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Laser assisted crystallization of ferromagnetic amorphous ribbons: A multimodal characterization and thermal model study

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This paper focuses on laser-based de-vitrification of amorphous soft magnetic Fe-Si-B ribbons and its consequent influence on the magnetic properties. Laser processing resulted in a finer scale of crystallites due to rapid heating and cooling during laser annealing compared to conventional furnace annealing process. A significant increase in saturation magnetization is observed for laser-annealed ribbons compared to both as-received and furnace annealed samples coupled with an increase in coercivity compared to the as received samples. The combined effect of thermal histories and stresses developed during laser annealing results in the formation of nano-crystalline phase along the laser track. The phase evolution is studied by micro-XRD and TEM analysis. Solute partitioning and compositional variation within the phases are obtained by Local Electrode Atom probe analysis. The evolution of microstructure is rationalized using a Finite Element based heat transfer multi-physics model. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4829279>]

I. INTRODUCTION

With increasing global warming and increasing consumption of energy resources, there is tremendous research interest in developing energy saving technologies. One possibility to meet the increasing demand is by efficient utilization of generated energy. Significant amount of energy is wasted during electrical power transmission and distribution, these losses including core loss can be greatly reduced by developing materials with superior electromagnetic properties. Fe-Si steels are soft magnetic alloys that are extensively used in transformer cores mainly due to their high saturation flux density and high permeability.¹ Core losses in transformers can be much higher in these conventional crystalline alloys compared to similar alloy compositions in amorphous and nano-crystalline states. This has triggered tremendous interest in developing amorphous and nano-crystalline materials for soft magnetic applications^{2–6} and has been extensively reviewed in the literature.^{7–9}

Amorphous materials have been a topic of interest since their invention due to their exceptional properties as compared to their crystalline counterparts. Their unusual properties like high yield strength,¹⁰ corrosion resistance,¹¹ wear resistance, and exceptionally good soft magnetic properties can be attributed to their disordered long range structure. In particular, the amorphous materials possess excellent soft magnetic properties due to averaging out of magneto-crystalline anisotropy as explained in the random anisotropy model.⁸

Iron based amorphous and nano-crystalline soft magnetic materials have been extensively studied for soft magnetic applications owing to their much lower coercivity values compared to the grain oriented Fe-Si steels, this result

in significant reduction in core losses.^{2,12,13} However, the saturation magnetization of these Fe-based amorphous (ribbon) materials is less than that of Fe-Si steel. Hence, there have been many attempts to increase the saturation magnetization of these amorphous steel ribbons without compromising coercivity.

Yoshizawa and coworkers² have developed Finemet steel ribbons by addition of Nb and Cu to Fe-Si, extremely low coercivity values were obtained due to a very fine nano-crystalline microstructure that develops in these ribbons. Nonetheless, the saturation magnetization of these ribbons continues to be rather low, many attempts have been made to increase the saturation magnetization. More recently, many new systems have been proposed to improve the magnetic properties by choosing different alloying elements. This in turn increases the cost due to expensive alloying elements.

One possible way to improve the saturation magnetization without enhancing the coercivity is by synthesizing nano-crystalline material from high iron content precursor amorphous alloy without alloying additions. It has been reported that the Fe-Si-B ternary system (without Cu and Nb alloying additions) can be crystallized by annealing at low temperatures.^{14–17} However, it requires prolonged annealing (~300 h) due to sluggish kinetics that is not suitable to produce nanocrystalline material on a industrial scale. It has also been reported that high temperature flash annealing can result in a nano-crystalline microstructure.¹⁸ This is attributed to associated high heating and cooling rates, resulting in increased nucleation density and low growth rates.¹⁹ The increase in nucleation density can result in overlap of diffusion fields impeding grain growth and resulting in very fine microstructures.

