perpendicular to the applied field of magnetometer. The maximum field in the magnetometer was 1.59×10^3 kA/m. The microstructure of the demagnetized specimen was observed under scanning electron microscope (SEM) (Model: JEOL 840 A).

3. Results and discussion

The particle size distributions of the starting powders, viz. samarium oxide and cobalt were determined. Both the powders were found to be fine with about 90% particles lying below $7.5 \mu\text{m}$ size. Flow rate and apparent density of starting powders could not be determined as powders were not found to flow freely through Hall funnel. The SEM (figures 1a and b) reveal the morphology of these powders.

The X-ray diffraction patterns of the powder blend before reduction and after calciothermic reduction followed by leaching out of calcium and calcium oxide are shown in figures 2a and b, respectively. All the diffraction peaks in the diffractogram for reduced powder were found to correspond to SmCo_5 phase. Diffraction peaks due to calcium oxide, samarium oxide or free cobalt were conspicuous by their absence. The absence of calcium in the reduced powder was also confirmed by energy dispersive spectrometer. Similar experiments were repeated with varying excess quantities of samarium oxide. The reduced powders were mixed with perspex powder to obtain isotropic magnets by compression moulding. In all the compression moulded compacts the volume percentage of the polymer was kept constant. The coercivity of these compacts was determined by PAR vibration sample magnetometer (Model: 150 A). The variation of coercivity with excess quantity of samarium oxide is shown in figure 3. It is evident from the figure that maximum coercivity is attained for 10 wt% excess of samarium oxide. Apparently, on taking 10 wt% excess of samarium oxide, the composition obtained after reduction is optimum so as to minimize the formation of $\text{Sm}_2\text{Co}_{17}$ and Sm_2Co_7 phases. These phases are reported to adversely affect the coercivity values as they provide easy nucleation sites for reverse domains (Wohlfarth and Buschow 1988).

The particle size distribution of SmCo_5 powders after ball milling is shown in figure 4. It may be noted that under the chosen conditions of ball milling, 60 min is sufficient to get more than 95% powders below $10 \mu\text{m}$ size. In fact, it is reported that particles below the grain size of $10 \mu\text{m}$ are desirable from the point of view of good magnetic properties. This stems from higher probability of nucleating defects in coarser particles. The SEM picture of the ball milled SmCo_5 powder is shown in figure 5. This further corroborates the results of the particle size distribution.

Figure 1. a. SEM micrograph of Sm_2O_3 and b. SEM micrograph of Co powder.

The demagnetization curves for metal-bonded magnets are shown in figure 6. It is evident from the figure that best magnetic properties are obtained for the indium-bonded magnets. The higher melting temperature of the matrix seems to affect the magnetic properties of bonded magnets. Moreover, in spite of the same wt% of soft metal matrix, the volume percentages of chosen matrix metal are different. The volume percentage is the lowest (14.9%) for Pb–Sn alloy and highest (20.2%) for tin. The higher volume percentage of matrix effectively decouples the magnetic particles and is,

Figure 2. a. XRD pattern of powder blend before reduction and b. XRD pattern of reduced and washed powder.

Figure 3. Variation of coercivity with excess quantity of samarium oxide.

Figure 4. Particle size distribution of SmCo_5 powder after ball milling.

therefore, expected to give better magnetic properties. On the contrary, the best results are obtained for indium-bonded magnets. It may be mentioned that loss of magnetic properties at moderately high temperatures is principally due to two reasons: The magnetic particle may lose its high intrinsic coercive force through slight corrosion of the particle surface. Such surface changes in SmCo_5 give rise to easy domain nucleation

Figure 5. SEM micrograph of ball milled SmCo_5 powder.

Figure 6. Demagnetization curves for various metal-bonded SmCo_5 magnets.

sites. From these, the magnetization reversal of the entire particle proceeds at progressively lower reverse applied fields. The second mechanism is due to softening of binder on heating. This permits physical rotation of some of the particles in response to the internal demagnetizing fields. It appears from figure 6 that the first effect predominantly controls the magnetic properties of the bonded magnets. Undoubtedly, the conditions are worse in the case of Pb-Sn alloy bonded magnets as there is a greater

Table 1. Magnetic properties of SmCo_5 magnets pressed in the direction of magnetic field.

Type	Magnetic properties			
	m.p. of soft metal matrix (K)	Br(T)	H_{c1} (kA/m)	(B.H.)max (kJ/m ³)
SmCo_5 (sintered)	—	0.7–0.9	550–1190	119–151
$\text{SmCo}_5 + 15\% \text{ In}$	429	0.25	481.5	27.8
$\text{SmCo}_5 + 15\% \text{ Sn}$	504	0.24	318.2	20.4
$\text{SmCo}_5 + 15\% (\text{Pb}-17 \text{ Sn})$	550	0.13	116.8	3.5

demagnetizing field due to the lower volume percentage of non-magnetic matrix coupled with the higher melting temperature as compared to the other two matrices. The B_r values for tin- and indium-bonded magnets are almost equal but H_{c1} values differ substantially. This may be attributed to higher volume percentage of tin (20.2%), as compared to indium (17%), for 15 wt% of each metal. Thus, the effect due to demagnetizing fields in tin-bonded magnets is weaker than indium-bonded magnets. The demagnetization effect brings about rotation of magnetic particles which, in turn, affects the flux density. However, the wide difference in coercivity values may be accounted for the higher corrosive action at the higher temperatures. The SmCo_5 particles get oxidized to some extent during bonding due to poor vacuum level. The extent of oxidation is more for higher melting point matrix. The oxidized particles are the sites for nucleation of reverse domains.

