Formation mechanisms of NaZn₁₃-type phase in giant magnetocaloric La-Fe-Si compounds during rapid solidification and annealing

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The promise of the La-Fe-Si alloys for energy efficient magnetic refrigeration devices stems from a strong magneto-structural transition in the La(Fe,Si)₁₃ (1:13) phase near room temperature. The formation of the 1:13 phase during rapid solidification was compared in detailed microstructural studies of the wheel-side and free-side surfaces of melt-spun ribbons. On the free-side, clusters of similarly-oriented crystallites are observed; chemical segregation of La, Fe, and Si leads to a nanoscale texturing of α -Fe and LaFeSi. In contrast, equiaxed 1:13 grains ~100 – 400 nm form the microstructure of the wheel-side surface, with a minor α -Fe phase precipitated in the matrix. Upon annealing, the 1:13 phase grows via dissolution of the α -Fe phase on the wheel side and a peritectoid reaction from the free side. For longer annealing times, the completion of the peritectoid reaction improves the magnetic entropy change under a magnetic field change of 1.5 T from 12 J/kg K (2 min) to 17 J/kg K (2 h), and increases the Curie temperature of the ribbons from 189 K to 201 K.

Keywords: La-Fe-Si, NaZn₁₃-type phase, Microstructure, Rapid solidification, Annealing

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1. Introduction

A sustainable solution to the problem of limited fossil fuel resources in the face of growing global energy demands must involve not only increased adoption of renewable sources of energy, but improvements in the efficiency of end-use devices and applications. In developed countries such as the United States, refrigeration accounts for 7% of total energy use in the commercial sector and 5% in the residential sector [1]. Conventional refrigerators involve volatile organic compounds (VOCs) and ozone-depleting gases in a vapor compression cycle. In recent years magnetic refrigeration based on the magnetocaloric effect (MCE) has become a promising alternative technology due to greater efficiencies than conventional refrigerators and environmentally friendly components [2-4].

The MCE refers to the heating or cooling of magnetic materials subject to a varying magnetic field. In the last decade, compounds with a large MCE have attracted a great deal of interest due to their potential applications in refrigeration devices [5-10]. Giant magnetocaloric effects have been identified near first-order magneto-structural or magneto-elastic transitions in materials such as $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ [8], MnAs-based compounds [11], $(\text{Mn,Fe})_2(\text{P,As,Ge})$ [8,10], and $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ [12-14]. The La-Fe-Si systems with a cubic NaZn_{13} -type (Fm3-c) structure are among the most promising candidates for magnetic refrigeration due to cheap and non-toxic constituents, giant MCE, small thermal/magnetic hysteresis, large relative cooling power, and high thermal conductivity [10, 15-18]. Consequently, $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ is regarded as a favorable refrigerant material for state-of-the-art magnetic cooling technology, and a number of works have explored fabrication and processing routes to optimize material properties for device applications [17-19].

The binary phase LaFe_{13} does not form because of positive enthalpy between La and Fe. However, the NaZn_{13} -type structure can be stabilized by substituting a small amount ($1.0 \leq x \leq 1.6$) of Si on the Fe site, forming $\text{LaFe}_{13-x}\text{Si}_x$. This stable 1:13 phase undergoes a first order magneto-structural transition accompanied by a typical itinerant electron meta-magnetic transition and a large volume change in the vicinity of its Curie temperature T_C [12,13,20,21]. These characteristics contribute to a giant magnetocaloric effect in $\text{La}(\text{FeSi})_{13}$. Under equilibrium solidification conditions, many reports using conventional melting techniques (e.g. arc melting or induction melting) have found that the 1:13 phase does not form directly from the melt upon cooling, but rather forms during subsequent heat treatments via a peritectoid reaction between an α -Fe and a La-rich phase [22,23]. As-cast La-Fe-Si alloys show a biphasic structure consisting of α -Fe (A2: $\text{Im}3\text{m}$) and La-Fe-Si (Cu_2Sb -type: P4/nmm); a single 1:13 phase is difficult to obtain because of its low stability at elevated temperatures and low atomic diffusivity [24]. To eliminate undesired minority phases in arc-melted ingots, the ingots must be annealed under vacuum at high temperature for an extended period of time (~ 1323 K, 30 days) [25,26]. Melt-spinning is an alternative and efficient route to producing the desired phase with minimal annealing time, as the formation of the 1:13 phase can significantly accelerate in the rapid solidification process or peritectoid reaction [27, 28]. In addition to a drastic reduction of fabrication time, melt-spinning of La-Fe-Si has been found to increase the Curie temperature while decreasing magnetic and thermal hysteresis [13,20,29]. Melt-spun $\text{La}(\text{FeSi})_{13}$ hot-compacted into a porous morphology is more tolerant of the large magneto-elastic effects at the first order transition than the

