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BULK NANOCOMPOSITE $LaCo_5/LaCo_{13}$ MAGNETS (POSTPRINT)

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14. ABSTRACT
The effects of processing parameters and composition on the magnetic properties and microstructure of nanocrystalline La-Co-based hard magnetic materials were investigated. Bulk nanocomposite $LaCo_5/LaCo_{13}$ magnets were fabricated by mechanical alloying of $LaCo_5$ and La_2Co_7 powder mixtures and subsequent hot pressing at 580–810 °C. A high coercive field (H_c) of over 16 kOe with a smooth demagnetization curve was obtained in a composition range of 25–30 wt. % La_2Co_7 when hot-pressed at 660–760 °C. Microstructural investigations indicated that the magnets consist of a primary $LaCo_5$ phase with grain sizes of 200–400 nm, coexisting with 20–100 nm grains of $LaCo_{13}$ located both at the grain boundaries and within the hard $LaCo_5$ grains.

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Bulk nanocomposite $LaCo_5/LaCo_{13}$ magnets

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The effects of processing parameters and composition on the magnetic properties and microstructure of nanocrystalline La-Co based hard magnetic materials were investigated. Bulk nanocomposite $LaCo_5/LaCo_{13}$ magnets were fabricated by mechanical alloying of $LaCo_5$ and La_2Co_7 powder mixtures and subsequent hot pressing at 580–810 °C. A high coercive field (H_c) of over 16 kOe with a smooth demagnetization curve was obtained in a composition range of 25–30 wt. % La_2Co_7 when hot-pressed at 660–760 °C. Microstructural investigations indicated that the magnets consist of a primary $LaCo_5$ phase with grain sizes of 200–400 nm, coexisting with 20–100 nm grains of $LaCo_{13}$ located both at the grain boundaries and within the hard $LaCo_5$ grains.
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I. INTRODUCTION

Among the intermetallic compounds of the La-Co system, the $LaCo_5$ phase (hexagonal $CaCu_5$-type structure) has a strong uniaxial magnetocrystalline anisotropy field (H_A) of 175 kOe and a high Curie temperature (T_c) of 840 K.[1] The value of saturation magnetization, $4\pi M_s$, of 900 G (G) is relatively low.[1] The $NaZn_{13}$-type $LaCo_{13}$ phase has a higher Co content, resulting in a larger magnetization of 1300 G and a higher T_c of 1297 K.[2] The cubic structure and relatively low H_A of the $LaCo_{13}$ phase (~12 kOe) compared to that of the $LaCo_5$ phase makes it unsuitable as a permanent magnet.[3,4] However, composites of $LaCo_5$(hard)/$LaCo_{13}$(soft), similar to those of the FePt(hard)/Fe_3Pt(soft) system, could be a promising permanent magnet system for high temperature applications. Previous research showed that sintered micro-scale $LaCo_5$ magnets had coercivities, H_c, of 11-12 kOe at room temperature.[5] Recently, a nanoscale $LaCo_5$-based powder with a record high H_c of 17 kOe was produced by mechanical milling and subsequent annealing.[6]

In the present study, bulk nanocomposites of $LaCo_5$/$LaCo_{13}$ were fabricated by mechanical alloying followed by hot pressing. The effects of compositional variations and processing parameters on the magnetic properties and microstructure were investigated.

II. EXPERIMENTAL DETAILS

The $LaCo_5$ and La_2Co_7 alloys were prepared by arc melting then crushed to a powder with particle sizes less than 250 μm. Powder mixtures with different weight ratios of La_2Co_7 between approximately 0 to 50% (La content of 32 to 36 wt.%), were mechanically milled for 16 hs using a Spex 8000M high energy mill to form amorphous precursors. Samples were then hot pressed (HP) at temperatures between 580–810 °C for 30 s under 25 kpsi load to form fully dense, crystalline nanocomposite magnets. Magnetic properties at room temperature were measured by a closed-loop hysteresis graph. The crystal structure, phase fractions, and microstructure were characterized by x-ray diffraction (XRD) with Cu radiation, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