Laser processing can be used to successfully synthesize very fine nano-crystalline phase by selection of appropriate combinations of laser parameters. Rapid heating rates and desired temperatures can be achieved with the help of laser annealing resulting in high quench rates and high nucleation rates that in turn aid in restricting the grain growth. Thus, in principle, it should be possible to achieve superior soft magnetic properties via laser annealing of soft magnetic amorphous ribbons. In addition, as laser annealing is a localized phenomenon, it can be extended to synthesize patterned nanostructures for sensing, data storage, and spintronics applications. Furthermore, EMI (Electro Magnetic Induction) shielding of complex shapes has been a challenge and laser processing can be a potential route to weld complex shapes. The present work focuses on the microstructural evolution in laser annealed amorphous Fe-Si-B ribbons and its correlation with magnetization behavior. Thorough microstructural characterization has been carried out and the magnetization behavior of the laser annealed samples has also been compared with the conventionally furnace annealed Fe-Si-B alloys.

II. EXPERIMENTAL PROCEDURE

A. Annealing

Iron-based amorphous ribbons (MetglasInc, Product No.: 2605 SA1) with a nominal composition of $\text{Fe}_{80}\text{Si}_{12}\text{B}_8$ in atomic percent and thickness of $28\text{ }\mu\text{m}$ were used for the laser-patterning experiments. The ribbons were cut into $4\text{ cm} \times 2\text{ cm}$ dimensions for the experiments. The laser patterning was carried by scanning parallel tracks with a continuous wave ytterbium doped Nd-YAG laser beam with a diameter of 0.6 mm at a wavelength of $1.064\text{ }\mu\text{m}$. A 100 W laser power was chosen and the laser beam was scanned 20 times with a velocity of 500 mm/s resulting in 0.33 J/mm^2 laser energy density. The lateral spacing between the centers of two consecutive laser-scanned tracks was maintained at 1 mm , thereby retaining an untreated track of width 0.4 mm between consecutive laser tracks (Figure 1).

The sample for conventional furnace annealing was prepared by sealing the sample in a glass tube in an Argon atmosphere, the glass tube was placed inside the furnace at 823 K . The heat treatment was done for 1 h in order to achieve considerable amount of crystallization as short term annealing results in very less amount of phase

transformed.^{16,17} The time and temperature of heat treatment are reported in many earlier reports.^{2,20,21}

B. Microstructure, phase analysis, and magnetic measurements

Phases after laser annealing were characterized by Rigaku III Ultima X-ray diffractometer (XRD) with Cu K_α radiation of wavelength 0.15418 nm . The XRD system was operated at 40 kV and 44 mA in a 2θ range of $20\text{--}90^\circ$ using a step size of 0.025° and a scan speed of $2^\circ/\text{min}$. Spatially resolved micro-XRD was performed using a Rigaku Rapid II system equipped with a rotating Cr anode (35 kV , 25 mA , $\lambda = 0.22910\text{ nm}$) and a 2-dimensional image plate detector. The sample was positioned perpendicular to the $10\text{ }\mu\text{m}$ diameter incident beam and was moved in $10\text{ }\mu\text{m}$ steps to record patterns across the laser tracks. The phases present were identified by comparing the XRD patterns with standard ICDD (International center for diffraction data) patterns. For detailed microstructure analysis, transmission electron microscopy (TEM) was conducted using FEI Tecnai F20 field emission gun TEM operated at 200 kV . A site specific TEM samples were prepared using a FEI Nova 200 Nano Lab—dual beam focused ion beam (FIB).