polycrystalline bulk material, extending the lifetime of the refrigerant which is subject to continuous field cycling during operation [19].

Despite its technological significance, a detailed knowledge of the formation mechanism and growth of the 1:13 phase in melt-spun La-Fe-Si alloys is lacking. These properties are closely related to the microstructure and solidification path. During the melt-spinning process, areas of the melt in direct contact with the wheel solidify most rapidly, and a gradient in the cooling rate exists across the thickness of the melt. As a result, structural inhomogeneities such as chemical segregation, **non-uniform distributions of crystal nucleation**, and varying degrees of structural relaxation are found in the solidified ribbon [30-32]. The non-uniform structure lowers the threshold temperature for crystallization in certain parts of the ribbon, and the final crystal microstructure and size varies throughout the material.

In this work, $\text{LaFe}_{11.5}\text{Si}_{1.5}$ melt-spun ribbons were prepared and studied via X-ray diffraction (XRD), scanning electron microscopy (SEM) and transition electron microscopy (TEM) in the as-spun state and after annealing for different times. The phase formation and microstructure of the ribbons were observed on the surface far from the copper wheel during solidification (Side 1) and on the surface in contact with the wheel (Side 2) (See Fig. 1). A strikingly different phase makeup was found between Side 1, where no 1:13 phase is present in the as-spun state, and Side 2, on which 1:13 is the majority phase. The microstructure also evolves along the thickness of the ribbon, with small equiaxed grains formed on Side 2 giving way to larger clusters of similarly oriented grains away from the wheel on Side 1. The contrast in as-quenched microstructure results in distinct formation mechanisms and speeds for

the 1:13 phase from the two surfaces upon subsequent annealing at 1273 K. After annealing for 2 h, the peritectoid reaction is complete and the 1:13 phase forms the majority of the ribbon.

2. Experimental Section

Ingots with a nominal composition of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ were fabricated by arc melting in an argon gas atmosphere. The ingots were re-melted four times and each time the ingot was turned over to obtain a homogeneous composition. The ingots were melt-spun into ribbons using a rotating copper wheel with a surface speed of 35 m/s. In order to prevent oxidation, the ribbons were sealed in quartz tubes under a high vacuum. The as-spun ribbons were annealed at 1273 K for 2 min and 2 h, respectively, then quenched to room temperature in cool water.

The phases and crystal structures of the materials were characterized by powder X-ray diffraction (XRD) using $\text{Cu-K}\alpha$ radiation. The microstructural analysis was carried out by scanning electron microscope (SEM) with an energy dispersive spectrometer (EDS) attached, model JSM-6700 F, and transmission electron microscope (TEM), model JEM-2010 F. The TEM specimen was prepared by dual-beam focused ion beam (FIB) on a model 600 i. Magnetic measurements were performed using a vibrating sample magnetometer (VSM, Lakeshore 7407) with a maximum magnetic field of 1.5 T. The T_C of all samples was determined from the peak value in $dM(T)/dT$, based on $M(T)$ curves measured in an applied magnetic field of 0.1 T.

