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# Abnormal crystal structure stability of nanocrystalline $\text{Sm}_2\text{Co}_{17}$ permanent magnet

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Abnormal crystal structure stability is discovered in the single-phase nanocrystalline  $\text{Sm}_2\text{Co}_{17}$  permanent magnet. Three kinds of crystal structures, namely the rhombohedral  $\text{Th}_2\text{Zn}_{17}$ -type (2:17 R), the hexagonal  $\text{TbCu}_7$ -type (1:7 H), and the hexagonal  $\text{Th}_2\text{Ni}_{17}$ -type (2:17 H), are claimed to exist at room temperature in the  $\text{Sm}_2\text{Co}_{17}$  alloy system. The strong dependence of the magnetic properties on the structure characteristics in the single-phase  $\text{Sm}_2\text{Co}_{17}$  alloy is interpreted in view of the atom space occupancy and the exchange coupling between substructures especially in the nanocrystalline alloy. © 2009 American Institute of Physics. [DOI: 10.1063/1.3040316]

The  $\text{Sm}_2\text{Co}_{17}$ -type permanent magnets are a kind of ideal candidate materials for applications in servomotors, pump couplings, and sensors,<sup>1</sup> particularly as magnets, which are required to operate at high temperature or across a broad temperature range.<sup>2</sup> This is owing to their excellent intrinsic magnetic properties that combine the high Curie temperature and the crystalline anisotropy.<sup>1-3</sup> As generally accepted, the permanent magnet properties of  $\text{Sm}_2\text{Co}_{17}$ -type alloys, usually containing Fe, Cu, and Zr,<sup>2-4</sup> are attributed to the formation of a cellular precipitate microstructure achieved through a multistage heat-treatment process,<sup>5,6</sup> which involves sequential procedures of solid-solution treatment, isothermal aging, and slow cooling. The nanostructured  $\text{Sm}_2\text{Co}_{17}$ -type magnets are of special importance and attract increasing interests, not only because they are potentially superior high-temperature magnets owing to the repulsive and attractive pinning as well as the nucleation mechanisms for improving the permanent magnet properties<sup>6-8</sup> but also because completely new physics (e.g., nanomagnetism<sup>9</sup>) and relevant applications may be exploited. However, the nanocrystalline  $\text{Sm}_2\text{Co}_{17}$ -type magnets can hardly be obtained by the multistage heat-treatment process, as the fairly complicated procedures easily lead to the coarsening of the grain structure. Therefore, comprehensive studies on the crystal structure characteristics, phase stability, and their influences on the magnetic performance for the nanocrystalline  $\text{Sm}_2\text{Co}_{17}$  alloys have been scarce so far.

We demonstrate in this report the preparation of the single-phase nanocrystalline  $\text{Sm}_2\text{Co}_{17}$  alloy by a simple route, where we take advantage of a specially home-designed configuration of the “oxygen-free” *in situ* fabrication system.<sup>10</sup> This system protects effectively the samples from being oxidized or contaminated, which has ever been a big challenge in the field of nanoscale magnetic materials.<sup>11</sup> More importantly, abnormal crystal structure stability of the  $\text{Sm}_2\text{Co}_{17}$  nanocrystals is discovered. The strong dependence of the magnetic performance on the structure characteristics is further analyzed.

The Sm-Co cast ingots at the 2:17 stoichiometry were prepared by induction melting in the water-cooled copper hearth under the purified argon atmosphere. Some ingots were annealed at 1320 °C for 24 h in the quartz capsules filled with highly purified argon gas, whereafter they were quenched in liquid  $\text{N}_2$  to obtain the supersaturation solid solution. The other ingots were crushed into the coarse powder with a typical particle size of approximately 500  $\mu\text{m}$ . In order to avoid introducing the contaminations, the following procedures were all performed in an entirely closed system filled with highly purified argon gas, which combined the powder treatment with the spark plasma sintering (SPS) technology. The fine amorphous powder was produced by the high-energy milling with a ball to powder weight ratio of 16:1 at a constant rotation rate of 500 rpm for 12 h. Subsequently, the amorphous powder was fed into a high-strength cermet die in the glovebox and immediately sent to the sintering chamber of the SPS equipment by a sliding rail. To obtain the nanocrystalline  $\text{Sm}_2\text{Co}_{17}$  bulk from the alloy powder, the sintering parameters were optimized as a final sintering temperature of 1000 K, a heating rate of 50 K/min, and no isothermal holding time.