Samples for Atom Probe Tomography (APT) studies were prepared by the focused ion beam milling technique. For this purpose, samples were prepared by dual-beam FIB FEI Quanta 3D FEG system using Ga ion beam. The ion beam thinning was carried out in multiple steps, starting with 30 kV ions, followed by finishing with 5 kV ions to reduce surface damage caused by the higher energy ions.²² The final tip diameter of the atom probe specimen was $\sim (50\text{--}80)\text{ nm}$. The APT experiments were carried out in voltage evaporation mode with 25% voltage pulse fraction at sample temperature of 40 K and evaporation rate of 0.5% using either LEAP 3000XHR or LEAP 4000XHR local electrode atom probe system from CAMECA Instruments Inc. The reconstruction of the APT data was performed using IVAS software and the tip diameter and shank angle during reconstruction were determined using a high magnification SEM image taken after final milling. De-convolution of overlapping peaks in mass to charge spectra were performed using the ion counts of the non-overlapping isotope peaks. The overlap of Si_{28}^{+1} and Fe_{56}^{+2} peaks in the mass to charge spectrum was de-convoluted using the ionic count of non-overlapping Si_{30}^{+1} isotope peak to estimate the count of Si_{28}^{+1} peak based on expected natural abundance ratio of isotopes. The phase transformation temperatures of the initial amorphous ribbon were tested using Differential Scanning Calorimetry (DSC). A NETZSCHDSC-404C was employed for calorimetric study. The DSC experiments were performed in Argon atmosphere using Alumina (Al_2O_3) crucibles. The sample weight was about 7 mg . The sample was heated to a temperature of 873 K at a heating rate of 20 K/min . The measurements of the saturation magnetization and coercivity of the materials were conducted employing a LakeShore7300 VSM. For laser annealed samples, the magnetization data are the average of the laser annealed region and the regions that have not been exposed to laser

FIG. 1. Schematic of laser treatment.

annealing. All the measurements were conducted three times to reduce errors.

C. Thermal model

The thermal histories experienced during laser annealing will have an effect on the microstructural evolution. In light of this, attempts were made to estimate the temperatures and their effects on microstructural evolution during laser annealing, through development of a multi-physics based computational model based on heat-transfer mechanisms in COMSOL'sTM heat transient mode. The equation governing the heat transfer model is given by

$$\rho C_p \frac{\partial T(x, y, z, t)}{\partial t} = k \left[\left(\frac{\partial T(x, y, z, t)}{\partial x} \right) + \left(\frac{\partial T(x, y, z, t)}{\partial y} \right) + \left(\frac{\partial T(x, y, z, t)}{\partial z} \right) \right]. \quad (1)$$

Here, k is the thermal conductivity, C_p is the specific heat, and ρ is the density of the material.

The model is governed by assigning different boundary conditions which in turn combine different heat transfer phenomena. The following equation takes into account all three boundary conditions; heat flux, convection, and surface to ambient radiation.

$$-k \left[\left(\frac{\partial T}{\partial x} \right) + \left(\frac{\partial T}{\partial y} \right) + \left(\frac{\partial T}{\partial z} \right) \right] = P_g - \varepsilon \sigma [T^4 - T_0^4] - h[T - T_0], \quad (2)$$

here h is heat transfer coefficient, ε is emissivity, P_g is three dimensional Gaussian laser beam distribution, σ is Stefan-Boltzmann constant, and T_0 is ambient temperature. The heat transfer in the laser track is governed by Eq. (2) and all other boundaries exhibit convective heat transfer and surface to ambient radiation. The physical constants related to the material can be found elsewhere.²³ A detailed description of the model can be found in our previous publication.²⁴

III. RESULTS

A. Phase transformation and microstructural evolution

The DSC results of the as received amorphous ribbon indicate the presence of two strong exothermic peaks at ~ 780 K (T_{x1}) and ~ 830 K (T_{x2}) (Figure 2), respectively. This is indicative of the decomposition of the amorphous phase through two crystallization events. The first crystallization temperature corresponds to the formation of the primary BCC α -Fe(Si) phase and the second crystallization peak corresponds to the formation of intermetallic phases. It has been reported that the initial amorphous phase decomposes into primary α -Fe(Si) and Fe_3B intermetallic and further decomposition of metastable Fe_3B phase occurs to Fe_2B .^{25,26} The peaks corresponding to the formation of Fe_3B and the transformation from Fe_3B to Fe_2B overlap and hence

FIG. 2. DSC of as received amorphous ribbon.

only two exothermic peaks are observed in the DSC curve. The formation of these phases is further confirmed by XRD and TEM analyses discussed in the following section.