3. Results and Discussion

3.1. XRD and SEM studies of structure and microstructure

The room-temperature XRD patterns for the two ribbon surfaces (Side 1 and Side 2) after rapid solidification, and for ribbon pieces ground into a powder are shown in Fig. 2. Using Jade 5.0 software, the major phase in the XRD pattern of Side 1 is identified as α -Fe, with a minority LaFeSi phase (hereafter referred to as 1:1:1). But for Side 2, in contact with the copper wheel, a large amount of the 1:13 phase was identified in addition to α -Fe and a minor 1:1:1 phase. This indicates that the rapid solidification process favors the direct formation of the 1:13 phase from the liquid melt of La-Fe-Si [12]. Under equilibrium solidification conditions, the 1:13 phase is formed by a peritectic reaction process between nascent α -Fe and liquid (L) phase ($1:13 \rightarrow \alpha\text{-Fe} + \text{L}$). However, the nucleation mechanisms involved in rapid solidification are entirely different from equilibrium solidification processes. The cooling rates of the melt are a significant factor in the nucleation rates of each phase during rapid solidification. Based on the XRD results, the nucleation rate of the 1:13 phase on Side 2 is significantly greater than that of Side 1 during competitive nucleation between the 1:13 and α -Fe phases, correlating with the faster cooling rate on Side 2 due to direct contact with the wheel.

In the XRD patterns of the annealed ribbons, the intensity of the α -Fe peaks are greatly reduced when the annealing time is increased from 2 min to 2 h. As the α -Fe contribution is diminished, the diffraction peaks corresponding to the cubic 1:13 phase become stronger. When the annealing time reaches 2 h, the 1:13 phase becomes dominant and α -Fe appears as a small minority phase in the XRD patterns. A similar peritectic solidification process is known to occur in other alloys, such as Ni-B, Nd-Fe-B and Fe-Ni [33-35]. Away from the wheel (Side 1), the as-spun ribbon appears smooth and uniform in SEM micrographs (Fig. 3a).

Some indistinct clusters of grains are visible, indicated by an arrow, formed due to similar growth orientation during rapid solidification. The ribbon surface in contact with the wheel (Side 2) is much rougher in comparison (Fig. 3d). Deep stripes with irregular grooves can be seen (arrow, Fig. 3d), caused by gas pockets introduced as the melt is spun against the surface of the copper wheel. By altering the local cooling rates during rapid solidification, these gas pockets affect the final microstructure of Side 2. Regions in the immediate vicinity of pockets will have a coarser microstructure than the rest of the ribbon. These observations are very similar to those of Ref. 36 for a $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ nanocomposite formed by melt-spinning and other alloy solidification processes [37-39].

After annealing the ribbons at 1273 K for 2 min, a few areas of a precipitate phase (white contrast, Fig. 3b and Fig. 3e) appeared on each side. On Side 2 the precipitation occurred near the gas pockets in the ribbon surface (Fig. 3e). When the annealing time was increased to 2 h, the density of spherical precipitates was greatly increased (Fig. 3c and Fig. 3f). Energy dispersive X-ray spectroscopy (EDS) analysis (See Supplemental Information) identified these white regions as a La-rich oxide phase. Elemental La accumulates preferentially at grain boundaries during rapid solidification, rendering these areas highly susceptible to oxidation during heat treatment. As the result of poor bonding between the oxide and matrix, the La oxide phase can easily fall away from the surface of the ribbon. Residual pits that formed around the oxide spheres as the sample cooled can be seen in Fig. 3c and Fig. 3e (black arrows). The number of the empty pits is higher on Side 2 than on Side 1. In addition to the precipitate, lathe-like substructures are also observed within the cluster grains in Fig. 3c (black dotted line), the emergence of which is attributed to self-adjusting reorientation of

grains during growth at 1273 K. In Fig. 3f, inhomogeneous regions of microstructure indicated by a dotted line appear on Side 2 after the 2 h annealing process, originating from gas pockets on the wheel-side surface.

