2014

Effect of annealing on nanostructure and magnetic properties of Zr_2Co_{11} material

Wenyong Zhang
University of Nebraska-Lincoln, wenyong.zhang@unl.edu

Xingzhong Li
University of Nebraska-Lincoln, xli2@unl.edu

Shah R. Valloppilly
University of Nebraska-Lincoln, svalloppilly2@unl.edu

Ralph A. Skomski
University of Nebraska - Lincoln, rskomski2@unl.edu

David J. Sellmyer
University of Nebraska-Lincoln, dsellmyer@unl.edu

Published in *Materials Science and Engineering B* 186 (2014), pp. 64–67;
doi: 10.1016/j.mseb.2014.02.012 0921-5107

Submitted October 17, 2013; revised January 29, 2014; accepted February 18, 2014; published online March 1, 2014.

Effect of annealing on nanostructure and magnetic properties of Zr_2Co_{11} material

W. Y. Zhang,[1,2] X. Z. Li,[2] S. Valloppilly,[2] R. Skomski,[1,2] and D. J. Sellmyer[1,2]

1. Department of Physics and Astronomy, University of Nebraska, Lincoln, NE 68588, USA
2. Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, NE 68588, USA

Corresponding author – W. Y. Zhang, Nebraska Center for Materials and Nanoscience, University of Nebraska, 855 N. 16th Street, Lincoln, NE 68588, 402-472-6818, email wenyong.zhang@unl.edu, wyzhang2005@yahoo.com

Abstract

Single-phase Zr_2Co_{11} nanomagnetic materials with high coercivity have been fabricated by melt spinning with subsequent annealing under Ar, N_2, and vacuum. Annealing coarsens the grains and decreases the density of defects, leading to intergrain decoupling action and the enhancement of the magnetocrystalline anisotropy field of the hard magnetic phase. Therefore, coercivity increases 44.7% from 6.7 kOe for the as-spun to 9.7 kOe for the annealed, which is the highest among Zr–Co alloys so far. The results show that the magnetic-hardening mechanism is primarily dominated by domain-wall pinning. In addition, annealing clearly increases the saturation magnetization. The above results indicate that Zr_2Co_{11} has potential for fabricating rare-earth-free permanent-magnet nanocomposites.

Keywords: annealing, nanostructure, magnetic-hardening, coercivity

1. Introduction

Zr_2Co_{11} is a potential candidate for developing rare-earth-free hard magnetic materials due to its strong magnetocrystalline anisotropy and high Curie temperature.[1,2] Depending on the preparation process, the crystal structure of Zr_2Co_{11} may be pseudohexagonal, rhombohedral, or orthorhombic.[3–5] Rhombohedral Zr_2Co_{11} was found to be the hard magnetic phase. Although the basic structure is denoted as Zr_2Co_{11}, a range of composition exists and it is often found that the stoichiometry corresponds to$ZrCo_{5.1}$. The room-temperature saturation polarization of Zr_2Co_{11} can be increased up to 12 kG by adding Fe.[6] However, the coercivity is much lower than $M_s/2$, the minimum needed to approach the theoretical maximum energy product. Recent work has focused on studying effects of the quench rate and element addition on nanostructure and hard magnetism of Zr_2Co_{11}-based alloys. It was reported that a high quench rate is required in order to obtain good magnetic properties because it increases the volume fraction of the hard magnetic phase.[7] B addition was found to refine the grain size and increase the coercivity.[8] Ti addition suppressed the formation of Zr_2Co_{11} dendrites upon solidification, refined the structure, and enhanced the coercivity.[9,10] A high coercivity of 6.7 kOe was achieved for the as-spun Zr_2Co_{11}-based nanocomposites with the additions of Si and B.[11] The coercivity was further increased up to 7.9 kOe for the single-phase Zr_2Co_{11} alloy due to Mo addition.[12] Up to now, few studies have been done on the effect of annealing condition on nanostructure and hard magnetism of the single-phase Zr_2Co_{11} materials. In this letter, we report that annealing optimizes the nanostructure of the single-phase Zr_2Co_{11} materials, and thus significantly enhances the coercivity and increases the saturation magnetization. We also analyze the nanostructure-property relationship.