XRD results from the furnace-annealed and laser-annealed Fe-Si-B ribbons, shown in Figure 3(a), reveal the formation of the BCC α -Fe(Si) phase along with the Fe_2B phase. In addition to phase analysis, the crystallite size distribution and also the volume fraction transformed across the laser-annealed region were evaluated using micro-XRD (Figures 3(c) and 3(d)). The area of the α -Fe(Si) (200) peak increases towards the edge of the laser track compared to the center, as seen from the XRD pattern (Figure 3(d)). It is also worth noting that significant peak intensity of α -Fe(Si) phase is observed in the unprocessed region (Figure 3(b)). The average crystallite sizes were estimated in the laser annealed regions using the Scherrer equation. The crystallite size at the laser annealed region was higher having a mean crystallite size of 70 nm with a standard deviation of 16 compared to the unprocessed region having a mean crystallite size of 35 nm with a standard deviation of 4. In addition, the presence of BCC α -Fe(Si) and Fe_2B phases is further confirmed from the TEM diffraction patterns shown as insets in Figures 4(a) and 5(a), respectively, in both laser-annealed as well as furnace-annealed samples. Furthermore, the analysis of morphology and distribution of different phases was also carried out using TEM analysis, as discussed in the following section.

The distribution of phases and the respective crystallite sizes have a strong influence on the magnetic properties. TEM bright field images and corresponding diffraction patterns show that significant crystallization took place after laser annealing (Figures 4(a) and 4(c)). The average precipitate size was estimated by measuring individual precipitate sizes employing commercially available ImageJ software. The TEM micrographs reveal a clear difference in the crystallite size between the furnace-annealed sample (average particle size ~ 100 nm) (Figure 5) compared to the laser-annealed sample (70 nm) (Figure 4). In addition, the equiaxed morphology is associated with the laser-annealed sample (Figure 4), whereas the furnace-annealed sample exhibits precipitates with a dendritic morphology (Figure 5). Further, the laser-annealed sample exhibits a wide distribution for precipitate

FIG. 3. (a) XRD patterns (b) Micro-XRD spectra corresponding to laser annealed sample across laser track (c) crystallite size distribution across laser track (d) area of the 200 peak across the laser track.

size (~ 20 nm– 200 nm) in both center and the edge of the laser track (Figure 4). The transformations are accompanied via partition of different alloying elements, as investigated using atom probe tomography (APT).

The APT results from edge and center regions of the laser track show clear segregation of B and Si to these distinct regions within the reconstructed volume (Figures 6 and 7). A suitable isoconcentration (isosurface) is chosen in such a way that it delineated both the phases, and then a

proximity histogram is generated across the interface to determine partitioning of the elements into the respective phases.^{27,28} The 80 at. % Fe isocomposition surface delineating the boundary between boron rich regions and silicon rich regions within the reconstruction are shown in Figures 6(b)–6(d) and 7(b)–7(d). For better understanding of elemental distribution a 5 nm slice of the entire APT reconstruction is shown with Fe ions (Figures 6(b) and 7(b)), B ions (Figures 6(c) and 7(c)) and Si ions (Figures 6(d) and 7(d)) overlaid on the 80 at. % Fe isocomposition surface. A proximity histogram plotted perpendicular to the 80 at. % Fe isocomposition surface is used to quantify the compositional partitioning between the B rich regions and Si rich regions. It can be observed that within the laser track (center and edge regions) boron concentration reaches ~ 33 at. % (Figures 6(e) and 7(e)) which is equivalent to the Fe₂B composition, in agreement with the XRD results. Similarly it can also be observed that the silicon concentration is about 15 at. % in the α-Fe(Si) phase for both at the edge region as well as

FIG. 4. TEM micrograph of laser annealed sample. (a) bright field image with corresponding SAD of center region of laser track, (b) dark field image of center region of laser track (c) bright field image with corresponding SAD of edge region of laser track, (d) dark field image of edge region of laser track.