The important magnetic properties of the three types of bonded magnets are summed up in table 1. It is apparent that indium-bonded magnet has the best magnetic properties. Further improvement in properties is underway by grading the powders in different sieve fractions and then mixing it in the right proportion. This will help attain higher packing density than the present value of 70–75% theoretical density. Also, it is possible to obtain better magnetic properties by carrying out final magnetization at higher magnetic fields.

The low and high magnification microstructure of the indium-bonded magnets is shown in figures 7a and b, respectively. In the low magnification microstructure the porosities, bright patches, are seen. These pores have entrapped air in them which reacts with the neighbouring particles resulting in nucleation sites of reverse domains. The higher magnification micrograph, taken in the backscattered electron mode, shows the distribution of indium in the material. It appears that indium is not present between all the SmCo_5 particles. It is, therefore, possible to reduce the demagnetization effect and hence improve the magnetic properties by increasing the volume percentage of indium.

4. Conclusions

The above study shows that it is possible to make good bonded magnets using the indigenously available raw materials. Also, use can be made of the SmCo_5 powders, generated during machining of sintered magnets, for making bonded magnets.

Figure 7. **a.** Low magnification microstructure of indium-bonded magnets and **b.** high magnification microstructure of indium-bonded magnets.

It has been shown that melting point of chosen matrix and its volume percentage have significant effect on irreversible losses. The corrosion reactions at high temperatures are major causes of degradation in magnetic properties and the porosity plays a significant role in this. A proper volume percentage of non-magnetic matrix (about 20%) and special precautions to reduce the porosity and oxidation during diffusion bonding are expected to give magnets with improved properties. The better mechanical properties of bonded magnets compared to their sintered counterparts make them suitable for application in some motors and electromechanical devices where moderate energy density and complex shapes are the main considerations.

Acknowledgements

The authors thank Prof. K P Gupta and Dr Sanjay Gupta, Advanced Centre for Materials Science, IIT, Kanpur for allowing use of the magnetic characterization facility and for providing other logistic support.

References

- Bachmann K and Nagel H 1976 *Prog. 2nd int. workshop on rare earth cobalt permanent magnets and their applications* (Ohio: Dayton) p. 347
- Cech R-E 1974 *J. Metals* **1** 33
- Croat J J, Herbst J F, Lee R W and Pinkerton F W 1984 *J. Appl. Phys.* **55** 2078
- Hadjipanayis G C, Hazelton R C and Lawless K R 1983 *Appl. Phys. Lett.* **43** 797
- Herget C and Domazer H G 1975 *Goldschmidt informiert* **35** 3
- Hsi H W, Miao Y W and Horng J S 1987 *Proc. 9th int. workshop on rare earth magnets and their applications* (FGR: Bad Soden) p. 347
- Jones F G 1987 *Proc. 9th int. workshop on rare earth magnets and their application* (FRG: Bad Soden) p. 737
- Kamino K and Yamane T 1976 *Proc. 2nd int. workshop on rare earth cobalt permanent magnets and their applications* (Ohio: Dayton) p. 364
- Luo Y 1990 *Proc. 11th int. workshop on rare earth magnets and their applications* (Pittsburgh) p. 270
- Martin D L, Laforce R P, Rockwood A C, Mcfarland C M and Valentine L 1973 *Proc. 10th rare earth res. conf.* (Arizona: Carefree) p. 105
- Mcfarland C M 1973 *Proc. 10th rare earth res. conf.* (Arizona: Carefree) p. 692
- Sagawa M, Fujimura S, Togawa N, Yamamoto H and Matsuura Y 1984 *J. Appl. Phys.* **55** 2083
- Sooner J P 1985 *Proc. 8th int. workshop on rare earth magnets and their applications* (Ohio: Dayton) p. 377
- Strnat K J 1967 *Cobalt* **36** 133
- Strnat K J 1976 US Patent No. 3998669
- Strnat K J, Kleman A J and Blaettner H 1976 *Proc. 2nd int. workshop on rare earth cobalt permanent magnets and their applications* (Ohio: Dayton) p. 387
- Strnat R M W, Liu S and Strnat K 1981 *Proc. 5th int. workshop on rare earth magnets and their applications* (Ohio: Dayton) p. 609
- Strnat R M W 1987 *Proc. 9th int. workshop on rare earth magnets and their applications* (FRG: Bad Soden) p. 675
- Taylor R J and Wainwright D P 1976 *Proc. 2nd int. workshop on rare earth cobalt permanent magnets and their applications* (Ohio: Dayton) p. 364
- Wohlfarth E P and Buschow K H J (eds) 1988 *Ferromagnetic materials* (Amsterdam: North Holland Physics Publishing) Vol. 4, p. 163