NOTE TO USERS

CRYSTAL STRUCTURE, MICROSTRUCTURE AND MAGNETIC PROPERTIES OF RAPIDLY SOLIDIFIED SAMARIUM-COBALT BASED ALLOYS

By

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Crystal Structure, Microstructure And Magnetic Properties Of Rapidly Solidified Samarium-Cobalt-Based Alloys

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CRYSTAL STRUCTURE, MICROSTRUCTURE AND MAGNETIC PROPERTIES OF RAPIDLY SOLIDIFIED SAMARIUM-COBALT BASED ALLOYS

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University Of Nebraska – Lincoln, 2005

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The SmCo-based permanent magnets are drawing much more attention since the early 1970's for their highly attractive features such as, high energy product (15 MGOe–30 MGOe), reliable coercive force, best temperature characteristics and excellent corrosion and oxidation resistance. These interesting and highly demanding features have made Sm-Co the ideal material in dynamic applications such as generators and motors. The melt-spun ribbons of Sm-Co-based magnetic materials produced by rapid solidification exhibited higher anisotropy, improved microstructures and better magnetic properties ($M_r \sim 8.5$ kG, $H_c \sim 4.1$ kOe and $(BH)_{max} \sim 18.2$ MGOe and a high remanence ratio of 0.9).

This research reports the structure and magnetic properties of rapidly solidified Sm-Co permanent magnets of simple binary alloy systems modified with Nb and C additions. Melt spinning at 40 m/s resulted in the formation of the metastable $TbCu_7$-type structure in all instances regardless of alloying additions. While the unalloyed $Sm_{12}Co_{88}$ alloy displayed a coercivity of 0.5 kOe, alloying additions resulted in a systematic and profound increase in coercivity, with maximum values exceeding 37 kOe. TEM revealed the presence of fcc Co, formed as a result of the non-equilibrium processing. The

alloying additions had a profound influence on the scale of the microstructure, reducing the $SmCo_7$ grains from the micron-scale to the 100 nm range and the scale of the Co from 80 nm to 10 nm. The nanoscale Co soft magnetic phase enables exchange coupling to the hard magnetic phase, resulting in high remanence ratios (~0.7).

For a range of compositions, from $SmCo_{5.67}$ to $SmCo_8$, the coercivity was highest in Sm-rich compositions (17.5 kOe) and decreased to ~3 kOe as Sm content decreased.

At higher wheel speed during melt-spinning, the higher chances of formation of Co precipitate and the reduced size of Co precipitates helped to improve the remanence. At higher wheel speed and at higher concentration of alloying additions the magnetization process was dominated by pinning mechanism.

During the order-disorder phase transformations, the as-solidified alloys in the $TbCu_7$-type structure exhibited coercivity as high as 7.85 kOe, which increased to greater than 9 kOe by heat-treatment. The magnetization processes were also strongly influenced by the structural state during order-disorder phase transformations, initially it was totally controlled by nucleation followed by the domain wall pinning.

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CHAPTER I :: INTRODUCTION

1.1 Significance of The Study

Since the discovery of the naturally occurring mineral, magnetite (Fe_3O_4), magnetism and magnetic materials have been playing an important role in modern science and technology. In ancient times, the Chinese and the Greeks were using lodestones or "waystones" in guiding mariners. In 1600, physicist, William Gilbert, experimented with lodestone, iron magnets and the magnetic field of the earth. His experiments laid the foundation for current scientific applications, and dispelled the folklore surrounding magnetism and magnetic material [1]. Research about magnetic materials expanded after the invention of electromagnets by physicist Hans Christian Oersted in 1820 [1]. Permanent magnets have brought much more attention to the field, because unlike powerful electromagnets, they can be used without any consumption of electricity or generation of heat.

Permanent magnets are used and extensively studied in academic and military research and energy laboratories. Another important area of application is in medical industries (MRI, hematology laboratories and magnetic hyperthermia technique). About 160 magnets are used for different purposes in our daily lives. The applications range from refrigerator magnets, kitchen appliances, television, telephone, watches, computer, audio systems, to microelectronics. Another 100 magnets are used in the automobile industry. Permanent magnets are behind some of the most important inventions of our modern lives. They make our lives pleasant, comfortable and easier. They have a promising future, because a number of new devices are waiting for them. Ultimately,

there is a basic necessity to understand and improve their properties, as well as to look for new applications for them.