The x-ray diffraction (XRD) analyses on the phases and structures of the  $\text{Sm}_2\text{Co}_{17}$  alloys at different preparation stages are shown in Fig. 1. As indicated by curve (a) in Fig.

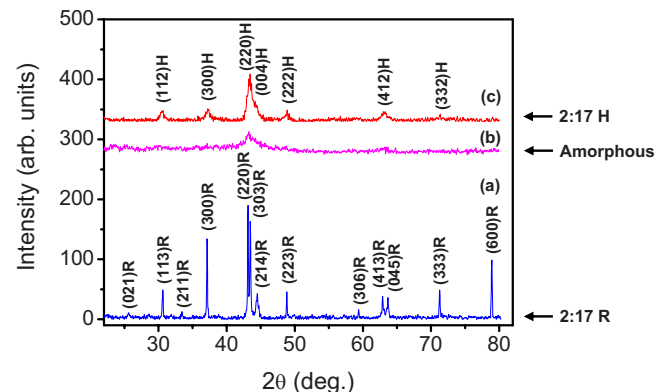


FIG. 1. (Color online) XRD analyses on the phases and structures of the  $\text{Sm}_2\text{Co}_{17}$  alloys at different preparation stages: (a) the as-cast alloy, (b) the ball-milled powder, and (c) the prepared nanocrystalline bulk.

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1, the as-cast alloy consists of the single  $\text{Sm}_2\text{Co}_{17}$  phase having a rhombohedral  $\text{Th}_2\text{Zn}_{17}$ -type (2:17 R) crystal structure, which is the normal crystal structure of the conventional polycrystalline  $\text{Sm}_2\text{Co}_{17}$  alloy at the equilibrium state. The amorphous structure of the alloy powder produced by the high-energy ball milling is characterized by the curve (b) in Fig. 1. Using the amorphous powder as a matrix and taking advantage of the consolidation as well as the concurrent nanocrystallization during the SPS process, we prepared the nanocrystalline  $\text{Sm}_2\text{Co}_{17}$  bulk with nearly a theoretical density. As shown by the curve (c) in Fig. 1, the nanocrystalline  $\text{Sm}_2\text{Co}_{17}$  bulk consists of a single phase, which has a hexagonal  $\text{Th}_2\text{Ni}_{17}$ -type (2:17 H) crystal structure [our deposited data CSD-420006 (Ref. 12)]. The broadened diffraction peaks indicate that the prepared  $\text{Sm}_2\text{Co}_{17}$  bulk has a very fine nanograin structure.

