Magnetism and magnetocaloric effect of melt-spun, nanostructured GdAl2

Mitali Madhusmita Prusty1, J Arout Chelvane2 and R Nirmala1

1 Department of Physics, Indian Institute of Technology Madras, Chennai 600 036, India
2 Defence Metallurgical Research Laboratory, Hyderabad 500 058, India
E-mail: nirmala@physics.iitm.ac.in

Keywords: magnetic properties, magnetocaloric effect, rare earth intermetallics, melt-spinning

Abstract
Magnetocaloric effect (MCE) of melt-spun rare earth intermetallic compound GdAl2 (Cubic, MgCu2-type) has been studied. The sample becomes nanostructured upon melt-spinning and the crystallite size obtained from the powder x-ray diffraction data is about 48 nm. A sluggish paramagnetic to ferromagnetic transition occurs at a Curie temperature ($T_C$) of about 136 K. This value is about 30 K lower than the ferromagnetic transition temperature of the arc-melted GdAl2. The maximum isothermal magnetic entropy change ($\Delta S_m$) is found to be $\sim -8.3 \text{ J kg}^{-1} \text{ K}^{-1}$ at 133 K for 70 kOe field change around $T_C$. This value is quite comparable to that of bulk sample prepared by arc-melting which is about $-8.5 \text{ J kg}^{-1} \text{ K}^{-1}$ at 168 K for the same field change. Thus melt-spinning process results in broadening of the peak in the isothermal magnetic entropy change versus temperature plot without compromising on the magnetocaloric effect.

Introduction
Melt-spinning is a non-equilibrium synthesis process and is generally used to stabilize metastable phases. Also this technique is known to yield highly crystalline rare earth based giant magnetocaloric materials with improved magnetic properties [1–3]. Laves phase intermetallic compounds RaAl2 (R = heavy rare earth) are considered as model systems to understand the role of various magnetic interactions including indirect Rudermann-Kittel-Kasuya-Yoshida (RKKY) exchange, crystalline electric fields, magnetoelastic interactions and magnetocrystalline anisotropy [4]. These compounds exhibit large magnetocaloric effect near their ferromagnetic ordering temperatures [3]. Recent studies on melt-spun rare earth intermetallic compounds such as RNi, RNi2, and RCu2 [6–8] have revealed micro-granularity and preferred orientation while polycrystalline nature of the samples was preserved. Most importantly, the melt-spun samples displayed comparable magnetocaloric effect with the corresponding arc-melted samples. Since the melt-spun samples are expected to show superior heat transfer properties over the arc-melted analogues, studies on magnetocaloric materials in melt-spin form assume importance. In the present work, the rare earth dialuminide GdAl2 has been prepared by melt-spinning technique and characterized. A nanostructured sample is obtained and it shows a slow paramagnetic to ferromagnetic transition. However, substantial isothermal magnetic entropy change values are obtained near the transition in melt-spun GdAl2 and these are comparable to that of the arc-melted GdAl2.

Experimental details
Polycrystalline GdAl2 has been prepared by arc-melting starting from stoichiometric amounts of pure elements [Gd (3N pure), Al (4N pure), Goodfellow, UK] under Ar atmosphere. The sample was remelted four times for better homogeneity. The mass loss after melting was less than 0.5%. The arc-melted ingot was used for...
melt-spinning in the same inert atmosphere. The linear speed of the copper wheel used for melt-spinning is \( \sim 17 \text{ m s}^{-1} \). The melt-spun samples were studied as-prepared, without any further heat treatment. The samples were characterized by powder x-ray diffraction (XRD) (Rigaku, CuK\(_\alpha\) radiation, \( \lambda = 1.5406 \) Å), scanning electron microscopy and energy dispersive x-ray analysis (SEM-EDAX) (FEI Inspect) and high-resolution transmission electron microscopy (HRTEM) (Tecnai G2 T20). DC magnetization data have been collected using a commercial SQUID magnetometer (MPMS, Quantum Design) and a SQUID based vibrating sample magnetometer (MPMS 3, Quantum Design) in the temperature range of 5 K to 300 K in applied magnetic fields up to 70 kOe.

