Formation of tree-like and vortex magnetic domains of nanocrystalline α -(Fe,Si) in La-Fe-Si ribbons during rapid solidification and subsequent annealing

Xueling Hou,^{1,2,a)} Yue Tian,^{1,2,3} Yun Xue,^{1,2} Chunyu Liu,^{1,2} Weixing Xia,³ Hui Xu,^{1,2} Paula Lampen-Kelley,^{4,b)} Hariharan Srikanth,⁴ Manh-Huong Phan^{4,c)}

¹ *Laboratory for Microstructures of Shanghai University, Shanghai, 200444, China*

² *School of Materials Science and Engineering, Shanghai University, Shanghai, 200072 China*

³ *Ningbo Institute of Industrial Technology, Nongbao, ZheJiang 201620, China*

⁴ *Department of Physics, University of South Florida, Tampa, FL 33620, USA*

The characteristic magnetic domains at the surfaces of melt-spun La-Fe-Si ribbons under different thermal processing conditions are explored using room-temperature Lorentz force microscopy and electron holography. In as-quenched ribbons, the magnetic domain structure is found to change from a tree-like morphology on the surface far from the copper wheel during quenching to a vortex-type domain structure on the surface in contact with the wheel. In the initial stages of annealing, domains on both surfaces developed a vortex behavior. Detailed microstructural observations demonstrated nanocrystalline α -(Fe,Si) regions embedded in the majority La(Fe,Si)_{13} phase due to a partially completed peritectoid reaction between α -(Fe,Si) and LaFeSi . The room temperature magnetic domains disappeared along with the residual α -(Fe,Si) upon extended heat treatment, yielding a homogeneous La(Fe,Si)_{13} material. Magnetometry measurements and analysis reveal the absence of strong coupling between the α -(Fe,Si) and La(Fe,Si)_{13} phases, so that the presence of α -(Fe,Si) nanocrystallites with a vortex-type structure does not favor an enhanced magnetocaloric response in the ribbons.

Introduction

Room temperature magnetic refrigeration based on the magnetocaloric effect (MCE) has

^a Electronic mail: xhou@staff.shu.edu.cn

^b Electronic mail: plampen@utk.edu

^c Electronic mail: phanm@usf.edu

attracted much attention due to its potential for improved energy efficiency over conventional gas compression cycles and its environmental friendliness [1-3]. In recent years, a number of magnetic compounds have been studied because of their prospects for refrigeration device applications, e.g. $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})$ [4], $(\text{Mn,Fe})_2(\text{P,As,Ge})$ [5], $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ [6-8], $\varepsilon\text{-(Mn}_{0.83}\text{Fe}_{0.17})_{3.25}\text{Ge}$ [9], and $\text{Gd}_{55}\text{Co}_{20}\text{Al}_{25}$ [10]. Among these materials, the cubic NaZn_{13} -type compounds $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ are particularly promising candidates for room temperature magnetic refrigerants due to their low cost and large magnetocaloric effect [6-8, 11-13]. However, obtaining the NaZn_{13} -type phase of $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ with $1.0 \leq x \leq 2.0$ during the solidification process is problematic due to the intrinsic incompleteness of a peritectic reaction with $\alpha\text{-Fe}$ or $\gamma\text{-Fe} + L \rightarrow \text{La}(\text{Fe,Si})_{13}$, which often results in a mixed microstructure of $\alpha\text{-Fe}$, $\gamma\text{-Fe}$, $\text{La}(\text{Fe,Si})_{13}$, and/or LaFeSi [14,15]. Fabrication of $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ with a pure cubic NaZn_{13} -type structure (referred to hereafter as the 1:13 phase) by conventional casting methods requires extended annealing steps at 1173 – 1323 K [16,17]. The pure 1:13 structure is more easily achieved through a melt-spinning technique in which the peritectoid reaction is completed during a short (20 min – 2 h) post-quenching annealing step [18, 19]. However, the process of phase change between $\alpha\text{-Fe}$ or $\gamma\text{-Fe}$ and the 1:13 phase in melt-spun La-Fe-Si is quite complex and the evolution of the phases during the initial solidification process and the subsequent heat treatment is not fully understood.

In this context, such a study of the evolution of $\alpha\text{-Fe}(\text{Si})$ domains in as-cast and annealed ribbons holds particular relevance for a full understanding of the 1:13 phase formation process as diversification between $\alpha\text{-Fe}/\gamma\text{-Fe}$ and 1:13 phases, post-solidification and during the initial minutes of heat treatment will produce corresponding changes in the magnetic domain structure of melt-spun La-Fe-Si ribbons. In this letter, we present the relationships between domain structure, phase composition, and microstructure in melt-spun La-Fe-Si ribbons are explored using

conventional and Lorentz force TEM and electron holography. Such relationships have important implications for the magnetocaloric figures of merit in La-Fe-Si alloys prepared using different processing routes.

