Institute of Physics Publishing — Journal of Physics D: Applied Physics
J. Phys. D: Appl. Phys. **39** (2006) 437–440 doi:10.1088/0022-3727/39/3/002

Effects of annealing on the coercivity of Sm(Co,Fe,Cu,Zr)$_z$ ribbons and its temperature dependence

Chuan-bing Rong[1,2], Hong-wei Zhang[1], Ren-jie Chen[1], Bao-gen Shen[1], Shu-li He[3] and J Ping Liu[2]

[1] State Key Laboratory of Magnetism, Institute of Physics and Center for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China
[2] Department of Physics, University of Texas at Arlington, Arlington, TX 76019, USA
[3] Department of Physics, Capital Normal University, Beijing 100037, People's Republic of China

Received 31 October 2005, in final form 15 December 2005
Published 20 January 2006
Online at stacks.iop.org/JPhysD/39/437

Abstract
Sm(Co$_{bal}$Fe$_{0.1}$Cu$_x$Zr$_{0.03}$)$_7$ ($x = 0.0$–0.25) ribbons have been prepared by melt spinning. The effects of annealing parameters on coercivity and its temperature dependence have been studied systematically. It is found that the melt-spinning technique remarkably improves the magnetic properties and simplifies the annealing process. The high-performance precipitation-hardened magnets can be obtained by only short-time ageing and slow cooling from 850 to 400 °C, without the standard solid solution. More interestingly, the temperature coefficient of coercivity of the ribbons can be tuned through adjustments of the processing parameters.

1. Introduction

Precipitation-hardened Sm(Co,Fe,Cu,Zr)$_z$ magnets have large anisotropy fields and high Curie temperatures which make them ideal candidates for high temperature applications [1–3]. Their high coercivity originates from a complex microstructure consisting of a superposition of cellular structure (2 : 17 cells with 1 : 5 cell boundaries) and a lamellar structure known as the Z phase. Recently, the interests of these precipitation-hardened magnets were mainly focused on the low or even positive temperature coefficients of coercivity, $\beta = \mathrm{d}(\mu_0 H_c)/\mathrm{d}T$ [4–11], which is a very large negative for the Nd$_2$Fe$_{14}$B-type magnets. However, the complex cellular microstructure in these magnets is usually obtained by a lengthy heat treatment consisting of homogenization at high temperatures followed by long-time ageing at temperatures in the range 800–850 °C and slow cooling to 400 °C. Therefore, some efforts have been undertaken to simplify the above processing procedure [12, 13]. Our recent work shows that the melt-spinning technique can not only simplify the annealing conditions but also produce the crystallographic texture in the Sm(Co,Fe,Cu,Zr)$_z$ ribbons [14]. This may be important technologically for the fabrication of more economical precipitation-hardened magnets. In this work, we systematically studied the effects of the melt-spinning technique and annealing parameters on the coercivity of Sm(Co,Cu,Fe,Zr)$_z$ ribbons and its temperature dependence.

2. Experiments

Ingots with nominal composition Sm(Co$_{bal}$Fe$_{0.1}$Cu$_x$Zr$_{0.03}$)$_7$ ($x = 0.0$–0.25) were prepared by the arc-melting technique. The ribbons were obtained using the single-roller melt-spinning technique with the surface speeds of the Cu wheel about 5 m s^{-1}. Subsequently, without the lengthy solid solution treatment, they were isothermally aged at temperatures T_a = 600–950 °C for time t_a = 0–25 h followed by slow cooling at rate v_c = 0.25–5 °C min^{-1} and then quenched at temperature T_q = 300–850 °C. It should be mentioned that all other annealing parameters are fixed to study the influences of T_a, t_a, v_c or T_q on coercivity. The crystalline structure was determined by x-ray diffraction (XRD) with Cu Kα radiation. The RT magnetic properties were measured using a superconducting quantum interference device (SQUID) magnetometer with a maximum applied field of 5 T. The high temperature magnetic properties were measured using a vibrating sample magnetometer with a maximum applied field of 2.4 T.

