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Structural, microstructural and magnetic properties of nanocomposite isotropic $Sm(Co_{bal}Fe_{0.1}M_yZr_{0.04}B_{0.04})_{7.5}$ ribbons with M = Ni, Cu and $y = 0.09$ and 0.12

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ABSTRACT

In boron-substituted melt-spun $Sm(Co,Fe,Cu,Zr)_{7.5}$-type alloys a nanocomposite microstructure and high coercivities in both as-spun and short-time annealed ribbons can be obtained. In the present study three different compositions, namely $Sm(Co_{0.73}Fe_{0.1}Cu_{0.09}Zr_{0.04}B_{0.04})_{7.5}$, $Sm(Co_{0.70}Fe_{0.1}Cu_{0.12}Zr_{0.04}B_{0.04})_{7.5}$ and $Sm(Co_{0.70}Fe_{0.1}Ni_{0.12}Zr_{0.04}B_{0.04})_{7.5}$ have been examined in order to investigate the influence of composition on the magnetic properties and the microstructure. Melt-spun ribbons have been obtained and annealing has been followed under argon atmosphere for 30–75 min at 600–870 °C. For the as-spun ribbons the $TbCu_7$-type of structure and fcc-Co as a secondary phase have been identified in the X-ray diffraction patterns. For the annealed ribbons above 700 °C the 1:7 phase transforms into 2:17 and 1:5 phases. The TEM studies have shown a homogeneous nanocrystalline microstructure with average grain size of 30–80 nm. Coercivity values of 15–27 kOe have been obtained from hysteresis loops traced in non-saturating fields. The coercivity decreases with temperature, but it is sufficiently large to maintain values higher than 5 kOe at 380 °C.

1. Introduction

$Sm(Co,Fe,Cu,Zr)_z$ alloys are established as permanent magnet materials with high energy product and high Curie temperature. Optimization studies for use at high temperatures, performed recently, resulted in compositions with intrinsic coercivity H_c of 10 kOe at 450 °C [1]. In these materials, coercivity is obtained by a precipitation hardening process, which comprises solid solution treatment at 1100–1200 °C for 4–24 h, isothermal aging at 850 °C for 10–24 h and slow cooling to 400 °C at a cooling rate <1 °C/min. This prolonged and complicated heat treatment is necessary for the development of the typical cellular–lamellar microstructure, with cells having a rhombohedral Th_2Zn_{17} (2:17R)-type structure, Cu-rich cell boundaries and Zr-rich lamellae perpendicular to the *c*-axis. The presence of Cu and Zr is considered to be requirement for the formation of the complex microstructure. Substitution of Ni for Cu does not prevent the formation of the cellular–lamellar microstructure, but the resulting coercivity is very low at room temperature, although it increases with temperature [2]. In melt-spun $Sm(Co,Fe,Cu,Zr)_z$ alloys, the cellular–lamellar microstructure and high coercivity (28 kOe) have been achieved simply by slow cooling from 850 to 400 °C, without the conventional solid solution and aging treatments [3]. Precipitation hardening with cellular features and H_c up to 10 kOe have also been obtained in melt-spun ribbons after a short-time anneal [4].

Alternative processing routes for nanostructured magnets with high coercivity have been explored in several recent studies. By mechanical milling and subsequent annealing, samples with 1:7 or 2:17 stoichiometries have been prepared with coercivities up to 20–25 kOe [5–7]. Lower H_c values (from 5 to 14 kOe) have been obtained by rapid solidification by melt spinning followed by short heat treatment [4,8–11]. Much higher coercivities, ranging from 16 to 27 kOe have been obtained, in boron-substituted

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$Sm(Co_{bal}Fe_{0.1}Cu_{0.12}Zr_{0.04}B_x)_{7.5}$ as-spun ribbons or after short annealing [12,13]. These compositions are typical of bulk precipitation hardened Sm–Co magnets, but the presence of B and the different synthesis process lead to the formation of a different microstructure. Several studies have also been focused in this direction [14–18]. In our series, the samples with a boron content $x = 0.04$ and spun at a moderate wheel speed (~40 m/s) showed very good magnetic properties and provide a promising starting point for further optimization studies. In the present work, we investigate the effect of Cu and Ni on the structure, microstructure and magnetic properties of these materials.

2. Experimental

Three bulk alloys, with compositions $Sm(Co_{bal}Fe_{0.1}Cu_{0.09}Zr_{0.04}B_{0.04})_{7.5}$, $Sm(Co_{bal}Fe_{0.1}Cu_{0.12}Zr_{0.04}B_{0.04})_{7.5}$ and $Sm(Co_{bal}Fe_{0.1}Ni_{0.12}Zr_{0.04}B_{0.04})_{7.5}$, which are denoted as compositions A(Cu009), B(Cu012) and C(Ni012), respectively, were prepared by arc melting under a flow of argon. These three compositions were selected for the connection of our previous work on melt-spun ribbons for high-temperature applications. To compensate for the Sm losses during processing, an excess of 5–10% Sm was added in all samples. Ribbons were obtained from master alloys by melt spinning using a quartz tube with an orifice diameter of 0.5 mm under 2 atm pressure of 99.999% pure argon. The wheel velocity was adjusted to 39 m/s with the use of a stroboscope. The ribbons were wrapped in with tantalum foil and sealed in a quartz tube—after three purges with pure argon to avoid oxidization—and then annealed at temperatures in the range of 600–870 °C for different times. The phases in as-spun and annealed ribbons were determined by powder X-ray diffraction (XRD) using Fe-Kα radiation. The magnetic measurements were performed with a SQUID magnetometer with a maximum applied field $H_{appl,max} = 52$ kOe. The high-temperature measurements were performed in a VSM with a maximum field of 20 kOe at temperatures up to 600 °C. The recrystallization behaviour was examined by differential thermal analysis (DTA), monitoring the heat flow versus temperature in a Setaram Setsys TG-DTA 1750 unit. The microstructure of the ribbons was determined by transmission electron microscopy using a Jeol JEM 2000FX microscope. SEM/EDAX with microprobe analysis was used to examine the composition at the wheel-contact surface of the ribbons.