III. RESULTS AND DISCUSSION

The magnetic properties exhibited a strong dependence on hot pressing temperature and composition. Figure 1(a) shows typical demagnetization curves of the bulk La-Co magnets, with the La_2Co_7 ratio ranging from 0 to 50 wt. %. Among the studied compositions, a high H_c of over 15 kOe with a smooth demagnetization curve was obtained for the samples with La_2Co_7 weight fraction of 25–30% (La content of 34–34.5 wt. %) when hot pressed at 760 °C. The ratio of the remanence magnetization (M_r) to the magnetization at 1.5 T, Mr/M (1.5 T), is roughly 0.9. The ratio H_k/H_c (where H_k is the reversal field when the moment $4\pi M$ drops down to 90% of the remanent $4\pi M_r$) quantifies the squareness of the

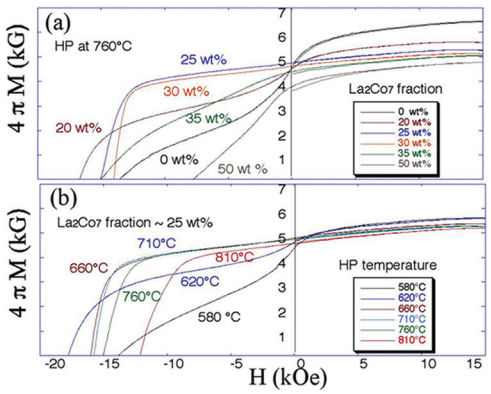

FIG. 1. (Color online) (a) Demagnetization curves of the bulk La-Co magnets as a function of La_2Co_7 weight fraction after hot pressing at 760 °C, and (b) as a function of hot pressing temperature for 25 wt. percent La_2Co_7.

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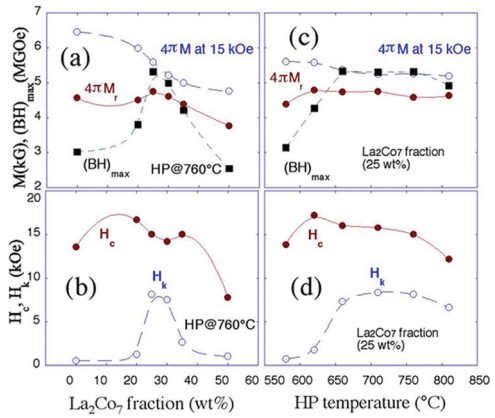

FIG. 2. (Color online) (a), (b) Magnetic properties of the bulk La-Co magnets as a function of La_2Co_7 weight fraction after hot pressing at 760 °C, and (c), (d) as a function of hot pressing temperature for 25 wt. percent La_2Co_7.

M-H loop. Values of H_k/H_c for these samples are close to 0.54 at room temperature. Magnets that are outside of this composition range exhibited lower H_c values and a shoulder in their demagnetization curves, indicative of a magnetically uncoupled structure. A similar uncoupling behavior is also observed for magnets that were hot pressed below 660 °C [Fig. 1(b)]. An optimum HP temperature window for the magnets with La_2Co_7 weight fraction of 25% is determined to be 660–760 °C. For higher processing temperatures, the coercivity is significantly reduced, while maintaining a single phase behavior. The overall hard magnetic properties with respect to composition and HP temperatures are summarized in Figs. 2(a)–2(d), respectively. In general, magnets that are hot pressed at 660–760 °C and contained 25–30 wt. percent of La_2Co_7 exhibited the highest H_c up to 16.6 kOe, with maximum energy products, $(BH)_{max}$, of approximately 5 MGOe. Outside of these optimal conditions, a shoulder in the demagnetization curve or lower H_c values significantly reduces $(BH)_{max}$.

X-ray diffraction and SEM indicated that the magnets are comprised of a multi-phase structure. The hot pressed samples were ground to a powder for XRD, with the resulting patterns presented in Fig. 3. The patterns indicate the

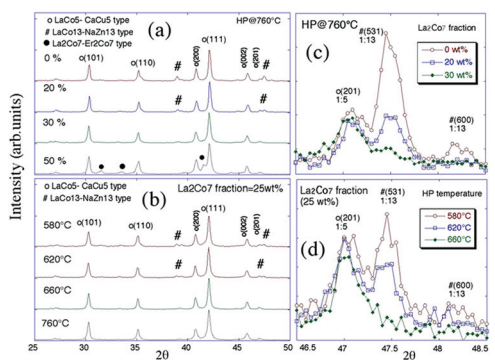

FIG. 3. (Color online) X-ray diffraction patterns of random powders as a function of La_2Co_7 weight percent for samples hot pressed at 760 °C (a), and as a function of hot press temperature for samples containing 25 wt. % La_2Co_7 (b). (c) and (d) show reflections from 1:13 phase (a) and (b), respectively, in detail.