3.2. TEM observations of NaZn₁₃-type phase formation

3.2.1 As-spun ribbons

Figure 4 presents the high angle annular dark field (HAADF) TEM micrographs of Side 1. It is clear that grain clustering occurred during the rapid solidification stage. The boundaries of the grain clusters are marked by dashed lines in Fig. 4a; an expanded view of the cluster boundary region encompassed by the white box in Fig. 4a is shown in Fig. 4b. The internal region of a cluster was also examined at higher magnification (Fig. 4c), revealing alternating nanoscale regions of dark and light contrast. To understand this observation, line scan EDS-TEM analysis was performed for the circular region marked in Fig. 4a. From the results, (Fig. 4d and Fig. 4e) it can be seen that the elemental composition of La, Fe and Si varies periodically along the line scan. The dark regions (e.g. positions 2 and 3) correspond to peaks in the Fe content and minima in both La and Si, while the light regions (e.g. position 1) correspond to maxima in La and Si content and a minimum in Fe. At position 1, the composition is consistent with the 1:1:1 phase. Recalling the phases identified in the XRD patterns of Fig. 2c, the adjacent Fe-rich regions (positions 2 and 3) can be assigned to the majority α -Fe phase. This observed nanoscale alternating arrangement of α -Fe and 1:1:1 phases on Side 1 is beneficial in promoting the peritectoid reaction that forms the 1:13 phase upon annealing.

The TEM micrograph of Side 2 of the ribbon is shown in Fig. 5a, and with increased

magnification in Fig. 5b and Fig. 5c. The global microstructure of equiaxed crystals is a very typical morphology in rapidly solidified materials. However, it can be seen that in addition to the equiaxed crystal matrix with a characteristic size of $\sim 100 \text{ nm} - 400 \text{ nm}$, a number of fine spherical precipitates ($\sim 20 \text{ nm} - 100 \text{ nm}$) with darker contrast are present. Several representative regions are labeled in Fig. 5c for high-resolution imaging. The HRTEM micrographs and corresponding Fourier transforms for areas A – part of the equiaxed crystal matrix, and B – a large dark precipitate region, are shown in Fig. 5d and Fig. 5e, respectively. The transformed micrograph of the matrix (A) can be indexed to the structure of the 1:13 phase with a composition of 8.84 at. % La, 77.9 at. % Fe, and 13.26 at. % Si determined by EDS analysis. The precipitate (B) can be indexed to the α -Fe phase with chemical composition of ~ 97.26 at. % Fe and 2.74 at. % Si. Similar analysis (Fig. 5f) also identified region 1, a smaller spherical precipitate within A, as α -Fe with a chemical composition of ~ 95.07 at. % Fe and 4.93 at. % Si. Finally, HRTEM near the well-defined border (region 2) of a precipitated sphere within a crystal neighboring A confirmed the crystal matrix to be the 1:13 phase, with α -Fe as the precipitated phase (Fig. 5g). Results of EDS analysis on the precipitated areas (Fig. 5e - Fig. 5g) yield an elemental composition of ~ 95 -98 at.% Fe and ~ 2 -5 at.% Si, consistent with the α -(Fe,Si) phase identified by HRTEM. These observations of a majority 1:13 phase with a small amount of secondary α -Fe are in good agreement with the XRD patterns for Side 2 of the as-spun ribbon in Fig. 2b.

3.2.2 Annealed ribbons

The microstructure and phase compositions of Side 1 and Side 2 after annealing were investigated using TEM and HRTEM. From Fig. 6, it is clear that annealing at 1273 K for 2 min has a strong effect on the microstructure. On Side 1, large areas of the nanoscale phase texturing observed in Fig. 4 were replaced by a homogeneous phase during annealing, in a peritectoid reaction between the α -Fe and 1:1:1 phases. Two types of interface transition zone between the reacted and unreacted phases can be distinguished in the annealed ribbons, one curved (Fig. 6a, arrows) and the other straight (Fig. 6a, dotted line). In selected area electron diffraction (SAED) patterns of the curved interface, two groups of diffraction spots (Fig. 6a, inset) confirm that crystallites of the 1:13 and α -Fe phases were mixed, with zone axes of [001] and $[\bar{1}\bar{2}3]$, respectively. The HRTEM micrograph and FFT pattern of region M are shown in Fig. 6c. A single 1:13 phase was identified, indicating a perfect peritectoid reaction. Near a straight interface (region N), a further HRTEM micrograph effectively illustrates the transition from a completed peritectoid reaction in location 1 to an imperfect reaction in location 2 to unreacted material in location 3 (Fig. 6e). Comparison of regions M, N, and O demonstrates that a straight interface transition zone includes three types of phase structure: 1:13, 1:1:1, and α -Fe, with zone axes of [001], $[11\bar{1}]$, and $[\bar{1}01]$, respectively. With sufficient heat treatment time, the peritectoid reaction will continue, eventually converting region O to a perfect 1:13 phase.