FIG. 5. TEM micrographs of furnace annealed sample. (a) Bright field image with corresponding SAD image and (b) dark field image.

FIG. 6. Atom probe reconstruction from the edge of laser track with (a) all ions (b) slice view of tip with iron ions (c) slice view of tip with boron ions (d) slice view of tip with silicon ions (e) proximity histogram across 80 at. % iso-surface.

at the center region of the laser track (Figures 6(e) and 7(e)). The atom probe analysis for the furnace annealed sample also revealed the formation of silicon rich and boron rich phases (Figure 8(a)). The segregation of alloying elements is further emphasized in the 5 nm slice view (Figures 8(b)–8(d)). The isoconcentration surface at 77 at. % of iron delineates the boron and silicon rich phases, a proximity histogram is generated across the interface to quantify the compositional partitioning. Although boron concentration (32 at. %) in the boron rich phase is similar to Fe_2B region concentration in laser annealed sample, the partitioning of silicon (~ 20 at. %) (Figure 8(e)) to the $\alpha\text{-Fe}(\text{Si})$ phase shows a significant change compared to the silicon partitioning in the laser annealed samples (~ 15 at. %). The evolution of microstructure and the partitioning behavior can be explained in terms of difference in their thermal histories. The thermal histories during laser annealing have been evaluated using a thermal model and the results are discussed in the next section.

B. Thermal modeling

Using a computational model, the thermal histories have been generated at the center region, edge region and the region, between the consecutive tracks. It can be clearly seen that the peak temperature (~ 850 K) at the center of the laser track for the first laser track reaches above the crystallization temperature (780 K) and lower temperatures (~ 720 K) are obtained at the edge of the laser track (Figure 9(a)). The

temperature profiles generated for the second laser track indicate a substantial increase in temperature above crystallization temperature (780 K) both at center region (950 K) as well as at the edge region (850 K) of the laser track (Figure 9(b)). Moreover, it can be noted that the temperature in the unprocessed region (~ 760 K) is close to the primary crystallization temperature (780 K) (Figure 9(b)) for the second laser track. This explains the low intensity in micro-XRD data for the un-processed region between two consecutive laser tracks (Figure 3(b)). In addition to temperature evolution during laser annealing, the heating and cooling rates are also estimated using the thermal model (Table I). The high cooling rates experienced during laser annealing (10^3 K/s) (Table I) are expected to have a strong influence on the partitioning of silicon as explained subsequently in this paper.

C. Magnetic response

The hysteresis curves (Figure 10) clearly indicate that the saturation magnetization of both furnace annealed as well as laser annealed samples increased compared to the as-received amorphous ribbon. In addition, a sharp increase in coercivity is observed for both laser and furnace annealing samples compared to as-received amorphous ribbon (Table I). For laser-annealed sample, the coercivity is smaller ($\sim 42\%$) and the saturation magnetization is greater (by 12%) compared to that of furnace-annealed sample (Table I). It is interesting to note that the remanent magnetization remains

FIG. 7. Atom probe reconstruction from the center of laser track with (a) all ions (b) slice view of tip with iron ions (c) slice view of tip with boron ions (d) slice view of tip with Si ions (e) proximity histogram across 80 at. % iso-surface.

FIG. 8. Atom probe reconstruction from the furnace annealed sample (a) all ions (b) slice view with iron ions (c) slice view with boron ions (d) slice view with silicon ions (e) proximity histogram across 77 at. % iso-surface.

the same for both furnace and laser annealed samples (Figure 10).