2. Experimental methods

Ingots of $Zr_{16}Co_{74}Mo_4Si_3B_3$ were arc melted from high-purity elements in an argon atmosphere. The ribbons were made by ejecting molten alloys in a quartz tube onto the surface of a copper wheel rotating with a speed of 16 m/s. The as-spun ribbons are about 2 mm wide and 50 μm thick. Some ribbons wrapped in the Ta foil were put in the middle of the stainless steel tube for annealing in Ar or N_2. The flowing rate is 100 sccm. The others were put in the middle of the quartz tube for annealing under vacuum. The heating rate is10°C/min. All the ribbons are annealed at temperatures of from 400 to 700°C for 30–120 min. The magnetic properties were found to be almost independent of the annealing atmosphere. The optimum conditions where the coercivity is the largest is 600°C for 90 min. As-annealed ribbons point to the ribbons annealed at the optimum condition. The phase components were examined by a RigakuD/Max-B X-ray diffraction (XRD) system with Cu Kα radiation and also by thermomagnetic measurements using a Quantum Design Physical Property Measurement System (PPMS) at temperatures up to 1000 K. The Curie temperature corresponds to the temperature where a minimum value in the differentiated $M(T)$ curves occurs. The nanostructure was observed by the JEOL 2010 Transmission Electron Microscope (TEM). The hysteresis loops were measured by a Quantum Design Superconducting Quantum Interference Device(SQUID) magnetometer at fields up to 7 T. The applied field is parallel to the long direction of the ribbon.

3. Results and discussion

Figure 1(a) shows XRD patterns of the as-spun and annealed ribbons. All the diffraction peaks were indexed to the rhombohedral Zr_2Co_{11} structure. The lattice parameters of $Zr_2(Co,Mo,Si,B)_{11}$ for two samples are a = b = 4.7866 and c = 11.7658 Å. The cell volume is 233.46 Å^3, which is much smaller than that of Zr_2Co_{11}, which indicates that the smaller B and Si atoms occupy Zr_2Co_{11} lattice sites[10,13] It has been reported that the existence of dislocations is a prerequisite to launch recrystallization which often leads to a change of grain orientation, grain growth, and decrease of defect density.[14,15] Earlier work showed that dislocations were observed in nanocrystalline Zr_2Co_{11} materials.[16] Compared to the as-spun ribbons, some extra peaks exist in the annealed ribbons. It was concluded that annealing induces the appearance of recrystallization, which may coarsen the grain and decrease the density of structural disorder such as planar defects. Therefore, the magnetization and Curie temperature were significantly enhanced for the annealed ribbons, which are shown in figure 1b. The enhanced Curie temperature for the as-annealed ribbons may be attributed to the increase of atomic moment of Co due to the enhancement of chemical ordering. Figure 2 shows the TEM images of the as-spun and annealed ribbons and the corresponding grain-size statistical distribution. The mean grain size for the as-spun ribbons is 70 nm. However, the average grain size for the annealed is 120 nm. There are some grains with stripes (indicated by red arrows in figure 2(a)and (b)) consisting of the planar defects shown in High-Resolution TEM image in figure 3(c) which may be stacking faults or antiphase domain walls.[9] It is evident that the volume fraction of grains with stripes for the as-spun samples is much larger than that for the as-annealed. It indicates that annealing decreases the density of structural disorder in good agreement with the thermomagnetic measurement results shown in figure 1(b).

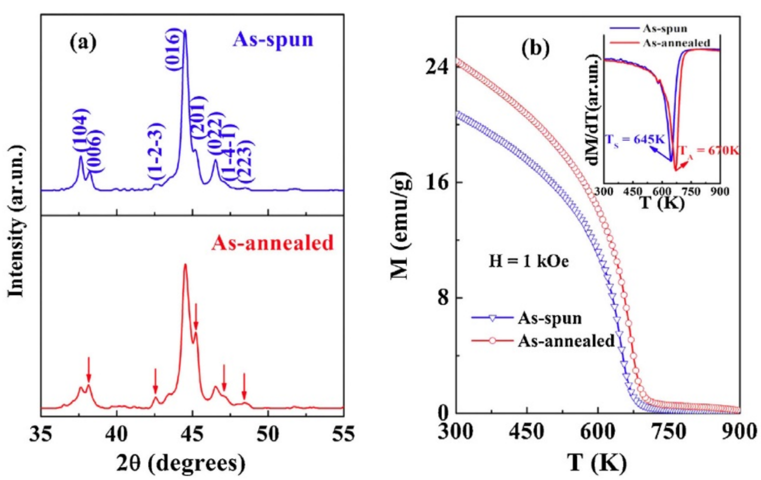

Figure 1. XRD patterns (a) and MT curves (b) of the as-spun and as-annealed ribbons. The inset in (b) is the differentiated MT curves showing the Curie temperatures of the Zr_2Co_{11}.