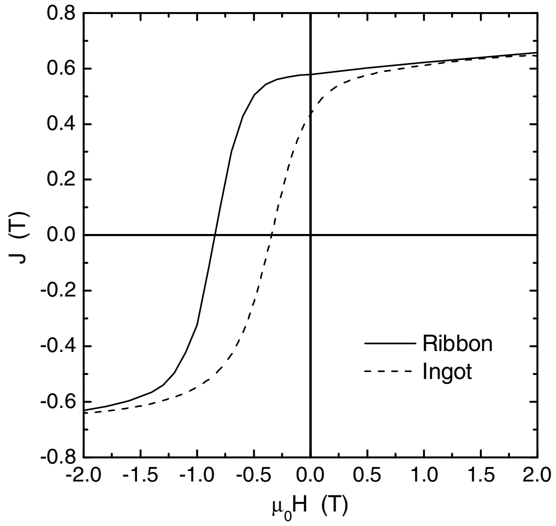

Figure 1. The demagnetization curves of the $Sm(Co_{bal}Fe_{0.1}Cu_{0.1}Zr_{0.03})_7$ ribbon and ingot annealed at the same conditions.

3. Results and discussions

To present the advantage of the melt-spinning technique, the ingots and ribbons have been annealed by the same process, i.e. aged for 3 h and slowly cooled from 850 to 400 °C without the lengthy solid solution treatment. Figure 1 gives the demagnetization curves of the precipitation-hardened $Sm(Co_{bal}Fe_{0.1}Cu_{0.1}Zr_{0.03})_7$ ribbon and ingot for an example. As can be seen the coercivity of ribbon is larger than that of ingot and the hysteresis loop of ribbon is more rectangular than that of ingot. In addition, we find that less Cu content x is needed in the ribbons to reach the same coercivity and rectangularity (the demagnetization curves of other composition are not given in figure 1). Thus, the magnetic properties of ribbons are better than those of ingots because less Cu content leads to higher saturation magnetization.

Figure 2(*a*) shows the RT coercivity of $Sm(Co_{bal}Fe_{0.1}Cu_x Zr_{0.03})_7$ ribbon as a function of T_a. To study the effect of T_a on H_c, $t_a = 3$ h, $v_c = 1\,°C\,min^{-1}$ and $T_q = 400\,°C$ are adopted. As can be seen H_c is low when $T_a \leqslant 750\,°C$, while it increases fast with varying T_a to 900 °C. Further increasing T_a to 950 °C leads to a drop in coercivity. Figure 2(*b*) shows the $H_c(T)$ curves of $Sm(Co_{bal}Fe_{0.1}Cu_{0.1}Zr_{0.03})_7$ ribbons aged at different T_a. One can find that H_c decreases monotonically with the temperature of the ribbon aged at $T_a = 600\,°C$. The abnormal temperature dependence of coercivity can be obtained only for the ribbon aged at about $T_a = 750\,°C$. This anomaly of coercivity will be discussed in the last paragraph of this section. A further increase in T_a leads to a near zero β at a wide temperature range. However, H_c decreases monotonically again if T_a is too high. Previous studies show that T_a has a significant effect on the microstructure of the $Sm(Co,Fe,Cu,Zr)_z$ magnets [15]. If T_a is too low, the cellular microstructure, which is the prerequisite to obtain high coercivity, is not developed. Upon ageing at an appropriately high temperature for a short time, a microstructure with a small cell size can be developed. A higher T_a leads to larger cells and higher coercivity. However, overhigh T_a will lead to the deterioration of cells and thus fast decrease in coercivity. The sensitive relations between the coercivity and T_a (shown in figure 2) prove the importance of the cellular microstructure in the precipitation-hardened magnets.