Experimental

La-Fe-Si ribbons with a nominal composition of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ were fabricated by a melt-spinning technique. Details of the preparation have been reported elsewhere [20,21]. The resulting (as-spun) ribbons were sealed in evacuated quartz ampoules and subjected to isothermal heat treatment at 1273 K for 3 min or 2 h before rapid quenching to room temperature. Microstructural analysis was carried out by a JSM-6700F scanning electron microscope with an energy dispersive spectrometer (EDS) attachment, and a JEM-2010F transmission electron microscope (TEM). TEM specimens were prepared by dual-beam focused ion beam milling. Magnetic domain structures were investigated by Lorentz microscopy using a JEM-2100F TEM with a field emission gun operating at 200 kV. A specialized pole piece reduced the magnetic field at the specimen position to less than 10 Oe during magnetic imaging and a biprism was equipped to perform holography to enable a direct visualization of the detailed distribution of magnetic flux lines. Magnetic measurements were performed using a Quantum Design Physical Property Measurement System.

Results and Discussion

TEM micrographs of the free- and wheel-side surfaces of an as-spun La-Fe-Si ribbon are shown in Fig. 1(a) and Fig. 1(b), respectively. Far from the copper wheel, two characteristic morphologies distinguished by black and grey contrast (labeled *A* and *B*, respectively, in Fig. 1a)

form during rapid solidification. EDS spectra indicate the darker contrast, i.e. more electronically dense *A* regions to be composed primarily of Fe (> 97 at.%), with small Si inclusions. Structural parameters obtained from Fourier-transformed HRTEM images within region *A* (Fig. 1a, upper inset) are consistent with the α -(Fe,Si) phase. In the lighter contrast *B* regions, EDS demonstrates an elemental composition of 37.7 at.% Fe, 37.5 at.% La and 28 at.% Si corresponding to the 1:1:1 LaFeSi phase. Selected area electron diffraction (SAED) patterns within the grey *B* regions were successfully indexed to the tetragonal unit cell of LaFeSi (Fig. 2a, lower inset). Within the 1:1:1 phase, additional embedded nanosized ($\sim 5 - 10$ nm) spherical α -Fe particles could be observed in many locations, e.g. the area enclosed by dashed lines in Fig. 1(a). The microstructure of the free side of the ribbon after melt spinning thus generates a large number of α -(Fe,Si)/LaFeSi interfaces that promote the peritectoid reaction of the two phases as seen below.

It can be seen from Fig. 1 that the microstructure of the as-spun ribbon differs significantly at its two surfaces. On the wheel side (Fig. 1b), well defined individual grains form following a log-normal size distribution centered at $0.25\ \mu\text{m}$. The light contrast grains are identified by SAED as the cubic 1:13 phase (Fig. 1b, upper inset), while α -(Fe,Si) forms a number smaller grains with dark contrast. Within the larger 1:13 grains, spherical α -(Fe,Si) precipitates (Fig. 1b, lower inset) $\sim 20 - 100$ nm in diameter are observed. The encapsulation of residual α -(Fe,Si) in the 1:13 matrix occurs as the result of an imperfect peritectic reaction $L + \alpha\text{-Fe} \rightarrow \text{La(Fe,Si)}_{13}$ during rapid solidification.

Micrographs of a La-Fe-Si ribbon annealed at 1273 K for 3 min are shown in Fig. 1(c)-(d). On the free surface of the ribbon (Fig. 1c), a reaction between the α -(Fe,Si) and 1:1:1 phases occurs during heating, forming the 1:13 phase according to $\alpha\text{-(Fe,Si)} + \text{LaFeSi} \rightarrow \text{La(Fe,Si)}_{13}$. In the initial stage of annealing arrested by quenching after 3 min, the peritectoid reaction is

incomplete and spatially non-uniform, producing boundaries between reacted and unreacted areas as indicated by arrows in Fig. 1(c). Within the reacted area a homogeneous 1:13 matrix is established, while mixed α -(Fe,Si) and 1:1:1 phases remain outside the boundary. In the transition region marked by a black square in Fig. 1(c), two groups of diffraction spots identified in the SAED pattern (inset) indicate a coexistence of 1:13 and α -(Fe,Si) structures. On the wheel-side ribbon surface (Fig. 2d) annealing promotes grain growth and an increase in the homogeneity of the pre-existing 1:13 regions as α -(Fe,Si) is partially dissolved into the 1:13 structure, becoming more spheroidal in the process. EDS line scans in Fig. 1(d) show residual α -(Fe,Si) regions $\sim 100 - 280$ nm are distributed in 1:13 matrix. The results of Fig. 1 demonstrate a sensitive dependence of the ribbon microstructure to conditions during the quench and initial thermal processing.