On Side 2, an annealing time of 2 min is too short to allow a peritectoid reaction to occur. Instead the effects of annealing are grain growth and increased homogeneity of the pre-existing 1:13 phase as the α -Fe phase and 1:1:1 phase dissolve into the crystal structure of the 1:13. In the process of dissolution, the α -Fe phase becomes spheroidal while the 1:1:1

phase assumes irregular elongated shapes due to more favorable infiltration between the 1:1:1 and 1:13 phases than between α -Fe and the 1:13 phase. EDS line scans along A and B in Fig. 6b show that the 1:1:1 phase is distributed in the grain boundaries of the 1:13 phase while the α -Fe is located within the grains. We observe that the boundaries between the 1:1:1 and 1:13 phases are quite straight, implying some orientation relationship between the phases, the nature of which will be explored in future work. Comparing the results from Side 1 and Side 2, it is clear that the development of the 1:13 phase proceeds according to different mechanisms in these locations at short annealing times.

We recall that the XRD patterns of each side of the ribbon showed a majority 1:13 phase with residual α -Fe after annealing for 2 h at 1273 K. Fig. 7 presents TEM micrographs of Side 1 (Fig. 7a) and Side 2 (Fig. 7b) of the ribbon after annealing at 1273 K for 2 h. On Side 1, the grain size is close to that of the grain clusters in the as-spun sample in Fig. 4a. This observation is consistent with a peritectoid reaction originating in the interior of the grain clusters, and subsequently growing toward the cluster boundary. The final grain boundaries in Fig. 7a form at the inter-cluster boundaries, and thus the cluster size of the as-spun ribbon determines the final grain size of the matrix. On Side 2, the ribbons exhibit uniform microstructures with a grain size of $\sim 0.5 \mu\text{m} - 1\mu\text{m}$. The grains are characterized by equiaxed crystals of the 1:13 phase, with no precipitate visible in the matrix (Fig. 7b). However on Side 1, a number of darker contrast particles are found within the 1:13 grains. By EDS analysis, the chemical composition of the matrix (region C) is consistent with the 1:13 phase (7.97 at. % La, 83.77 at. % Fe and 8.26 at. % Si), while black particle D is composed of α -Fe (3.79 at. % La, 93.06 at. % Fe and 3.15 at. % Si). Grey particle E was identified as a

La-rich phase with 37.74 at. % La, 55.51 at. % Fe and 6.75 at. % Si. The α -Fe and La-rich residual phases within the 1:13 matrix indicate that the peritectoid reaction is incomplete on Side 1 even after 2 h of annealing.

3.3 Magnetic properties

The magnetic properties of La-Fe-Si alloys are closely tied to phase coexistence and microstructure. As shown in Fig. 8a, the T_C of LaFe_{11.5}Si_{1.5} melt-spun ribbons increased from 189 K to 201 K as annealing time increased from 2 min to 2 h. The driving force behind the shift in T_C is the dissolution of more Fe and Si in the 1:13 matrix by solid diffusion or peritectoid reaction during the longer heat treatment. Compared to the sample annealed for 2 h, the decline of magnetic moment above T_C is more sluggish for the sample annealed for 2 min, and its isothermal magnetization curves in the vicinity of T_C show less magnetic hysteresis. The magnetic hysteresis loss, defined as the enclosed area between the ascending and descending branches of magnetization curve, is related to the strength of a first-order magnetic transition.^[40] The broader transition in the $M(T)$ curves and the reduction of the first-order signature in the $M(H)$ curves can be attributed to the large amount of secondary phases present in the sample annealed for 2 min, identified in the previous sections as α -Fe and the 1:1:1 phase.

