Indigenous Efforts on the Development of Samarium-Cobalt based Permanent Magnets

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D.K. Sahoo is the recipient of the DAE Young Applied Scientist/Technologist Award for the year 2015

Abstract:
The present invention deals with process of producing samarium-cobalt alloy powder which is useful as raw material in developing permanent magnets having high magnetic properties. A modified reduction-diffusion process has been adopted here to produce the alloy by choosing appropriate raw material and performing reduction process in a controlled way. The process essentially involves the calcothermic reduction of samarium oxide in presence of cobalt under argon atmosphere, followed by decalcification to get desired alloy product. The effect of processing parameters in obtaining the desired magnetic phases and on residual calcium has been studied in details. It was observed that the alloy powder with optimum samarium and lower calcium content is suitable to have improved the magnetic properties in the final product. The process has been successfully scaled up from 100g to 10kg batch level.

Introduction:
Permanent magnets i.e. hard magnetic materials are of great technological importance because they can maintain high level of constant magnetic fluxes without applying an external magnetic field or electrical current. Rare earth based permanent magnets are technologically important materials and have got significant uses in industry and science, i.e. electric motors, NMR scanners, wind-mills, compact discs, actuators for robotics and flight control, etc [1-3]. After the discovery of magnetic anisotropy in yttrium cobalt compound (YCo5) in 1966, an insurgent interest had been developed in the researchers to explore the magnetic properties of other rare earth metals with cobalt. The extensive research on this area has led to the discovery of SmCo5 based magnets with energy product which was referred to the first generation of rare earth based permanent magnets. Later Sm2Co17 and NdFeB type of magnets were discovered. Although NdFeB type of magnets are widely used in the market on account of their superior magnetic properties and low cost but they have some shortcomings like low curie temperature, low thermal stability and corrosiveness which often limits their uses [4-6]. Samarium-cobalt based magnets with high energy product and excellent coercive force are suitable to be used in highly efficient machine and components in which higher operation temperature, higher corrosion and oxidation resistance are crucial [7-8]. These magnets find use in atomic energy, space and defence industries for a variety of strategic and non-strategic applications. Industrially, rare earth alloys are produced by melting pure rare earth metals at high temperatures. It is, however, expensive due to high cost of rare earth metals, high melting temperature, and rare earth losses in the process. Moreover, it is obtained as a dense ingot, which requires further crushing and grinding before magnet making. All these processes are energy intensive. On the other hand, reduction-diffusion process yields the alloy powders directly from inexpensive oxides at much lower temperature, thereby resulting in lower cost magnets. The object of this invention is to develop indigenous technology for preparing Sm-Co magnetic alloy powder from the raw materials found in India suitable to make permanent magnets.
Experimental:
In the first step of process, the samarium oxide (99% pure) was thoroughly mixed with cobalt powder (99.4% pure) supplied by Indian Rare Earths Limited (IREL). The mixture was then admixed with calcium metal granules (99% pure procured from local market) to affect the reduction of the samarium oxide. Mixing of calcium into the charge mixture was carried out under protective cover of argon gas inside a glove box. In the process 10-100% stochiometric excess of calcium was used to ensure that all of the samarium metal oxide is reduced to samarium metal. The mixture of Sm$_2$O$_3$, Co and Ca was then charged into a specially designed crucible and then kept inside the furnace chamber. The furnace chamber was purged with argon gas for one hour to remove water moisture and entrained air before keeping the crucible containing charge mixture in it. The furnace was heated up to 1100-1200 °C and nominal flow of argon gas was maintained throughout the course of experiment. Optimum soaking period was given depending upon the quantity of charge mixture taken to ensure the complete diffusion of samarium into cobalt matrix. The crucible along with the reaction mixture was taken out after the furnace cool down to room temperature. The reactions involved in the RD process are given below:

$$ Sm_2O_3 + 10Co + 3Ca \rightarrow 2SmCO_5 + 3CaO $$ (1)

Fig.1: Sm-Co product obtained by R-D process

Fig.1 shows the product obtained after RD process. It is essentially a hard, black, clinker-like cake comprising Sm-Co intermetallics and CaO along with some unreacted calcium. The undesired Ca and CaO sometimes forms Ca (OH)$_2$ upon exposure to atmosphere. The main aim in the second step was to effectively leach out Ca from the RD products safeguarding the Sm and Co values. The reaction product was first cooled to room temperature and then subjected for leaching process.