The as-quenched  $\text{Sm}_2\text{Co}_{17}$  alloy is found to have a hexagonal  $\text{TbCu}_7$ -type (1:7 H) crystal structure, which is a metastable phase at room temperature in the polycrystalline  $\text{Sm}_2\text{Co}_{17}$  alloy. It was claimed by Khan and Mueller<sup>13</sup> and Khan<sup>14,15</sup> in their classic studies that the hexagonal  $\text{Sm}_2\text{Co}_{17}$  existed as a single phase only above 1300 °C, while at temperatures up to 1300 °C the  $\text{Sm}_2\text{Co}_{17}$  phase had only a  $\text{Th}_2\text{Zn}_{17}$ -type (2:17 R) crystal structure. They concluded from the quenching experiments that the high-temperature hexagonal phase had either a defect-type crystal structure of the  $\text{CaCu}_5$ -type (1:5 H) or a disordered structure of the  $\text{TbCu}_7$ -type (1:7 H), while the hexagonal  $\text{Th}_2\text{Ni}_{17}$ -type (2:17 H) phase did not exist in the  $\text{Sm}_2\text{Co}_{17}$  alloy.<sup>14</sup> It has been conventionally considered that only two kinds of crystal structures can exist at room temperature in the  $\text{Sm}_2\text{Co}_{17}$  alloys. One is 2:17 R, as a stable equilibrium phase and the other is 1:7 H, as a metastable supersaturation solid solution. However, the present work shows convincingly that the hexagonal  $\text{Th}_2\text{Ni}_{17}$ -type (2:17 H) crystal structure in the single-phase nanocrystalline  $\text{Sm}_2\text{Co}_{17}$  alloy can exist stably at room temperature. Accordingly, the  $\text{Sm}_2\text{Co}_{17}$  nanocrystals exhibit abnormal crystal structure stability in contrast to conventional polycrystalline  $\text{Sm}_2\text{Co}_{17}$  alloys.

Figure 2 shows the microstructures of the prepared nanocrystalline  $\text{Sm}_2\text{Co}_{17}$  alloy. From the dark-field transmission electron microscopy (TEM) image in Fig. 2(a), it is estimated that the mean grain size of the nanograin structure is approximately 15 nm. As revealed by the selected area diffraction pattern (SADP) and the corresponding indexing, the nanocrystalline  $\text{Sm}_2\text{Co}_{17}$  is composed of the randomly oriented nanograins having the single hexagonal phase with the  $\text{Th}_2\text{Ni}_{17}$ -type crystal structure. This agrees well with the XRD analysis. The high-magnification enlargement of a local region in the nanocrystalline  $\text{Sm}_2\text{Co}_{17}$  is shown in Fig. 2(b). The four nanograins are shown by the bright-field high-resolution TEM (HRTEM) image and the RGB amplitude image, respectively. The corresponding lattice fringes of the 2:17 H nanocrystals are shown in the upper right of Fig. 2(b). The TEM analysis confirms the stable 2:17 H crystal structure in the nanocrystalline  $\text{Sm}_2\text{Co}_{17}$  and indicates that the SPSed  $\text{Sm}_2\text{Co}_{17}$  bulk has a completely crystallized structure with the ultrafine nanograins. The energy dispersive x-ray detections at the nanograin boundaries indicate that there is no segregation of elements, which confirms the single phase of  $\text{Sm}_2\text{Co}_{17}$  in the nanocrystalline alloy. Therefore, the present preparation route (stoichiometric ingot