The magnetic entropy change $\Delta S_M(T, H)$ for the annealed ribbons was calculated from isothermal magnetization curves in the vicinity of the T_C using the thermodynamic Maxwell relation, [2,5]

$$\Delta S_M(T, H) = \mu_0 \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH. \quad (1)$$

For an applied magnetic field change of 1.5 T, the maximum values of $-\Delta S_M(T, H)$ are 12 J/kg K and 17 J/kg K near T_C for the ribbons annealed for 2 min and 2 h, respectively (Fig. 8d). The refrigerant capacity (RC) is a figure of merit in magnetic refrigeration materials representing the amount of heat that can be transferred between the hot and cold ends of a thermodynamic cycle, and is directly related to both the peak height and full-width at half maximum (FWHM) of the $-\Delta S_M(T)$ curve. The RC is calculated for the ribbons by integrating the $-\Delta S_M(T)$ peaks between the FWHM temperatures (inset, Fig. 8d). In the 2 min sample, the RC remains lower than in the 2 h sample across the field range investigated. This can be attributed to the fact that the peak $-\Delta S_M$ value is lower in the 2 min sample while the widths of the $-\Delta S_M(T)$ peaks are comparable in both samples.

The re-scaled magnetization curves of the ribbons annealed for 2 min and 2 h are shown in Fig. 9a and Fig. 9b, respectively. According to the Banerjee criterion, negative slopes in the curves of H/M vs. M^2 plots indicate the presence of a first-order magnetic transition [41]. This criterion is clearly satisfied for the ribbon annealed for 2 h (Fig. 9b). In the ribbon annealed for 2 min (Fig. 9a), the H/M vs. M^2 isotherms do not possess negative slopes near T_C . However, a strong curvature in the isotherms combined with the slight magnetic hysteresis observed in Fig. 8 suggests that a weakly first order characteristic exists in the 2 min sample. Upon further annealing, the first order nature of the transition is strengthened as the 1:13 phase develops, simultaneously enhancing the magnetocaloric effect in the $\text{LaFe}_{11.5}\text{Si}_{1.5}$ ribbons.

4. Conclusions

From our systematic study of the microstructure of melt-spun ribbons of the giant MCE material La-Fe-Si, we draw the following important conclusions:

1) The undercooled liquid during rapid solidification of melt-spun ribbons can change solidification path and crystallization process depending on proximity to the copper wheel, producing varying phase compositions and microstructures in the final ribbons. Large clusters of similarly oriented grains occurred on the surface of melt-spun La-Fe-Si ribbons far from copper wheel during rapid solidification. Within these clusters, nanoscale texturing between the α -Fe and 1:1:1 phases occurs, with a periodic variation in the elemental composition of La, Fe and Si. A large number of equiaxed 1:13 crystals with a size of $\sim 100 \text{ nm} - 400 \text{ nm}$ occurred on the surface of the ribbon in contact with the copper wheel during rapid solidification. Minor α -Fe and 1:1:1 phases were precipitated in the 1:13 matrix.

2) In the heat treatment process of La-Fe-Si alloys, the phase transition region of the peritectoid reaction between the α -Fe and 1:1:1 phases and their change of shape indicates that there are two formation mechanisms of the 1:13 phase. Firstly, the 1:13 phase can be obtained by a peritectoid reaction between the α -Fe and 1:1:1 phases due to easy atomic diffusivity between nano-sized regions of each phase on Side 1, along with good mixing of La, Fe and Si atoms. Secondly, where pre-existing grains of the NaZn_{13} -type structure are present, growth occurs during the heat treatment process and most of the α -Fe phase is dissolved into the 1:13 phase to form equiaxed 1:13 grains.

3) The maximum magnetic entropy change $-\Delta S_M$ of ribbons annealed at 1273 K for 2 h is 17 J/kg K at 201 K under an applied field change of 0 – 1.5 T. This represents an

improvement over the entropy change of the ribbons annealed at 1273 K for 2 min (12 J/kg K at 189 K). Longer heat treatments are beneficial for a homogeneous 1:13 phase via a peritectoid reaction or solid state diffusion in $\text{LaFe}_{11.5}\text{Si}_{1.5}$ melt-spun ribbons.