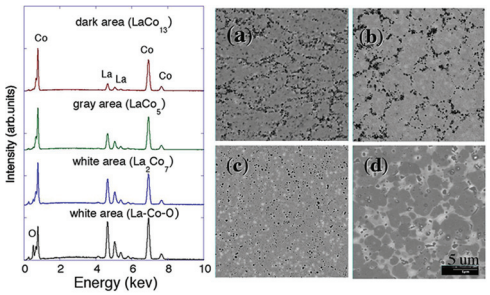

FIG. 4. (Color online) SEM/BSE images and corresponding EDS patterns for the bulk La-Co magnets with La_2Co_7 weight fractions of (a) 0%, (b) 20%, (c) 30%, and (d) 50% after hot pressing at 760 °C. The three composition areas are: (1) dark areas (Co-rich $LaCo_{13}$ phase), (2) gray areas ($LaCo_5$ phase), and (3) lighter areas (La-rich La-Co or La-O phases).

presence of three magnetic phases: (1) the $LaCo_5$ phase that dominates the structure of all magnets, (2) the $LaCo_{13}$ phase, detected as a minor phase in some of the samples, and (3) a La-rich phase in an Er_2Co_7 structure, detected when the La_2Co_7 content increases up to 50 wt %. The La-rich phase has a low $H_A \approx 50$ kOe (see Ref. 7), resulting in a decrease of the coercivity. Figure 3(a) shows the patterns for magnets hot pressed at 760 °C as a function of La_2Co_7 weight percent. The reflections shown in Fig. 3(c) indicate that the 1:13 phase decreases with increasing La_2Co_7 weight fraction, becoming almost undetectable at 30%. Similar behavior is observed as the HP temperature is increased for the magnets with the La_2Co_7 content of 25 wt. % [Figs. 3(b) and 3(d)]. The small amount of the 1:13 phase gradually decreases and almost disappears at temperatures of 660 °C and above. Existence of the magnetically uncoupled behavior in the demagnetization curves of the hot pressed magnets should be related to the presence of this detectable 1:13 phase. Even though it cannot be detected by XRD, magnets with a smooth demagnetization curves also contain a finely distributed small fraction of 1:13 phase evidenced by the SEM and TEM analysis. As it is discussed in detail by Kneller and Hawig,[8] the phase fraction and distribution of the low anisotropy phase greatly influences the coupling behavior.

Figure 4 depicts the SEM back-scattered electron (SEM/BSE) images and corresponding energy dispersive spectroscopy (EDS) patterns of the bulk La-Co magnets as a function of weight fraction for samples hot pressed at 760 °C. The

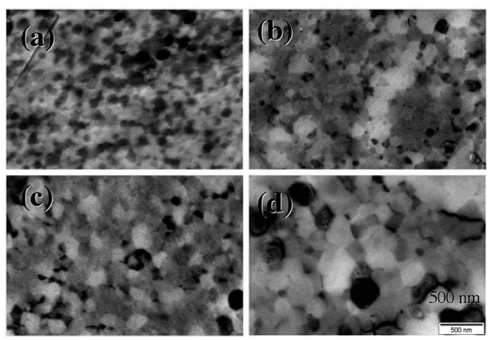

FIG. 5. SEM/BSE images for the bulk La-Co magnets with the La_2Co_7 weight fraction of 25% after hot pressing at (a) 580 °C, (b) 660 °C, (c) 710 °C, and (d) 760 °C.

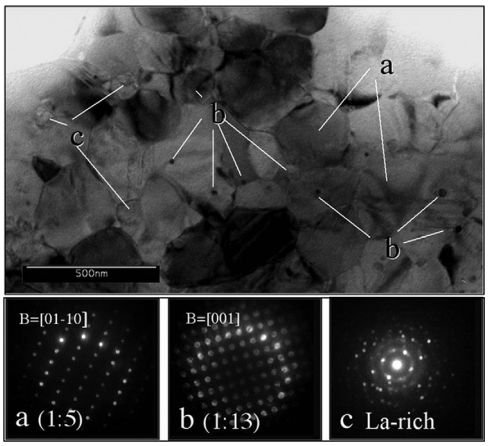

FIG. 6. TEM image and NBE diffraction patterns of bulk La-Co magnet with La_2Co_7 weight fraction of 25% after hot pressing at 660 °C; (a) $LaCo_5$-$CaCu_5$ type; B = 01-10, (b) $LaCo_{13}$-$NaZn_{13}$ type; B = 001, and (c) La rich phases.