**Results and discussion**

Powder XRD data obtained at room temperature confirm the single phase formation (cubic, \( Fd-3m \)) and the peaks match well with those of the crystallographic information file \# 19923 (figure 1). The broadening of XRD peaks suggests nanoparticle formation upon melt-spinning. The average crystallite size estimated using Scherrer formula is \( \sim 48 \) nm. The EDAX results confirm the sample composition is indeed 1:2 and the SEM micrograph indicates the presence of nanograins (figure 2(a)). The HRTEM image shows agglomerated nanoparticles which are polycrystalline in nature (figure 2(b)).

Magnetization data obtained in the temperature range of 300 K to 5 K indicate progressive transformation from a paramagnetic to a ferromagnetically ordered state at around 136 K (\( T_C \)) (figure 3(a)). It must be noted that the arc-melted, bulk GdAl\(_2\) sample orders ferromagnetically at 167 K through a second order transition \([5, 9]\). Although a small hysteresis is observed between the zero-field-cooled and field-cooled magnetization data measured in 100 Oe field, well below \( T_C \), there is no such irreversibility in the data obtained in 5 kOe field. The sluggish nature of the magnetic transition is attributed to the nanostructuring of the sample. Because the particle sizes could limit the long-range magnetic exchange interactions and also there is a non-negligible role played by disorder in the nanoparticle samples.

The paramagnetic susceptibility is fitted to the Curie-Weiss law. From the fit, the paramagnetic Curie temperature (\( \theta_p \)) and the effective paramagnetic moment values are obtained as \(+149 \) K and 8 \( \mu_B/\text{f.u.} \) respectively. The magnetization versus field measured at 5 K does reveal the soft ferromagnetic nature of the sample (figure 3(b)). The hysteresis is negligible and the saturation magnetization (\( M_s \)) value at 5 K is about 7.5 \( \mu_B/\text{f.u.} \). The \( M_s \) value is comparable to that of the arc-melted sample. This indicates that the size induced disorder is negligible in the melt-spun sample and the broadening of magnetic transition may be due to the distribution of particle sizes. However, particle size distribution could not be ascertained because the particles observed in HRTEM images are agglomerated (figure 2(b)). Broadening of the phase transition temperature due to a non-uniform size distribution of nanoparticles has been studied in detail, in order to optimize the performance of particulate matter in various applications \([10, 11]\).
The isothermal magnetic entropy change ($\Delta S_m$) has been computed using the magnetization versus field data measured around $T_c$ (figure 4(a)). For this, the following expression obtained from thermodynamic Maxwell relation has been used.
Figure 3. (a) Magnetization versus temperature of the melt-spun GdAl2 in 5 kOe field measured during zero-field-cooled (ZFC), field-cooled cooling (FCC) and field-cooled-warming (FCW) states and (b) magnetization versus magnetic field data at 5 K.

Figure 4. (a) Magnetization-field isotherms of the melt-spun GdAl2 sample in the temperature range of 70 K – 180 K in fields up to 70 kOe and (b) isothermal magnetic entropy change ($\Delta S_m$) versus temperature for various magnetic field changes.
Figure 5. Magnetization-field isotherms of the arc melted GdAl$_2$ sample in the temperature range of 140 K–195 K in fields up to 70 kOe and (b) isothermal magnetic entropy change ($\Delta S_m$) versus temperature for various magnetic field changes.

Figure 6. Field dependence of maximum value of isothermal magnetic entropy change ($\Delta S_m^{\text{max}}$) of melt-spun GdAl$_2$ at 133 K and the power law fit ($\Delta S_m^{\text{max}} \propto \Delta H^n$) with $n = 0.95$. 

Mater. Res. Express 7 (2020) 064001 M M Prusty et al
Here, $H_i$ and $H_f$ are the initial and final applied magnetic fields and $\mu_0$ is the permeability of free space [12]. The maximum value of $\Delta S_m$ for 70 kOe field change at 133 K is about $-8.3$ J kg$^{-1}$ K$^{-1}$ (figure 4(b)). This value is almost equal that in the arc-melted GdAl$_2$ near its $T_C$ i.e. $-8.5$ J kg$^{-1}$ K$^{-1}$ at 168 K for 70 kOe field change (figure 5) and these numbers are comparable to those obtained in the previous studies [5, 9]. The broad maximum in the isothermal magnetic entropy change versus temperature plot is in accordance with the slow increase of magnetization with the decrease of temperature.