The first commonly used permanent magnets were made of carbon steel and were shaped like a horseshoe. Although this type of magnet is now obsolete, the horseshoe represents the symbol for magnetism [2]. In the past sixty years the applications of permanent magnets have been diversified due to discoveries of new materials like Alnicos (alloys of Al, Ni, Co and Fe), ferrites (combination of iron oxide with another metal), Nd-Fe-B and Sm-Co magnets. Although the Alnicos were extensively used in the mid-twentieth century as general-purpose permanent magnets, for their moderate magnetic properties achieved by relatively easy processing, they were replaced by much cheaper ferrites which now occupy 55% of the permanent magnet world market.

The field of rare-earth permanent magnets was initiated by the discovery of $SmCo_5$ in the late 1960s. People were much more attentive to these Sm-Co magnets due to their high anisotropy field H_A. The anisotropy field was twice that of the contemporary ferromagnetic Alnico alloys. A higher anisotropy field increases the coercivity H_{ci}, which helps to increase the maximum energy product $(BH)_{max}$, the amount of energy stored inside the material, which is the maximum value of the product of the magnetic induction (B) and the applied field (H) in the second quadrant of the B versus H hysteresis curve (will be discussed in detail in the next chapter – Chapter II). However, to avoid using relatively expensive and vulnerable sources of Co, the search for the Fe-based permanent magnets continued. This led to the discovery of $Nd_2Fe_{14}B$-based materials in 1983, followed by interstitially modified Sm-Fe-N in 1992. But, both of these have some drawbacks compared to Sm-Co magnets. The Sm-Fe compounds are not useful as

permanent magnet materials (for their basal plane easy magnetization direction) unless nitrogen diffusion expands the crystal structure and produces $Sm_2Fe_{17}N_x$. The Nd-Fe-B magnets are not applicable at higher temperatures. Table 1.1 displays representative properties of various permanent magnet materials.

As the second generation of rare-earth permanent magnets, Sm-Co-based magnets have been available since the early 1970's. The most interesting features of these magnets are high energy products (14 MGOe – 30 MGOe), reliable coercive force and the best temperature characteristics in the rare-earth materials family. Sm-Co-based magnets not only have better corrosion and oxidation resistance, but also exhibit better temperature stability. This is the ideal material in applications such as pump couplings, sensors and servo-motors. The Sm-Co system forms two related equilibrium phases in Co-rich compositions: the $CaCu_5$-type $SmCo_5$ structure and the Th_2Zn_{17}- or Th_2Ni_{17}-type Sm_2Co_{17} structure. The $CaCu_5$ structure itself is rather simple, with one Ca (R) site and two distinct Cu (Co) sites. The Sm_2Co_{17} structure is related to the $SmCo_5$ structure through the ordered substitution of one Sm by a pair of Co atoms (commonly referred to as Co dumbbells) [3]. In addition to the ordered Sm_2Co_{17} dumbbell structures, the dumbbell arrangement can be randomized on the rare earth sites as the disordered $TbCu_7$-type structure [4]. This metastable structure has the same unit cell as the $CaCu_5$ structure. The suppression of the long-range order, leading to the formation of the $TbCu_7$-type $SmCo_7$ structure, has been accomplished by melt spinning [5], splat cooling [6], mechanical alloying [7], and dilute additions of Zr and Ti [8,9,10]. The formation of

Table 1.1 The crystal structures and magnetic properties of various permanent magnets.

Property	**Alnico**	**$BaFe_{12}O_{19}$**	**$SmCo_5$**	**$Nd_2Fe_{14}B$**	**$Sm_2Fe_{17}N_x$**
Structure	cubic	hexagonal	hexagonal	tetragonal	Rhombohedral
Anisotropy field H_A (kOe)	5		350	80	140
Saturation magnetization $4\pi M_S$ (kG)	19	6.3	11	16	15.4
Curie temperature T_C (K)	1120	745	1000	580	770
Maximum energy product $(BH)_{max}$ (MGOe)	5.5	4.3	18.1	36.4	10.936

the disordered $SmCo_7$ structure has provided pathways to the development of materials with novel structures, as exemplified by recent advancements in the elevated-temperature performance of Sm-Co-based materials.