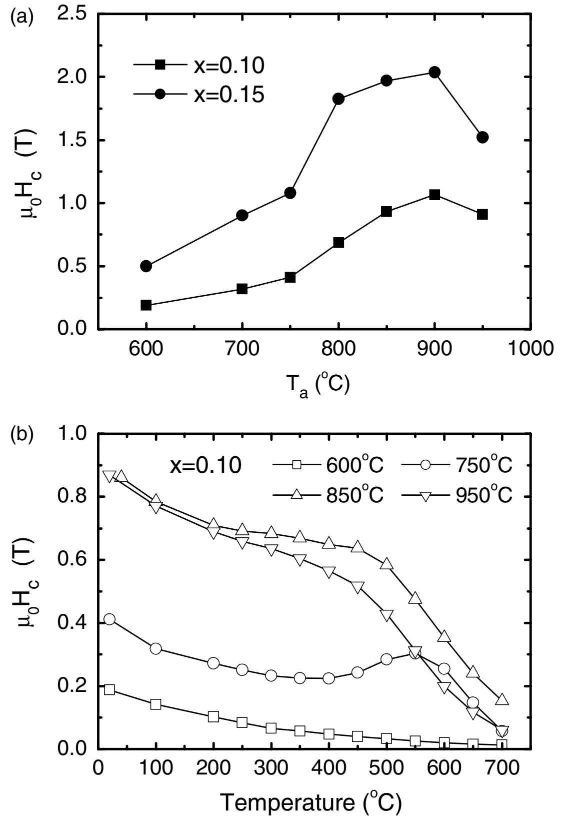

Figure 2. Coercivity of the $Sm(Co_{bal}Fe_{0.1}Cu_x Zr_{0.03})_7$ ribbons with different ageing temperature, T_a. (*a*) RT H_c versus T_a; (*b*) $H_c(T)$ curves of the magnet with $x = 0.10$.

Figure 3(*a*) shows the RT coercivity of $Sm(Co_{bal}Fe_{0.1}Cu_x Zr_{0.03})_7$ ribbon as a function of t_a. $T_a = 850\,°C$, $v_c = 1\,°C\,min^{-1}$ and $T_q = 400\,°C$ are fixed. For the ribbons with Cu content $x \leqslant 0.15$, H_c increases monotonically with t_a until $t_a = 3$–5 h and rarely changes with longer ageing time. However, for the ribbons with $x \geqslant 0.20$, H_c reaches a maximum at $t_a = 1$–3 h and decreases significantly with a further increase in t_a. That is to say, a short-time ageing is enough to develop the coercivity and a long-time ageing is disadvantageous for the ribbons. Previous transmission electron microscopy investigations show that the cellular microstructure is formed mainly during the isothermally ageing process [15–17]. After ageing for a short time, small 1 : 5 cells are developed first. Then the lamellar phase appears. With increasing t_a, the cell size and density of lamellar phase gradually increase. This leads to an increase in coercivity. Perfect and uniform cellular microstructures are always formed after ageing for about 2 h. However, further increasing t_a destroys the cellular microstructure and thus decreases the coercivity [15–18]. Figure 3(*b*) shows the $H_c(T)$ curves of $Sm(Co_{bal}Fe_{0.1}Cu_{0.1}Zr_{0.03})_7$ ribbon aged for different t_a. As can be seen the anomalous temperature dependence of coercivity is observed in the ribbon with short-time ageing. However, the coercivity is lower than that of the aged ribbons in the whole temperature range.