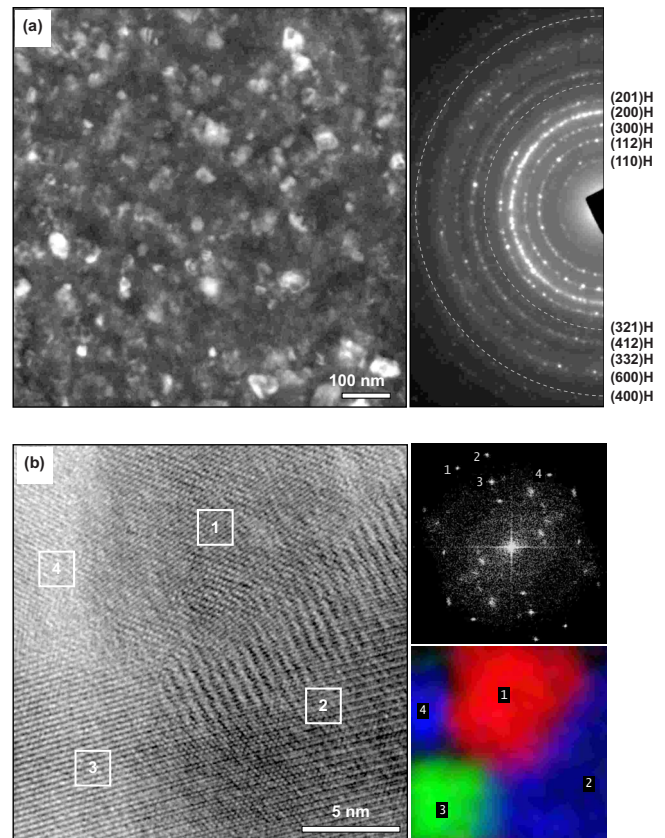


FIG. 2. (Color online) TEM analyses on the microstructure of the prepared nanocrystalline  $\text{Sm}_2\text{Co}_{17}$  alloy: (a) dark-field TEM image, the corresponding SADP and the indexing, (b) bright-field HRTEM image of the local nanograin structure, along with the corresponding lattice fringes of the nanocrystals (upper right) and the RGB amplitude image (lower right).

→ amorphous powder → nanocrystalline bulk) has been verified to be practical for fabricating the single-phase nanocrystalline alloy bulks with the ideal purity.

As described above, the  $\text{Sm}_2\text{Co}_{17}$  alloy can have three kinds of crystal structures at room temperature, i.e., 2:17 R, 1:7 H, and 2:17 H. The 1:7 H is a metastable crystal structure formed through the rapid quenching far from the thermodynamic equilibrium. However, both the polycrystalline 2:17 R and the nanocrystalline 2:17 H are the ordered stable phases at room temperature. The stable existence of the hexagonal phase instead of the conventional rhombohedral phase at room temperature could be better understood from the nanograin size effect on the phase stability. In a nanoscale thermodynamic model developed in our previous work,<sup>16</sup> the fundamental thermodynamic properties of the nanocrystalline materials, i.e., the enthalpy, the entropy, and the Gibbs free energy, were derived as the deterministic functions of the temperature and the nanograin size. The stability of the crystal structure of a certain nanocrystalline phase is dominated by the relative free energy with respect to other phases. Thus, the Gibbs free energies of different nanocrystalline phases, and further the thermodynamic equilibrium of the phases, are modulated by the variation in the nanograin size. Therefore, when the nanograin size is reduced to below a critical value, the Gibbs free energy of the hexagonal 2:17 H structure can be lower than that of the rhombohedral 2:17 R structure, thus the 2:17 H phase instead of the 2:17 R phase exists stably at room temperature. Hereby the abnormal phase stability in the nanocrystalline  $\text{Sm}_2\text{Co}_{17}$  is induced by

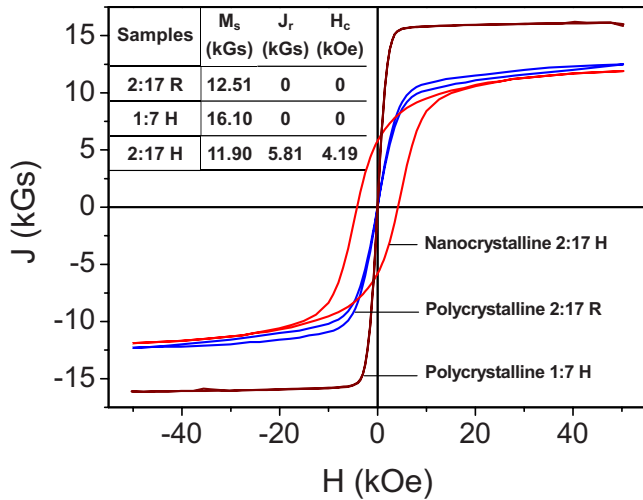


FIG. 3. (Color online) The magnetization hysteresis loops of the  $\text{Sm}_2\text{Co}_{17}$  alloys with different structures: (a) the as-cast polycrystalline 2:17 R alloy, (b) the as-quenched polycrystalline 1:7 H alloy, and (c) the nanocrystalline 2:17 H alloy. The characteristic values of magnetic performance for different samples are listed in the inset.

the ultrafine nanograin size, which results in the changes in the energy and the structure states of the nanocrystalline phase.