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References

- [1] *Annual Energy Outlook 2013*, Energy Information Administration, U.S. Department of Energy, 2013, p. 130-132.
- [2] K. A. Gschneidner Jr., V. K. Pecharsky, A. O. Tsokol, Rep. Prog. Phys. 2005;68:1479.
- [3] E. Bruck, in: K. H. J. Buschow (Ed.), *Handbook of Magnetic Materials*, vol. 17, North-Holland, Amsterdam, 2008.
- [4] V. Franco, J.S. Blázquez, B. Ingale, A. Conde, Annu. Rev. Mater. Res. 2012;42:305.
- [5] A. Smith, C. R. H. Bahl, R. Bjørk, K. Engelbrecht, K. K. Nielsen, N. Pryds, Adv. Energy Mater. 2012; 2:1288.
- [6] X. Moya S. Kar-Narayan, N. D. Mathur, Nature Mater. 2014;13:439.
- [7] J. Liu, T. Gottschall, K. P. Skokov, J. D. Moore, O. Gutfleisch, Nature Mater. 2012;11:620.
- [8] V. K. Pecharsky, K. A. Gschneidner, Phys. Rev. Lett. 1997;78:4494.
- [9] Z. B. Guo, Y. W. Du, J. S. Zhu, H. Huang, W. P. Ding, D. Feng, Phys. Rev. Lett. 1997;78:1142.
- [10] O. Tegus, E. Brück, K. H. J. Buschow, and F. R. de Boer, Nature 2002;415:150.
- [11] H. Wada, Y. Tanabe, Appl. Phys. Lett. 2001;79:3302.
- [12] A. Yan, K. H. Muller, L. Schultz, O. Gutfleisch, J. Appl. Phys. 2006;99:08K903.
- [13] O. Gutfleisch, A. Yan, K. H. Muller, J. Appl. Phys. 2005;97:10M305.
- [14] F. X. Hu, B. G. Shen, J. R. Sun, Z. H. Cheng, G. H. Rao, X. X. Zhang, Appl. Phys. Lett. 2001;78:3675.
- [15] B. G. Shen, J. R. Sun, F. X. Hu, H. W. Zhang, Z. H. Cheng, Adv. Mater. 2009;21:4545.
- [16] S. Fujieda, A. Fujita, K. Fukamichi, Appl. Phys. Lett. 2002;81:1276.

- [17] H. Zhang, Y. J. Sun, E. Niu, F. X. Hu, J. R. Sun, B. G. Shen, Appl. Phys. Lett. 2014;104:062407.
- [18] J. D. Moore, D. Klemm, D. Lindackers, S. Grasemann, R. Trager, J. Eckert, L. Lober, S. Scudino, M. Katter, A. Barcza, K. P. Skokov, O. Gutfleisch, J. Appl. Phys. 2013;114:043907.
- [19] J. Lyubina, R. Schäfer, N. Martin, L. Schultz, O. Gutfleisch, Adv. Mater. 2010;22:3735.
- [20] J. Lyubina, O. Gutfleisch, M. D. Kuz'min, M. J. Richter, J. Magn. Magn. Mater. 2008;320:2252.
- [21] A. Fujita, Y. Akamatsu, K. J. Fukamichi, J. Appl. Phys. 1999; 85:4756.
- [22] M. D. Kuz'min, M. Richter, Phys. Rev. B 2007;76:092401.
- [23] X.D. Liu, X.B. Liu, Z. Altounian, G. H. Tu, Appl. Phys. A 2006;82:339.
- [24] H. Zhang, B. Bao, P. Shi, B. Fu, L. Y. Long, Y. Chang, J. Rare Earths. 2008;26:727.
- [25] J. Liu, M. Krautz, K. Skokov, T. G. Woodcock, O. Gutfleisch, Acta Mater. 2011;59:3602.
- [26] F. X. Hu, J. Gao, X. L. Qian, J. R. Sun, B. G. Shen, J. Appl. Phys. 2005;97, 1.
- [27] X. B. Liu, X. D. Liu, Z. Altounian, G. H. Tu, J. Alloys Compd 2005;397:120.
- [28] X. B. Liu, Z. Altounian, G.H. Tu, J. Phys.: Condens. Matter 2004;16:8043.
- [29] A. Yan, K. H. Muller, O. Gutfleisch, J. Appl. Phys. 2005;97:036102.
- [30] J. E. Rout, P. E. Donovan in: S. Steeb and H. Warlimont (Eds.) *Rapidly Quenched Materials Volume I*, North Holland Physics Publishing Amsterdam, 1985.
- [31] B. Cantor, W. T. Kim, B. P. Belway, A. G. Gillen, J. Mater. Sci. 1991;26:1266.
- [32] M. L. Ovecoglu, N. Unlu, N. Eruslu, A. Genc, Mater. Lett. 2003;57:3296.
- [33] Y. Z. Chen, F. Liu, G. C. Yang, Y. H. Zhou, Intermetallics 2011;19:221.