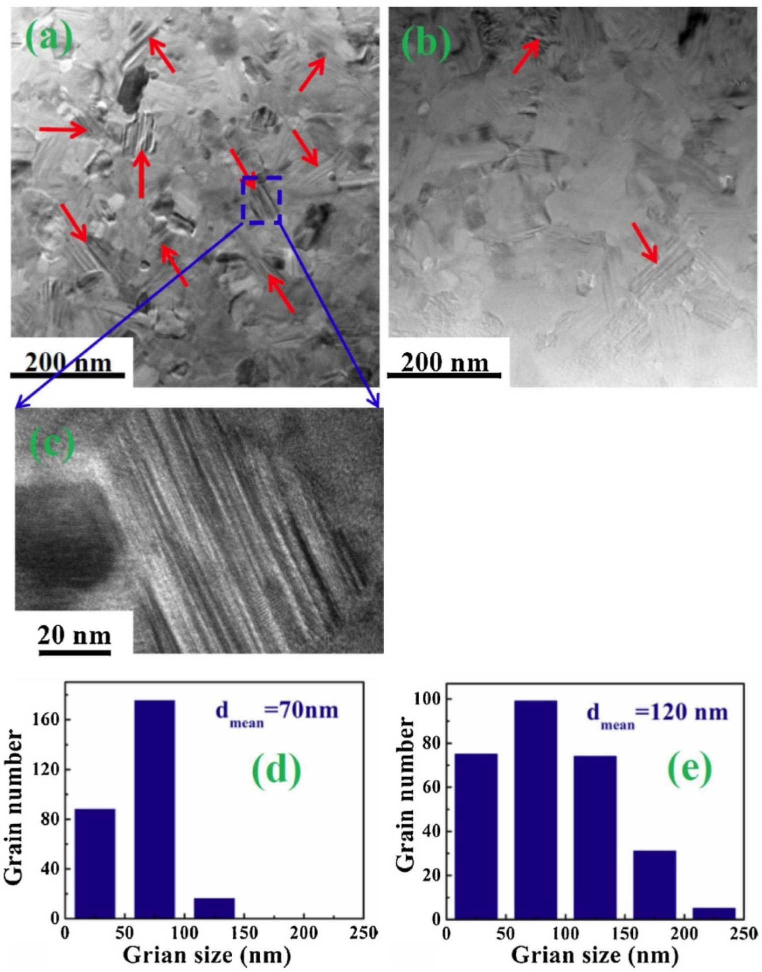

Figure 2. TEM images of the as-spun (a) and as-annealed (b) ribbons, the enlarged part (high-resolution TEM) (c), and the grain size distribution of the as-spun (c) and as-annealed(d) ribbons.

Figure 3 shows the hysteresis loops at 300 K of the as-spun and as-annealed ribbons. It is seen that the coercivity and remanence of the as-annealed ribbons were almost independent of the annealing atmosphere. Annealing obviously increases the saturation field of the sample. The law of the approach to saturation was employed to fit the high-field part of the hysteresis loops.[17] The anisotropy constant K and saturation magnetization M_s were determined. The magnetocrystalline anisotropy field, $H_a = 2K/M_s$, for the as-spun and annealed ribbons are 39.8 and 45 kOe, respectively. Annealing obviously enhances H_a, which is believed to arise from the decrease of the structural disorder. In addition, annealing coarsens the grains and tends to decouple exchange the grains. This significantly increases the coercivity up to 9.7 kOe, which is the highest value obtained so far for the Zr–Co alloys.

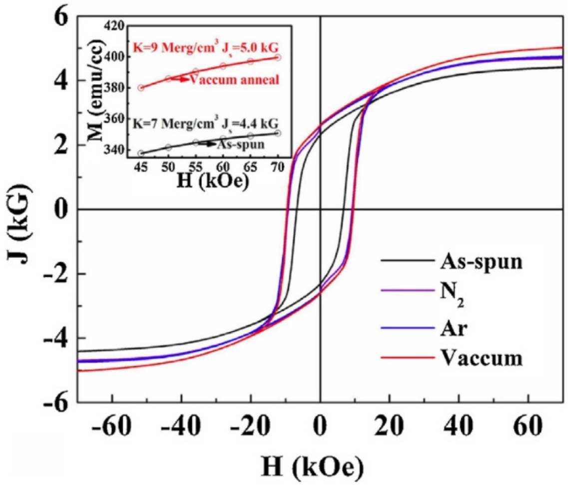

Figure 3. Hysteresis loops of the as-spun ribbon and as-annealed ribbons under different atmosphere. The upper left inset shows the K and J_s.