3. Results and discussion

In the X-ray diffraction patterns of bulk arc-melted samples, the 1:7-type structure was identified and refined as the $TbCu_7$-type of structure, as shown in Figs. 1(a)–(c). Some minor phases were present, while the (0 2 4) peak of the 2:17 rhombohedral structure was also identified in Fig. 1(b). As can be observed in Fig. 1, all diffraction peaks have the same relative intensities between samples, indicating that different levels of substitution of Ni for Cu do not change the electronic density dramatically. This may be due to the similarity of the atomic radii for the two transition metals ($r_{Cu} = 0.157$ nm and $r_{Ni} = 0.162$ nm).

The diffraction patterns for as-spun ribbons at 39 m/s for all compounds A(Cu009), B(Cu012) and C(Ni012), are presented in Fig. 2. The patterns are similar for all three compositions, while the increased breadths of the diffraction peaks indicate nanocrystallinity. In the as-spun samples, the $TbCu_7$-type structure (1:7) or Sm_2Co_{17} (PDF#26-0484) is dominant. The lattice parameters of the 1:7 ($SmCo_7$) phase have been calculated to be $a = b \approx 4.95$ Å, $c \approx 4.07$ Å. The diffraction peaks (1 1 1), (2 0 0) and (2 2 0) for the

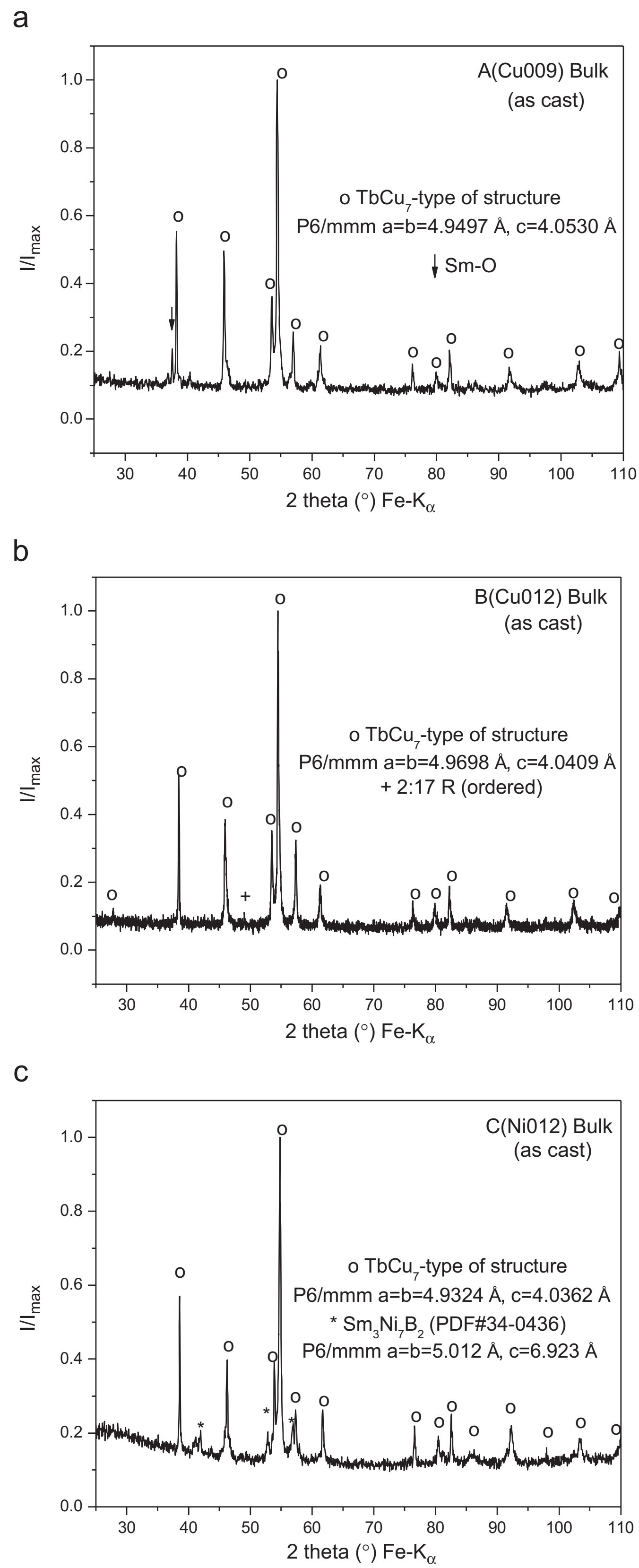

Fig. 1. X-ray diffraction patterns for bulk as-cast samples A(Cu009), B(Cu012) and C(Ni012).

fcc-Co (for $\lambda_{(Fe-K\alpha)}$) lay at 2θ values of ~56°, ~66° and ~101°, respectively. In some cases, these peaks were scarcely visible in the diffraction patterns for the as-spun ribbons.