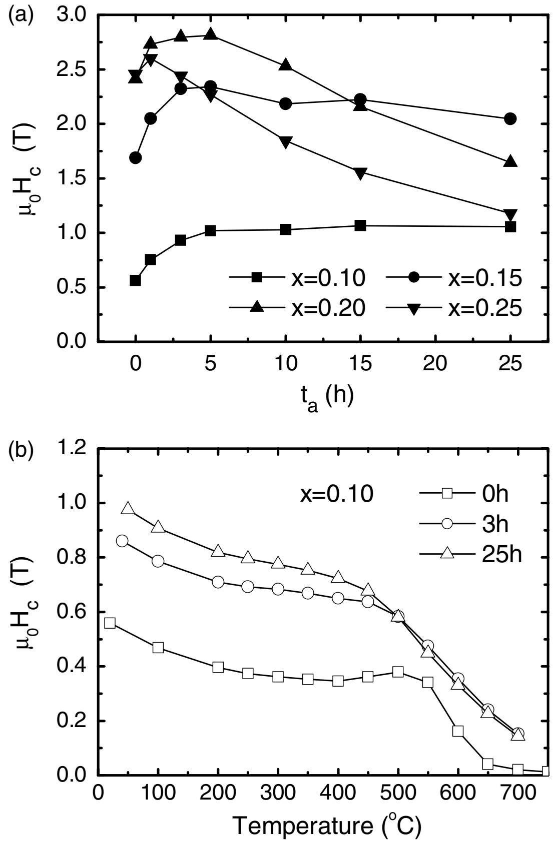

Figure 3. Coercivity of the Sm(Co$_{bal}$Fe$_{0.1}$Cu$_x$Zr$_{0.03}$)$_7$ ribbons with different ageing time, t_a. (*a*) RT H_c versus t_a; (*b*) $H_c(T)$ curves of the magnet with $x = 0.10$.

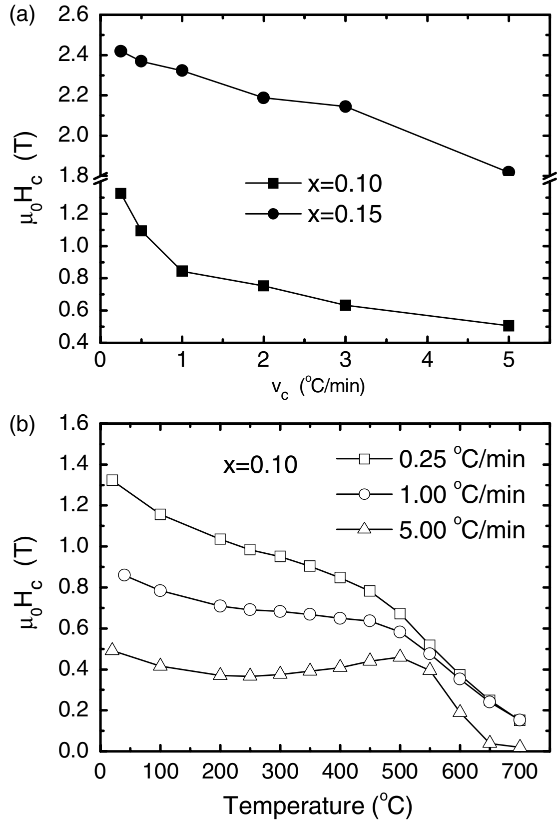

Figure 4. Coercivity of the Sm(Co$_{bal}$Fe$_{0.1}$Cu$_x$Zr$_{0.03}$)$_7$ ribbons with different v_c. (*a*) RT H_c versus v_c; (*b*) $H_c(T)$ curves of the magnet with $x = 0.10$.