TEM micrographs of the La-Fe-Si ribbon after annealing for a longer period of 2 h at 1273 K are shown in Fig. 1(e,f). Analysis of HRTEM images and their Fourier transforms on both surfaces of the ribbon show a single structure pattern corresponding to the 1:13 phase with no evidence of the significant α -Fe volume that remained after the 3 min annealing step. A perfect 120° intersection of three grains is shown in Fig. 1(f), indicating good crystallinity and equal grain boundary energies. Thus, the partial reaction observed in the sample annealed for 3 min is completed when the annealing time is extended to 2 h, resulting in a nearly homogeneous 1:13 phase.

The magnetic domain structures of the La-Fe-Si ribbons are observed by Lorentz microscopy, in which image intensity in a sample with nonzero spontaneous magnetization is modulated by Lorentz force deflection of the electron beam, producing bright or dark contrast regions in the vicinity of convergent or divergent domain walls, respectively. Reversing the sign of the defocus causes convergent magnetic features to become divergent and vice versa, allowing

domain walls to be imaged. Figs. 2(a,b) show slightly over- and under-focused images of the free surface of an as-spun La-Fe-Si ribbon. Magnetic domain walls (indicated by arrows) appear as contrast-reversed bright and dark lines in the images. The magnetic structure of the free surface after melt spinning consists of narrow, elongated domains with irregular branching. A clear preferred orientation transverse to the long axis of the ribbon can be seen in the tree-like domain structure, suggesting a weak anisotropy set in during rapid cooling.

Figure 2(c) shows the reconstructed phase image of the ribbon based on electron holography [22]. Contour lines provide a 2D mapping of in-plane magnetic flux, where contour line spacing is related to local magnetic flux density $|\vec{B}|$. Closely spaced magnetic flux lines can be seen running perpendicular to the domain walls of Fig. 2(a,b). This behavior is typical of tree-like domains, and serves to transport a part of the magnetic flux from one principal domain to the adjacent principal domain, thus decreasing the magnetic charges and hence the demagnetizing energy [23].

In contrast to the uniform domain structure on the free side, Lorentz micrographs of the wheel side of the as-spun ribbon show magnetic features concentrated around α -(Fe,Si) grains and nanoprecipitates (Fig. 2d-f). Domain walls (white arrows) of both 90° and 180° - type occur within grains up to several hundred nanometers in size, producing a flux closure vortex structure (inset, Fig. 2e). In addition to domain walls, the contrast of a number of points (red ellipses) transforms with the focusing mode, suggesting a magnetic origin. The corresponding magnetic flux map (Fig. 2f) shows that these points correspond to core locations of vortices formed within isolated single-domain Fe nanoprecipitates. Widely spaced contour lines within the paramagnetic La-Fe-Si matrix indicate weak magnetostatic interaction fields between Fe-rich regions.

Figure 3 shows the reconstructed phase images of the La-Fe-Si ribbon after the initial 3 min

annealing step. On the free side of the ribbon following the heat treatment, magnetic domain walls can no longer be identified in Lorentz micrographs. Outside the 1:13 regions isolated vortex cores are identified in areas where the peritectoid reaction is incomplete (Fig. 3a). The change from tree-like domain walls to large vortices in areas of nanoscale textured Fe and 1:1:1 phase signifies an increased homogeneity in the distribution of magnetic Fe so that a single flux-closure structure is formed within regions that appear unreacted in Fig. 1(c). On the wheel side (Fig. 3b) annealing decreases the number and size of unreacted Fe regions, leaving a small number of single-domain magnetic flux vortices. The absence of contour lines in the intervening La(Fe,Si)_{13} matrix indicates that the residual Fe particles are isolated and non-interacting. After annealing for 2 h, no magnetic features are observed in Lorentz TEM or electron holography images, consistent with the paramagnetic behavior expected from the uniform 1:13 phase at room temperature.

The temperature dependence of magnetization in the annealed La-Fe-Si ribbons between 100 K and 300 K under a 100 Oe dc magnetic field is shown in Fig. 4(a). The Curie temperatures $T_C \sim 188$ K and ~ 194 K determined from the inflection points of the $M(T)$ curves (inset, Fig. 4a) for the ribbons annealed at 1273 K for 3 min and 2 h, respectively, are near the expected value for the La(Fe,Si)_{13} phase. Above the ferromagnetic T_C of La(Fe,Si)_{13} , a small temperature-independent magnetization (~ 1.4 emu/g) is observed in the ribbons annealed for 3 min due to the presence of residual nanoscopic α -Fe with a T_C well above room temperature. When the annealing time is increased to 2 hours, the magnetization above T_C becomes vanishingly small. Simultaneously, the low field ordered moment increases, and the transition sharpens and shifts upward as the remaining α -Fe and LaFeSi regions are incorporated into the La(Fe,Si)_{13} structure. These results are in full agreement with the TEM and domain observations.