The magnetic field dependence of magnetocaloric effect is studied by fitting the maximum isothermal magnetic entropy change values for a given field change ($\Delta H$) to a power law i.e. $\Delta S_{m_{\text{max}}} \propto \Delta H^n$ (figure 6). The value of ‘n’ is found to be 0.95 for the melt-spun GdAl$_2$ sample at 133 K. A value of $n = 2/3$ is expected for a mean-field ferromagnet [13] and the same is observed near $T_C$ of the arc-melted GdAl$_2$ sample (figure 7). The small deviation of the exponent from the mean-field value in the melt-spun GdAl$_2$ suggests the role of disorder in the nanostructured sample. Such deviations have been observed earlier in the melt-spun FePd alloy and some rare earth based bulk metallic glasses [14, 15].

Previous studies on ball-milled GdAl$_2$ of much smaller size show a disorder broadened magnetic entropy change spread over a broad range of temperatures [16]. In fact, longtime mechanical milling of GdAl$_2$ has resulted in atomically disordered nanostructured sample that demonstrated a spin glass-like behaviour [17, 18]. However, melt-spinning method with wheel speed of 17 m s$^{-1}$ seems to yield crystalline rare earth intermetallic GdAl$_2$ nanoparticles without compromising much on the ferromagnetism and the associated magnetocaloric effect.

Conclusions

Melt-spun GdAl$_2$ (cubic, $Fd-3m$) is found to be crystalline, single phase and nanostructured. The ferromagnetic ordering temperature is about 136 K and this value is about 30 K lower than that of the corresponding arc-melted bulk sample. Using magnetization versus field data, magnetocaloric effect has been estimated. The maximum value of $\Delta S_m$ is found to be about $-8.3$ J kg$^{-1}$ K$^{-1}$ at 133 K for 70 kOe field change and it is nearly equal to that in the bulk, arc-melted sample.

Acknowledgments

Authors thank B Akshay Kumar for the help with HRTEM imaging and Prof A K Nigam, TIFR for helping us to record a few field-dependent magnetization data.
ORCID iDs

J Arout Chelvane  https://orcid.org/0000-0002-5106-7059
R Nirmala  https://orcid.org/0000-0001-6292-8769

References

[1] Yan A, Müller K-H and Gutleisch O 2005 J. Appl. Phys. 97 036102
[2] Lyubina J, Schäfer R, Martin N, Schultz L and Gutleisch O 2010 Adv. Mater. 22 3735 and references therein
[3] Bež H N, Pathak A K, Biswas A, Zarkevich N, Balema V, Mudryk Y, Johnson D D and Pecharsky V K 2019 Acta Mater. 173 225
[4] Purwins H and Leson A 1990 Adv. Phys. 39 309
[5] Tishin A M and Spichkin V I 2003 The Magnetocaloric Effect and its Applications (Bristol: Institute of Physics Publishing)
[6] Rajivgandhi R, Arout Chelvane J, Quezado S, Malik S K and Nirmala R 2017 J. Magn. Magn. Mater. 433 169
[7] Ibarra-Gaytan P J, Sánchez-Valdes C F, Sánchez Llamazaures J L, Álvarez-Alonso P, Gorria P and Blanco J A 2013 Appl. Phys. Lett. 103 152401
[8] Rajivgandhi R, Arout Chelvane J, Nigam A K, Malik S K and Nirmala R 2020 J. Alloys Compd. 815 152659
[9] Tishin A M 1999 Handbook of Magnetic Materials 12 (The Netherlands: Elsevier)
[10] Waters J, Berger A, Kramer D, Fangohr H and Hovorka O 2017 J. Phys. D: Appl. Phys. 50 35LT01
[11] Amaral J S and Amaral V S 2014 Phys. Status Solidi A 211 971
[12] Pecharsky V K and Gschneidner K A Jr 1999 J. Magn. Magn. Mater. 200 44
[13] Franco V, Blázquez J S and Condea A 2006 Appl. Phys. Lett. 89 222512
[14] Prida V M, Franco V, Vega V, Sánchez Llamazaures J L, Suñol J J, Conde A and Hernando B 2011 J. Alloys Compd. 509 190
[15] Luo Q and Wang W H 2010 J. Alloys Compd. 495 209
[16] de Paula V G, da Silva L M, dos Santos A O, Lang R, Otubo L, Coelho A A and Cardoso I P 2016 Phys. Rev. B 93 094427
[17] Zhou G F and Bakker H 1994 Phys. Rev. Lett. 73 344
[18] Zhou G F and Bakker H 1995 Phys. Rev. B 52 9437