To start the process, the resulted mass of the RD product was first crushed into smaller pieces with particle size of around 1 to 2 mm size. For small scale batch (up to 1 kg scale) crushing was carried out in mortar pestle, where as for large scale batch (more than 1 kg scale) jaw crusher was used for this purpose. After crushing into small pieces, the next step was to grind the small pieces to fine powder having particle size of 200 µ. For small scale batch (up to 100g scale) grinding was carried out in mortar pestle, where as for large scale batch (more than 1 kg scale) planetary ball mill was used.

The resulting mass after crushing and grinding is hydrated with water to alkalinize the Ca/CaO to form calcium hydroxide according to following equation.

$$ 2SmCO_5 + 3CaO + H_2O \xrightarrow{yields} 2SmCO_5 + 3Ca(OH)_2 $$ (2)

Here, the solution was stirred using a mechanical stirrer keeping a fixed rpm for optimum duration. In the process, the heavier intermetallic settled out while dissolved and un-dissolved Ca(OH)$_2$ floating in the supernatant liquid was removed by decantation. Water wash treatment was carried out in repeated cycles keeping with affixed solid to liquid ratio. In addition to water wash, the RD product is also subjected to acid treatment with solution of weak acid to get desired level of calcium content in the final product.

X-ray diffraction (XRD) (Inel France make, using Cr K$_\alpha$ radiation (λ = 2.29 Å) was employed to identify the phases of the alloy powder before and after the Ca leaching. Similarly, ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) technique was used to analyze residual calcium of the intermetallic powder. Wavelength Dispersive X-ray fluorescence (WD-XRF) spectroscopy was used to analyze the composition of Sm and Co in the alloy. The various phases and composition of the alloy were identified.
by means of scanning electron microscopy (SEM) analysis. Oxygen content in the alloy powder was determined by inert gas fusion method.

Results and Discussion:
Fig.2 shows the XRD pattern of final product obtained after leaching. It was evident from the XRD pattern that the decalcified under optimum conditions has peaks corresponding to required SmCo5 and Sm2Co7 only. Results obtained from WDXRF were also found to be consistent with the XRD result. Residual calcium and oxygen content in the alloy powder were found to be well within the permissible limit for making magnets.

Optimization of parameters in the RD process:
To study the effect of temperature on the performance of RD process, experiments were carried out at different temperature ranging from 900°C to 1300°C. It was observed that the reduction was incomplete when it was carried out below 1050°C and there was loss of samarium value when temperature crossed 1200°C. It was evident from the study that temperature must be kept above the melting point of samarium i.e.1070°C for faster diffusion to happen. A number of experiments were carried out to arrive at the optimum charge composition to get desired phases of the alloy. It was found that 5% excess Sm2O3 and 20% stoichiometric excess of Ca were necessary to get the desired phases.

Optimization of leaching conditions:
In the decalcification step, it was observed that almost 95% CaO was removed by leaching the product with demineralized (DM) water. For further decrease of residual calcium, leaching with acid solution was found to be necessary. In the leaching process, pH control is very important in the removal of trace amount of calcium by chemical reaction. High acidity may facilitate calcium removal but it leads to corrosion of alloy powder resulting in the deviation from targeted composition. Improper leaching results in loss of rare earth values. Typical SEM image the decalcined powder is shown in Fig.3.

Optimization of leaching conditions:
To select the effective leaching conditions for maximum yield of SmCo5 with minimum residual Ca in the alloy powder, four parameters have been identified. These are number of water wash cycle, number of acid wash cycle, pH of the solution and digestion time in each cycle. A number of experiments were carried out to reach at optimum conditions of leaching. These standardized leaching conditions were also experimentally validated for one kg and 10 kg scale batch.

Magnets were made out of this alloy powder and magnetic properties of these magnets were found to well match with the properties of the imported SmCo5 magnet (Recoma-18) with typical values of Br= 8.4 kGauss, Hc = 8.1 kOe, Hk = -12 kOe, BHmax = 19 MGOe.

Conclusion
Synthesis ofSm-Co (1:5) alloy powder by reduction-diffusion process has been optimized. Leaching conditions were also standardized for successful
removal of calcium from the products. XRD analysis confirmed the presence of required phases and WD-XRF analysis ensured the desired contents of the elements in the alloy powders. Oxygen and residual calcium content in the final products were well within the permissible limit for magnet preparation. Magnets made out of this material were found to be par with the recoma-18 grade magnets. The process has been successfully scaled up from 100g to 10kg batch level.

References: