Physica B 487 (2016) 25–30

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Magnetic-field-induced irreversible antiferromagnetic–ferromagnetic phase transition around room temperature in as-cast Sm–Co based $SmCo_{7-x}Si_x$ alloys

D.Y. Feng, L.Z. Zhao, Z.W. Liu *

School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, PR China

ARTICLE INFO

Article history:
Received 21 January 2016
Accepted 26 January 2016
Available online 26 January 2016

Keywords:
SmCo
AFM-FM phase transition
Magnetic field
Metastable

ABSTRACT

A magnetic-field-induced irreversible metamagnetic phase transition from antiferro- to ferromagnetism, which leads to an anomalous initial-magnetization curve lying outside the magnetic hysteresis loop, is reported in arc-melted $SmCo_{7-x}Si_x$ alloys. The transition temperatures are near room temperature, much higher than other compounds with similar initial curves. Detailed investigation shows that this phenomenon is dependent on temperature, magnetic field and Si content and shows some interesting characteristics. It is suggested that varying interactions between the Sm and Co layers in the crystal are responsible for the formation of a metastable AFM structure, which induces the anomalous phenomenon in as-cast alloys. The random occupation of 3*g* sites by Si and Co atoms also has an effect on this phenomenon.

1. Introduction

$SmCo_5$, $SmCo_7$ and Sm_2Co_{17} alloys have been extensively studied because of their excellent permanent-magnet properties [1–6]. Generally, these alloys are prepared by melt spinning, ball milling or sintering. The structures and properties of melt-spun ribbons, milled powders and sintered magnets have been well investigated, especially for $SmCo_5$- and Sm_2Co_{17}-based alloys [7–10]. However, the magnetic characteristics of as-cast Sm–Co based alloys have seldomly been reported, possibly due to their poor coercivity caused by the large grain size or non-optimized microstructure [11]. In the present work, we have investigated the magnetization curves of as-cast Sm–Co based alloys prepared by argon-arc-melting and have found that the initial magnetization curve is situated outside the magnetic hysteresis loop at a certain temperature range around room temperature. This unusual phenomenon has attracted our attention since it has never been reported for Sm–Co alloys before. Extensive literature search indicates that a similar anomalous initial magnetization curve has previously been reported for some other compounds, such as $Ga_{1-x}Zn_xCMn_3$ [12], $Ce(Fe_{0.96}Ru_{0.04})_2$ [13], $Ce(Fe_{0.96}Al_{0.04})_2$ [14], Gd_5Ge_4 [15], $Mn_2Sb_{0.95}Sn_{0.05}$ [16], Nd_7Rh_3 [17], $(PrCa/Na)MnO_3$ [18] and $Nd_{0.5}Sr_{0.5}MnO_3$ [19], but it generally occurs at very low temperatures, even close to 5 K, much lower than what we have found for Sm–Co alloys. In order to understand the underlying physics of this anomalous magnetization process, the magnetic hysteresis loops, magnetization *versus* temperature ($M \sim T$) curves, thermal-analysis curves and specific heat of as-cast $SmCo_{7-x}Si_x$ alloys at various temperatures are presented here. The origin of this unusual phenomenon is discussed. A magnetic-field-induced high-temperature irreversible antiferromagnetic–ferromagnetic (AFM-FM) phase transition is suggested.

2. Experimental

$SmCo_{7-x}Si_x$ ($x=0$–0.60) alloys have been prepared by argon arc-melting. From the as-cast ingots, samples have been taken. For some experiments, selected ingots were annealed at 600 and 900 °C for 96 h in argon atmosphere. For comparison, $SmCo_{6.85}Si_{0.15}$ ribbons were also prepared by melt spinning with a wheel speed of 50 m/s. Magnetic properties and specific heat C_p of the ingots were measured at various temperatures using a physical-property-measurement system (PPMS-9, Quantum Design). To measure the *M vs T* curves. The magnetization was then measured at magnetic fields of 40 kA/m, 800 kA/m, and 1600 kA/m in the following sequence: the samples were first cooled from room temperature to 150 K at zero field., then warming up the sample to the highest temperature of 350 K, cooling it in a field to the lowest temperature of 150 K (FC). Differential scanning calorimetry (DSC-Q200, TA, USA) has been carried out in nitrogen atmosphere. The phase structure was determined by X-ray diffraction (XRD, Philips X-pert) with Cu-K_α radiation.

* Corresponding author.
E-mail address: zwliu@scut.edu.cn (Z.W. Liu).

http://dx.doi.org/10.1016/j.physb.2016.01.028
0921-4526/

3. Experimental results

Fig. 1 shows the magnetic hysteresis loops (magnetic polarization *versus* magnetic field, $J \sim H$) of as-cast $SmCo_{7-x}Si_x$ alloys with various Si contents. All loops show very low coercivity because of the large grains formed during the arc-melting [11]. With increasing Si content from $x=0$ to 0.6, the saturation polarization J_s decreases from 1.13 to 0.74 T. Surprisingly, the initial magnetization curve is lying outside the hysteresis loop for the $SmCo_{7-x}Si_x$ alloys with $x \le 0.45$. This very unusual phenomenon has never been reported for Sm-Co alloys before. The largest field gap between the initial curve and the magnetization loop in the first quadrant, defined in Fig. 1 by H_g shown, decreases with increasing Si content, indicating that this phenomenon is sensitive to Si content.

Fig. 2 shows the *J vs H* loops of $SmCo_{6.85}Si_{0.15}$ at various temperatures. At 285 K, the initial magnetization curve is inside the magnetization envelope. At 290 K, it starts to reside out of the loop. H_g increases with the increasing temperature and reaches its largest value at 300 K. Above this temperature, H_g decreases afterwards and vanishes at 380 K. Also, J_s has its largest value at 300 K. The results indicate that this anomalous phenomenon is also sensitive to temperature.

Fig. 3 shows the ZFC–FC curves of $SmCo_{6.85}Si_{0.15}$ between 150 and 350 K at various magnetic fields. At all fields, the ZFC curve is different from the FC curves. At an applied field of 40 kA/m, the ZFC magnetization (M) increases from 10.7 to 12.3 A m^2/kg with temperature increasing from 150 to 350 K, as shown in Fig. 3(a). The FC magnetization increases with decreasing temperature. When the field is increased to 800 kA/m, the ZFC curve changes slightly from 150 to 260 K, as shown in Fig. 3(b). The magnetization increases rapidly from 73 to 105 A · m^2/kg in the temperature interval from 260 to 310 K and becomes about constant around 330 K. Around 290 K, where the anomalous initial magnetization curve starts to appear (Fig. 2), the magnetization increases most sharply. The FC curve obtained at 1600 kA/m (Fig. 3(c)) displays a similar temperature dependence as the one at 800 kA/m. It can be concluded that a large magnetic field (800 or 1600 kA/m) induces a drastic increase of M around 290 K.

Fig. 4 shows *M vs T* curves for $SmCo_{6.85}Si_{0.15}$ in the high-temperature range. In a field of 40 kA/m, M decreases slowly with increasing temperature. Close to 1000 K, M decreases sharply due to the FM-paramagnetic phase transition. Except for a larger M value, the behavior at 800 kA/m is similar. Around 380 K, where the anomalous initial magnetization curve disappears, no sharp increase or decrease of M is found, indicating that the disappearance of the anomalous initial curve is a continuous process.

Fig. 5 shows the DSC result for $SmCo_{6.85}Si_{0.15}$. After cooling down to 190 K, the sample was heated up to 720 K and then cooled down again. No clear exothermic or endothermic peak was found, indicating that there is no first-order phase transition in the temperature interval from 190 K to 720 K.

However, the temperature dependence of the specific heat C_p of $SmCo_{6.85}Si_{0.15}$ shows two peaks at 287 K and 357 K (Fig. 6), very close to 290 K and 380 where the anomalous phenomenon starts to appear and disappear, respectively. The results indicate that second-order phase transitions occur at these two temperatures.

Fig. 7 shows $J \sim H$ curves of as cast $SmCo_7$ and $SmCo_{6.85}Si_{0.15}$ before and after annealing. As shown in Fig. 7(a), the anomalous initial magnetization behavior of $SmCo_7$ has disappeared after annealing at 600 °C and 900 °C. For $SmCo_{6.85}Si_{0.15}$, H_g has become small after annealing at 600 °C and finally disappears after annealing at 900 °C (Fig. 7(b)). The disappearance of the anomalous initial magnetization behavior is accompanied by a decrease of J_s.

Fig. 8 shows the XRD patterns of $SmCo_7$ alloys before and after annealing. The phase structure of the as-cast alloy is dominated by Th_2Zn_{17}-type Sm_2Co_{17} (R-Sm_2Co_{17}) and $CaCu_5$-type $SmCo_5$ phases. Upon annealing at 600 °C, the patterns only slightly change. After annealing at 900 °C, the alloy is still dominated by $SmCo_5$ and R-Sm_2Co_{17} phases. However, the $CaCu_5$-type $SmCo_5$ (110), (200)

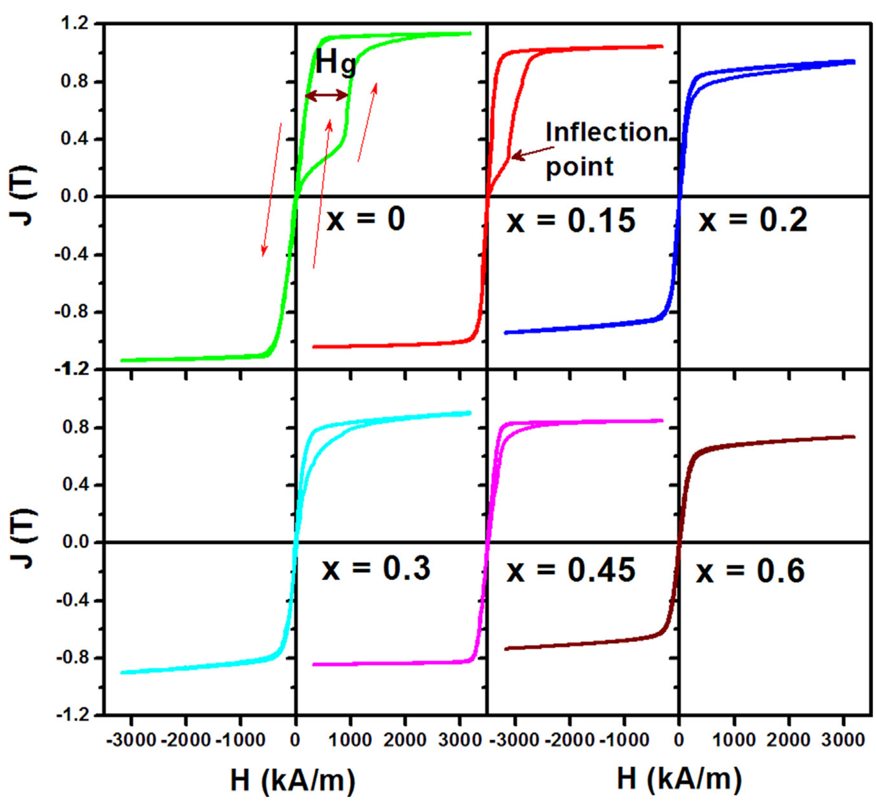

Fig. 1. Magnetic hysteresis loops at 300 K for as-cast $SmCo_{7-x}Si_x$ (x=0–0.60) alloys.