- [34] H. W. Kerr, W. Kurz, *Inter. Mater. Rev.* 1996;41:129.
- [35] Y. Arai, T. Emi, H. Fredriksson, H. Shibata, *Metal Mater. Trans. A* 2005;36:3065.
- [36] T. Umeda, T. Okane, W. Kurz, *Acta Mater.* 1996;44:4209.
- [37] R. Yapp, H. A. Davies, *Mater. Lett.* 1999;38:33.
- [38] M. J. Kramer, Y. Tang, K. W. Dennis, R.W. McCallum, *J. Mater. Res. Soc. Symp. Proc.* 1999;577:57.
- [39] C. Wang, M. Yan, *J. Mater. Sci. Eng. B* 2006;28:216.
- [40] M. J. Kramera, L. H. Lewis, Y. Tang, *J. Scr. Mater.* 2002;47:557.
- [41] S. K. Banerjee, *Phys. Lett.* 1964;12:16.

Figure Captions

Fig. 1 Illustration of melt-spinning fabrication process. Side 1 is the surface of the ribbon farthest from the copper wheel. Side 2 is the surface of the ribbon in contact with the wheel.

Fig. 2 XRD patterns of as-spun $\text{LaFe}_{11.5}\text{Si}_{1.5}$ for (a) powdered sample (b) ribbon Side 2 and (c) ribbon Side 1. XRD patterns after annealing at 1273 K for 2 min for (d) powdered sample (e) ribbon Side 2 and (f) ribbon Side 1. XRD patterns after annealing at 1273 K for 2 h for (g) powdered sample (h) ribbon Side 2 and (i) ribbon Side 1.

Fig. 3 SEM micrographs of Side 1 (a,b,c) and Side 2 (d,e,f) of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ ribbons with (a,d) no heat treatment, (b,e) 2 min annealing at 1273 K, and (c,f) 2 h annealing at 1273 K.

Fig. 4 (a) TEM micrograph of Side 1 of the as-spun ribbon. (b) Increased magnification of cluster boundary region enclosed by white box in (a). (c) Increased magnification of interior of grain cluster. (d) EDS line scan and (e) elemental distribution curves for the region indicated by white dashed circle in (a).

Fig. 5 (a) TEM micrograph of Side 2 of the as-spun ribbon, with higher magnification of the regions of the sample indicated by the dashed (b) box and (c) circle. HRTEM micrographs and corresponding FFT patterns of (d) region A, (e) region B, (f) region 1, and (g) region 2 as identified in panel (c).

Fig. 6 TEM micrographs of Side 1(a),(c),(e) and Side 2 (b),(d),(e) of the ribbon annealed at

1273 K for 2 min. HRTEM micrograph and FFT near (c) region M and (d) region N of Side 1.

(d) HRTEM micrograph and SAED pattern along lines (d) A and (f) B of Side 2.

Fig. 7 TEM micrograph of (a) Side 1 and (b) Side 2 of the ribbon annealed at 1273 K for 2 h.

EDS analysis for (c) region C, (d) region D, and (e) region E as marked in (a).

Fig. 8 (a) Magnetization vs. temperature curves under an applied field of 0.1 T and isothermal magnetization curves for ribbons annealed at 1273 K for (b) 2 min and (c) 2 h. (d)

Temperature dependence of magnetic entropy change under a magnetic field change of 0 – 1.5 T; lines are guide to the eye. Inset: Magnetic field dependence of refrigerant capacity.

Fig. 9 H/M vs. M^2 constructions for ribbons annealed for (a) 2 min and (b) 2 h.

Figures
Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9