Figure 4 shows the hysteresis loops at various temperatures of the as-spun and annealed ribbons. Many small grains with grain size of about 20 nm were observed in the as-spun and annealed samples (see fig. 2). They may have much smaller magnetocrystalline anisotropy constant than large grains and are regarded as the soft phase, whereas the large grains are the hard phase. The demagnetization curve for the as-spun exhibits the character of the single phase, indicating the existence of effective interphase exchange coupling. The coercivity has a little increase with the decrease of temperature because of a small increase of the magnetocrystalline anisotropy. However, we found that the coercivity of the annealed ribbon significantly increases with decreasing temperature due to a large increase of the magnetocrystalline anisotropy. A kink appears in the second quadrant of the hysteresis loop at 10 K for the annealed ribbon. This is because a large increase of K with the decrease of temperature leads to a decrease of the volume fraction of the small grains that are well exchange-coupled. The temperature coefficients of coercivity in 10–300 K for the as-spun and as-annealed ribbons are 0.07%/K and 0.15%/K, respectively. The difference in the change of the coercivity with the variation of temperature between the as-spun and as-annealed ribbons is believed to arise from the difference in the nanostructure such as the grain size and the degree of structural disorder.

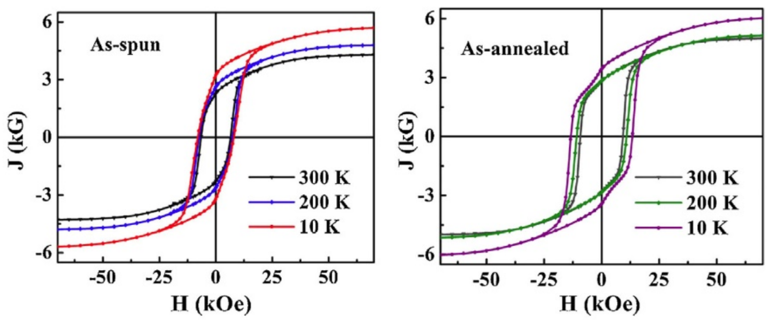

Figure 4. Hysteresis loops at different temperatures of the as-spun (a) and as-annealed (b) ribbons.

Figure 5 shows the initial magnetization curves for the as-spun and annealed ribbons, and maximum applied field dependence of the coercivity. For the two samples, the magnetization and coercivity increase slowly until the applied field exceeds a critical value. The saturation of the magnetization and coercivity is completed at fields much higher than the saturated coercivity. A change of slope indicated by the yellow arrows appears in the initial magnetization and ${}_iH_c(H)$ curves. This suggests that domain walls cannot move freely, and coercivity is mainly governed by the pinning of domain walls. The defects in the samples may act as the source of domain-wall pinning. Defects including dislocation, grain boundary, and stacking faults usually exist in the Zr–Co alloys.[16] Generally, dislocation defects and grain boundary may act as the nucleation center of reversed domain and decrease the coercivity. Stacking faults may act as the pinning center and increase the coercivity. Annealing deleted the dislocation defects, largely decreased the area of grain boundary, and increased the coercivity. Simultaneously, annealing decreased the density of the stacking fault and decreased the coercivity. Competing of two effects finally leads to the increase of the coercivity in the as-annealed ribbons.

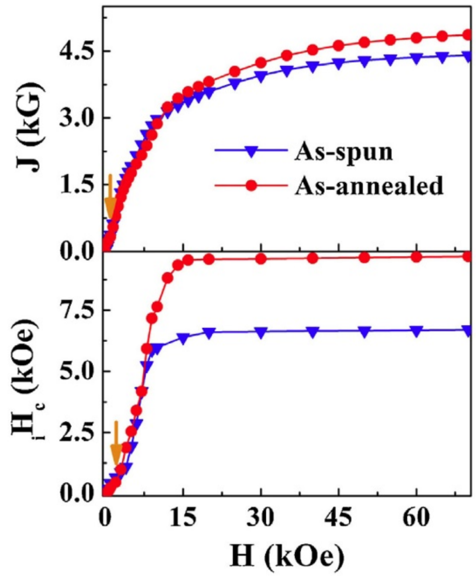

Figure 5. The initial magnetization curves of the as-spun and as-annealed ribbons and applied field dependence of coercivity.