Figure 4(*a*) shows the RT coercivity of Sm(Co$_{bal}$Fe$_{0.1}$Cu$_x$Zr$_{0.03}$)$_7$ ribbon as a function of v_c. To study the effect of v_c on H_c, $T_a = 850\,^\circ$C, $t_a = 3$ h and $T_q = 400\,^\circ$C are fixed. It is found that H_c increases monotonically with decreasing v_c regardless of the Cu content. Especially, the enhancement of H_c of $x = 0.10$ is faster than that of $x = 0.15$. For the Sm(Co,Fe,Cu,Zr)$_z$ magnets, the slow cooling is an important step to develop the coercivity of magnets. During this step, diffusion of Cu takes place and Cu is concentrated mainly in the 1 : 5 cell boundaries finally [15]. This dilutes the magnetic properties of the 1 : 5 phase and causes domain wall pinning at the cell boundaries or the magnetic isolation of the 2 : 17 cells. This is the reason why the slow cooling develops the coercivity of the precipitation-hardened magnets. Since more Cu enters the 1 : 5 cell boundaries with slower cooling rate, H_c increases with decreasing v_c. For the ribbons with high x, the Cu content in the 1 : 5 cell boundary phase may be saturated even with large v_c. Thus, H_c of the high x ribbons changes little since the Cu content in the 1 : 5 phase changes little with varying v_c. However, for the ribbons with small x, the saturation of Cu in the 1 : 5 phase needs small v_c. Thus, H_c of the ribbon with $x = 0.10$ increases dramatically when v_c is smaller than $1\,^\circ\mathrm{C\,min^{-1}}$. Figure 4(*b*) shows the $H_c(T)$ curves of Sm(Co$_{bal}$Fe$_{0.1}$Cu$_{0.1}$Zr$_{0.03}$)$_7$ ribbon treated with different v_c. The anomalous temperature dependence of coercivity can be obtained in the ribbon with $v_c = 5\,^\circ\mathrm{C\,min^{-1}}$. However, it prefers to disappear with the decrease in v_c.

Figure 5(*a*) gives the RT coercivity of Sm(Co$_{bal}$Fe$_{0.1}$Cu$_x$Zr$_{0.03}$)$_7$ ribbon as a function of T_q. $T_a = 850\,^\circ$C, $t_a = 3$ h and $v_c = 1\,^\circ\mathrm{C\,min^{-1}}$ are adopted to study the effect of T_q on H_c. As can be seen H_c increases fast with a decrease in T_q. Similar to the effects of v_c during the slow cooling, the increase in T_q leads to a decrease in the Cu content in the 1 : 5 cell boundary phase and thus a decrease in coercivity. Figure 5(*b*) shows the $H_c(T)$ curves of Sm(Co$_{bal}$Fe$_{0.1}$Cu$_{0.1}$Zr$_{0.03}$)$_7$ ribbon quenched at different T_q. The anomalous temperature dependence of coercivity can be obtained in the ribbons with $T_q \geqslant 500\,^\circ$C. In addition, the tendency of the abnormal temperature dependence of coercivity gradually disappears with decreasing T_q.

In fact, all the previous relations between β and the annealing parameters may be explained by the change of microstructure and microchemistry, which leads to a variation of the distribution and amount of Cu in the 1 : 5 cell boundaries. This controls the coercivity and its temperature dependence. The abnormal behaviours can be explained by the domain wall pinning [5–7], nucleation models [8, 10] and the mixture of both mechanisms [4, 19, 20]. Domain wall pinning assumes that H_c should be proportional to the difference in the domain wall energy density between the 2 : 17 and 1 : 5 phases [5–7,21], i.e. $H_c \propto \Delta\gamma = |\gamma_{2:17} - \gamma_{1:5}|$. When the Cu content in the 1 : 5 phase is low, $\gamma_{1:5} > \gamma_{2:17}$ at RT. $\Delta\gamma$ decreases with increasing temperature until some temperature T_0 where $\gamma_{2:17} = \gamma_{1:5}$ and then it climbs up to a maximum at $T_c^{1:5}$. This explains the minimum and maximum in $H_c(T)$