contrast in the images indicates increasing La concentration from dark to light. EDS indicates that the dark areas correspond to the Co-rich LaCo-1:13 phase, the gray areas correspond to the $LaCo_5$ phase, and lighter areas correspond to the La-rich La-Co or La-O phases. The microstructure is highly dependent on weight percent of La_2Co_7, where Fig. 3(c) shows the best distribution of the dark 1:13 phase in the gray 1:5 phase. This is consistent with the magnetization measurements, which indicated the optimum microstructure for exchange-spring behavior occurs for La_2Co_7 fractions of 25-30wt%. Increasing the La_2Co_7 content [Fig. 3(d)] results in an increase in the amount of the La-rich phase (white areas) as well as an increase in the grain size. The magnetization measurements show that this results in a lower H_c and/or a lower H_k. Figure 5 shows the SEM/BSE images of the bulk La-Co magnets with the La_2Co_7 weight fraction of 25% as a function of HP temperature. The amount of Co rich $LaCo_{13}$ phase (dark areas) reduces and their distribution improves as the HP temperatures increases from 580 to 660 °C, resulting in a better coupling behavior. Higher HP temperatures beyond 760 °C cause the grains to grow larger, resulting in a decrease of H_c. The La_2O_3 phase was also detected at higher HP temperatures, causing a reduction in H_c.

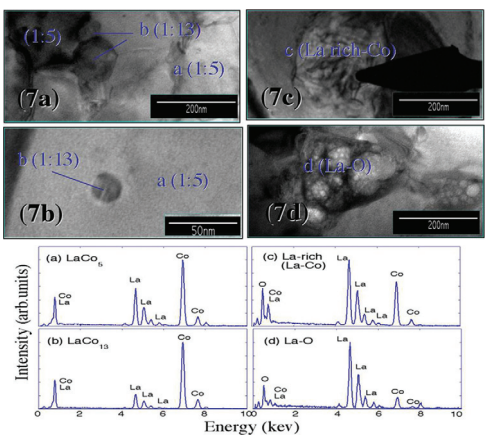

FIG. 7. (Color online) TEM images and corresponding EDS patterns of the phases present in the bulk La-Co magnet with La_2Co_7 weight fraction of 25% after hot pressing at 660 °C. (a) $LaCo_5$, (b) $LaCo_{13}$, (c) La rich La-Co, and (d) La-O.

Microstructural details of the 660 °C hot pressed magnet, with La_2Co_7 content of 25 wt. %, are presented in Figs. 6 and 7. TEM/EDS and nanobeam-electron (NBE) diffraction results suggest that the magnet exhibits a nanocomposite structure composed of four distinct phases: (a) the 1:5, (b) the 1:13, (c) the La-rich La-Co ($\sim La_2Co_7$), and (d) the La-O (near La_2O_3 stoichiometery) phases. These results are consistent with the findings from the XRD and SEM studies. The main $LaCo_5$ phase (grain sizes of 200–400 nm) coexists with the soft $LaCo_{13}$ phase (20–100 nm), located both at grain boundaries [see Fig. 7(a)], and within the hard 1:5 grains [see Fig. 7(b)]. The observed hard magnetic properties are attributed to the high anisotropy field and uniform grain size of the $LaCo_5$ phase, as well as its exchange coupling to the $LaCo_{13}$ phase. It is worth noting that the finely distributed La-rich La-Co and the La-O phases (or precipitates) have a subgrain structure [see images in Fig. 7(c) and 7(d)] and they are located among the 1:5 and 1:13 grains. The effects of these La-rich phases are not readily known. However, if they are paramagnetic in nature they are expected to act as pinning sites to impede the domain walls. If they are ferromagnetic, regardless of their anisotropy field, they are small enough to participate in the exchange coupling activity as a third party.

In summary, bulk $LaCo_5/LaCo_{13}$ nanocomposite magnets with maximum H_c values of 16 kOe have been successfully synthesized. The microstructure and magnetic properties are sensitive to initial powder weight ratios and hot pressing temperatures. This system shows promise as a permanent magnet system for high temperature applications.

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