4. Conclusions

The effect of annealing condition on nanostructure and magnetic properties of $Zr_{16}Co_{74}Mo_4Si_3B_3$ spun at 16 m/s has been investigated. Annealing did not change the phase components. Annealing leads to the appearance of the recrystallization, which coarsens the grains and decreases structural disorder such as planar defects. Thus the magnetocrystalline anisotropy field and coercivity were significantly enhanced. The highest coercivity of 9.7 kOe, which is about 9 times larger than that of alnico, was achieved for the ribbon annealed at 600°C for 90 min. The annealed sample exhibits a strong temperature dependence of coercivity. The above results indicate that Zr_2Co_{11} is an alternative hard magnetic phase for synthesizing rare-earth-free nanocomposite permanent magnets.

Acknowledgments – This work is supported by Department of Energy/BREM (DE-AC02-07CH11358, Subaward No. SC-10-343). The work was carried out in part in the Central Facilities of the Nebraska Center for Materials and Nanoscience, which is supported by the Nebraska Research Initiative.

Appendix A. Prime novelty statement

Annealing was found not only to enhance coercivity but also to increase saturation magnetization. The microstructure origin leading to magnetic property enhancement was investigated. A record value (9.7 kOe) of coercivity for Zr–Co alloys has been achieved in the annealed rare-earth-free $Zr_2(Co,Mo,Si,B)_{11}$.

References

[1] T. Ishikawa, K. Ohmori, *IEEE Transactions on Magnetics* 26 (1990) 1370.

[2] E. Burzo, R. Grössinger, P. Hundegger, H. R. Kirchmayr, R. Krewenka, R. Lemaire, *Journal of Applied Physics* 70 (1991) 6550.

[3] H. H. Stadelmaier, T. S. Jang, E. Th. Henig, *Materials Letters* 12 (1991) 295.

[4] G. V. Ivanova, N. N. Shchegoleva, A. M. Gabay, *Journal of Alloys and Compounds* 432 (2007) 135.

[5] B. G. Demczyk, S. F. Cheng, *Journal of Applied Crystallography* 24 (1991) 1023.

[6] E. Burzo, R. Grössinger, P. Hundegger, H. R. Kirchmayr, R. Krewenka, O. Mayerhofer, R. Lemaire, *Journal of Applied Physics* 70 (1991) 6550.

[7] W. Y. Zhang, X. Z. Li, S. Valloppilly, R. Skomski, J. E. Shield, D. J. Sellmyer, *Journal of Physics D: Applied Physics* 46 (2013) 135004.

[8] T. Saito, *Applied Physics Letters* 82 (2003) 2305.

[9] A. M. Gabay, N. N. Shchegoleva, V. S. Gaviko, G. V. Ivanova, *Physics of Metals and Metallography* 95 (2003) 122.

[10] W. Y. Zhang, S. Valloppilly, X. Z. Li, Y. Liu, S. Michalski, T. A. George, R. Skomski, D. J. Sellmyer, *Journal of Alloys and Compounds* 587 (2014) 578.

[11] C. Gao, H. Wan, G. C. Hadjipanayis, *Journal of Applied Physics* 67 (1990) 4960.

[12] W. Y. Zhang, S. R. Valloppilly, X. Z. Li, R. Skomski, J. E. Shield, D. J. Sellmyer, *IEEE Transactions on Magnetics* 48 (2012) 3603.

[13] H. H. Stadelmaier, et al., *Materials Letters* 12 (1991) 295.

[14] R. D. Doherty, D. A. Hughes, F. J. Humphreys, J. J. Johas, D. Juul Jensen, M. E. Kassner, W. E. King, T. R. McNelley, H. J. McQueen, A. D. Rollett, *Materials Science and Engineering A* 238 (1997) 219.

[15] I. Samajdar, B. Verlinden, P. Van Houtte, *Acta Materialia* 46 (1998) 2751.

[16] A. M. Gabay, Y. Zhang, G. C. Hadjipanayis, *Journal of Magnetism and Magnetic Materials* 236 (2001) 37.

[17] G. C. Hadjipanayis, D. J. Sellmyer, B. Brandt, *Physical Review B: Condensed Matter* 23 (1981) 3349.