Figure 3 shows the magnetization characteristics of the as-cast polycrystalline  $\text{Sm}_2\text{Co}_{17}$  alloy with the 2:17 R crystal structure, the as-quenched polycrystalline  $\text{Sm}_2\text{Co}_{17}$  alloy with the 1:7 H crystal structure, and the prepared nanocrystalline  $\text{Sm}_2\text{Co}_{17}$  alloy with the 2:17 H crystal structure, respectively. The magnetic characteristics of the three samples are distinctly different, as observed from the hysteresis loops. The polycrystalline 2:17 R and 1:7 H alloys have almost no coercivity ( $H_c$ ) and remanence ( $J_r$ ), which are the most important permanent magnet parameters. Whereas, the nanocrystalline 2:17 H alloy has evidently permanent magnet properties with greatly enhanced coercivity and remanence. On the other hand, the 1:7 H alloy has the highest saturation magnetization ( $M_s$ ), while the 2:17 R and 2:17 H alloys have the similar level of saturation magnetization with that of the 2:17 R alloy a bit larger (the detailed values listed in the inset in Fig. 3).

In the coarse-grained 2:17 R and 1:7 H alloys with a single-phase structure, there is no contribution from the pinning effect of the second-phase particles on the magnetic domain walls,<sup>17</sup> leading to the magnetization loop without the presence of coercivity and remanence. The high saturation magnetization of the 1:7 H alloy is owing to the strong uniaxial magnetocrystalline anisotropy, which originates from the Co atoms at the  $2c$  sites in the primary lattice cell, as well as their shrink deformation<sup>18</sup> during the formation of 1:7 H lattice structure through disordered (and asymmetric) substitution of Co–Co dumbbell pairs for Sm atoms. For the single-phase nanocrystalline 2:17 H alloy, the enhancement in the permanent magnet properties is achieved by the exchange coupling between the neighboring nanograins. The large coercivity of the 2:17 H alloy, as compared with the 2:17 R and 1:7 H alloys, should be attributed to the drastically increased volume fraction of the grain boundaries in the ultrafine nanocrystalline alloy, which act as the strong domain-wall pinning centers. Although both 2:17 R and 2:17

H crystal structures are constituted by long-range ordered lattices with specific Co “dumbbells” arrangement, the two lattice structures have different anisotropy. The larger anisotropy of the 2:17 R structure, as can be reflected by the deviation of the axial ratio from the unity (referring to  $c/a = 1.4624$  for 2:17 R and  $c/a = 0.9172$  for 2:17 H in the present work), leads to a relatively higher intrinsic saturation magnetization of the 2:17 R alloy than that of the 2:17 H alloy.

In summary, we produced the single-phase nanocrystalline  $\text{Sm}_2\text{Co}_{17}$  permanent magnet with ultrafine grain size by a simple fabrication route, which has primary advantages of oxygen-free and *in situ* rapid synthesis and is potentially applicable to a large variety of nanocrystalline alloys with the satisfying purity. The prepared nanocrystalline  $\text{Sm}_2\text{Co}_{17}$  alloy has a hexagonal  $\text{Th}_2\text{Ni}_{17}$ -type crystal structure existing stably at room temperature, which is abnormal phase stability in contrast to conventional polycrystalline  $\text{Sm}_2\text{Co}_{17}$  alloys. The remarkable differences in the magnetic performance of the alloys with different structures originate from the atom space occupancy and the exchange coupling between the nanoscale substructures. The unambiguous relationship between the structure characteristics and the magnetic performance enables more profound understanding of the magnetism of the  $\text{Sm}_2\text{Co}_{17}$ -based alloys, thus facilitates the development of nanocrystalline  $\text{Sm}_2\text{Co}_{17}$ -type alloys with superior permanent magnet properties.

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