The isothermal magnetization curves of the La-Fe-Si ribbons annealed for 3 min and 2 h

are shown in Fig. 4(b) and Fig. 4(c), respectively. It can be seen that the high-field magnetization of the sample annealed for 3 min is enhanced with respect to that of the sample annealed for 2 h. However, linear extrapolation from the high field region gives a spontaneous magnetization of $M_S = 48$ emu/g due to the high- T_C ferromagnetic contribution of minority Fe after the initial heat treatment (Fig. 4b). The change in sample magnetization due to the ordering of La(Fe,Si)_{13} is therefore $\Delta M_{3\text{min}} \sim 90$ emu/g, while on the other hand $\Delta M_{2\text{h}} \sim 120$ emu/g in the sample annealed for 2 h where La(Fe,Si)_{13} is the only magnetic phase present. While a large moment is a prerequisite for a strong MCE, the magnetic entropy change $-\Delta S_M(T, H)$ is most sensitive to changes in the magnetization as established by the thermodynamic Maxwell relation [1]:

$$\Delta S_M(T) = \mu_0 \int_{H_i}^{H_f} \frac{\partial M}{\partial T} dH$$

under a field change $\Delta H = H_f - H_i$. Figure 4(d) shows the $-\Delta S_M(T)$ curves for the annealed ribbons under field changes of 1 T and 6 T. The entropy change reaches maximum values of $-\Delta S_M = 16$ J/kg K and 22 J/kg K in the ribbons annealed for 3 min and 2 h, respectively, consistent with the differences in ΔM . In a number of materials, magnetic nanocomposite morphology or coupling between multiple magnetic phases has led to enhanced magnetocaloric properties [24, 25]. The magnetic properties of the nanocrystalline α -(Fe,Si)-embedded La(Fe,Si)_{13} ribbons in the present study do not indicate any significant coupling between the two magnetic phases. In the absence of interacting phases, poorer crystallinity and interfacial effects in the incompletely reacted ribbon lead to a drop in the magnitude of the MCE with respect to the homogeneous La(Fe,Si)_{13} ribbon.

In summary the microstructure, domain structure, and bulk magnetic properties of melt-spun La-Fe-Si alloys were reported in various stages of the complex rapid solidification

process. Small variations in cooling rate during rapid solidification produced strong differences in microstructure and distribution of the 1:13, 1:1:1, and α -Fe phases across the thickness of the ribbon. After an initial annealing step, tree-like transverse domains on the wheel-side surface were converted to vortex-type magnetic flux contours in regions of incompletely reacted LaFeSi and α -Fe. The residual nanocrystalline α -(Fe,Si) domains that persist in the early stages of the annealing process do not contribute to the change in magnetization at T_C or significantly broaden the transition, yielding diminished magnetocaloric properties compared to the single phase La(Fe,Si)_{13} ribbon.

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Figure Captions

Fig. 1 TEM images of the free-side (a),(c) and wheel-side (b),(d) surfaces of La-Fe-Si ribbons (a),(b) in the as-spun condition and (c),(d) after a 3 min annealing step at 1273 K. Red, blue, and green curves in (d) represent EDS linescans of Fe, La, and Si content, respectively. (e,f) TEM images of a La-Fe-Si ribbon after annealing for 2 h. Inset (f): HRTEM image and Fourier transform.

Fig. 2 Lorentz TEM images of the free-side surface of an as-spun La-Fe-Si ribbon acquired in (a) underfocused and (b) overfocused mode. Lorentz TEM images of the wheel-side surface of an as-spun La-Fe-Si ribbon acquired in (d) underfocused and (e) overfocused mode. Electron holography flux maps of (c) the free side and (f) the wheel side surfaces of an as-spun La-Fe-Si ribbon. White arrows and red circles indicate magnetic domain walls and vortex cores, respectively. Inset: magnification of the region marked by a blue box in (f); Arrows indicate the direction of the magnetic flux contours; 90°-type and 180°-type domain walls are marked by yellow and red dashed lines, respectively.

Fig. 3 Electron holography phase maps of (a) the free-side surface and (b) the wheel-side surface of La-Fe-Si ribbons after annealing at 1273 K for 3 min.

Fig. 4 (a) Temperature dependence of magnetization in La-Fe-Si ribbons annealed for 3 min and 2 h at 1273 K. Field-dependent magnetization isotherms collected around T_C at 1 K or 2 K intervals in ribbons annealed for (b) 3 min and (c) 2 h. (d) Magnetic entropy change curves collected under field changes of 1 T and 6 T. Inset(a): First derivative of magnetization.

Figure 1

Figure 2

Figure 3

Figure 4