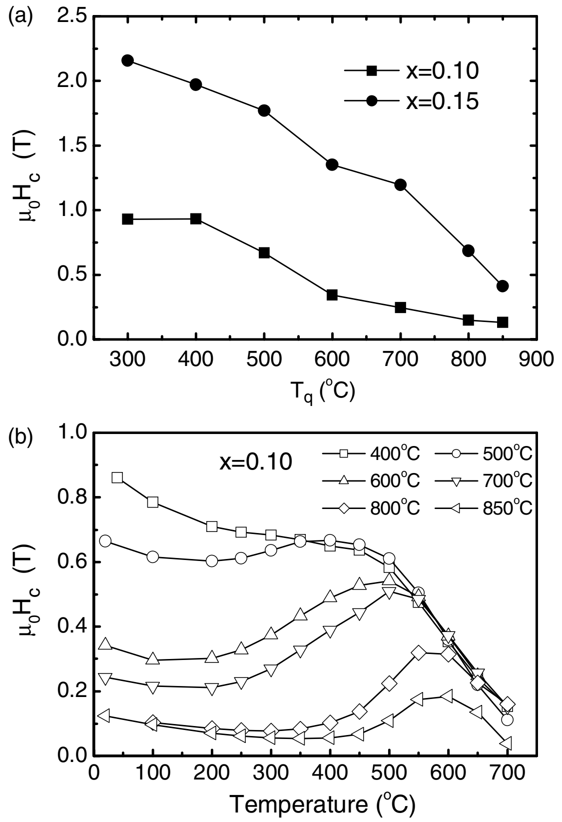

Figure 5. Coercivity of the $Sm(Co_{bal}Fe_{0.1}Cu_xZr_{0.03})_7$ ribbons with different T_q. (*a*) RT H_c versus T_q; (*b*) $H_c(T)$ curves of the magnet with $x = 0.10$.

curves appearing at T_0 and $T_c^{1:5}$, respectively. The nucleation model uses the assumption that H_c is controlled by nucleation of reversed domains [8, 10] and thus is sensitive to magnetic isolation of the single-domain regions. Since the 2 : 17 cells are surrounded by magnetic 1 : 5 boundaries and not isolated at RT, the RT coercivity is low. With increasing temperature up to $T_c^{1:5}$, the 1 : 5 boundaries become nonmagnetic, resulting in complete magnetic isolation of the 2 : 17 cells and thus a high coercivity. The nucleation model also explains the anomalous $H_c(T)$ successfully. According to both pinning and nucleation mechanisms, the temperature of the peak coercivity, T_{max}, should be equal to $T_c^{1:5}$. To study the relation between them, $T_c^{1:5}$ and T_{max} of the ribbons quenched at different T_q are listed in table 1. It can be clearly seen that there is a strong relation between T_{max} and $T_c^{1:5}$, i.e. both of them decrease with increasing T_q. This also indicates that Cu is mainly concentrated in the 1 : 5 cell boundaries during the slow cooling and plays an important role in the abnormal temperature dependence of coercivity. However, T_{max} is always lower than $T_c^{1:5}$. This can be attributed to the inhomogeneous distribution of Cu in the 1 : 5 cell boundaries [6].

4. Conclusion

$Sm(Co_{bal}Fe_yCu_xZr_w)_z$ ribbons have been prepared by melt spinning followed by different annealing conditions. The effects of processing parameters on coercivity and its temperature dependence have been studied systematically.

Table 1. The effect of T_q on $T_c^{1:5}$, $T_c^{2:17}$ and T_{max} of the $Sm(Co_{bal}Cu_xFe_{0.1}Zr_{0.03})_{7.0}$ ribbons.

T_q[°C]	$T_c^{2:17}$[°C]	$T_c^{1:5}$[°C]	T_{max}[°C]
850	855	665	550–600
800	855	655	550–600
700	855	630	500–550
600	850	610	400–550
500	850	605	350–500
400	850	600	—

It was found that the melt-spinning technique can improve the magnetic properties remarkably. More importantly, it can also simplify the annealing process. That is to say, we can develop a high-performance high-temperature magnet by only slow cooling the ribbons from 850 to 400 °C. In addition, the temperature coefficient of coercivity can be tuned through adjustment of annealing parameters, which should be attributed to the variation of the distribution and amount of Cu in the 1 : 5 cell boundaries.

Acknowledgment

The work was supported by the National Science Foundation of China.

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