IV. DISCUSSION

It can be seen from the XRD (Figure 3(a)) and TEM analyses (Figures 4(a)–5(a)) that Fe_2B and $\alpha\text{-Fe}(\text{Si})$ are the major crystallization products in both laser-annealed and furnace-annealed samples. Although the temperature at the edge region of the laser track is less than the temperature attained at the center region of the laser track, significant crystallization is observed in both the center and edge regions as seen from the electron diffraction pattern (Figures 4(a) and 4(c)). This is attributed to the steep thermal gradient and associated distribution of thermal stresses due to the Gaussian beam distribution of the laser beam intensity. The presence of stresses is likely to alter the amount of free volume and also the diffusion kinetics, leading to rapid crystallization.²⁹ It has been reported earlier that the phase fraction transformed in the edge region longer than that at the center of the laser track for isolated single laser pass.³⁰ Similarly, in the present case, it is likely that the phase fraction transformed is greater towards the edges of the laser track for multi-pass laser processing. This could be the reason for increase in area fraction of the crystalline peak (Figure 3(d)) at the edge of the laser annealed region. Thus, an increased fraction of amorphous material was transformed to the crystalline phase (due to enhanced diffusion kinetics). It has been reported from first principle calculations that the Fe_2B phase has a reduced magnetic moment due to anti-ferromagnetic

exchange interactions.³¹ Hence, the presence of Fe_2B reduces the saturation magnetization due to an overall reduction in magnetic moment. The saturation magnetization and magnetocrystalline anisotropy of $\alpha\text{-Fe}(\text{Si})$ depends on the solute content. Although boron has very little solubility in the BCC $\alpha\text{-Fe}$ phase, silicon can partition into the $\alpha\text{-Fe}$ phase. It has been reported that the partitioning of silicon into primary $\alpha\text{-Fe}$ is lower during initial stages of crystallization but as annealing progresses, more and more silicon partitions into the $\alpha\text{-Fe}$ phase. When the Si concentration reaches about 20 at. % of silicon, chemical ordering takes place resulting in the degradation of saturation magnetization and magnetostriction.³² It is also reported that lower concentration of silicon increases the saturation magnetization and reduction in saturation magnetization starts to occur above 16 at. % of silicon.⁵ Simulations based on Density Functional Theory (DFT) indicate that the magnetic moment of iron decreases with the increasing number of silicon atoms as nearest neighbors. Thus with an increase in silicon concentration in the $\alpha\text{-Fe}$ phase, the magnetic moment of one iron lattice site decreases due to hybridization between iron-d orbitals and silicon s,p orbitals.³³ The magnetization value can be calculated based on number of Fe nearest neighbors.^{34,35} The Magnetization (emu/gms) was estimated by calculating the magnetic moment of the DO_3 supercell for both furnace and laser annealed samples by considering the silicon content in the $\alpha\text{-Fe}(\text{Si})$ phase obtained from the Atom probe data (Figures 6–8). As mentioned earlier, the Si concentration in furnace annealed sample is ~ 20 at. % compared to ~ 15 at. % in laser annealed samples.

FIG. 9. Peak temperatures predicted by the thermal model (a) first laser track (b) second laser track.

TABLE I. Comparison of properties for different processing conditions.

Property	Furnace annealing	Laser annealing	As received
Coercivity H_c (Oe)	64	37	0.45
Saturation magnetization (emu/g)	155	175	136
M_r/M_s	0.42	0.37	0
Heating rate	isothermal	6×10^3 K/s	NA
Cooling rate	Air cooled	1.3×10^3 K/s	NA

Fe_3Si phase has a DO_3 structure formed by 4 interpenetrating FCC sublattices with their origins at A(0,0,0) B(1/2,1/2,1/2), C(1/4,1/4,1/4) and D(3/4,3/4,3/4).³⁶ As each FCC sublattice contains 4 atoms, there are 16 atoms in a supercell. Fe atoms occupy (A,C) sublattices with 4 Si atoms and 4 Fe atoms as NN (nearest neighbors). In addition, Fe atoms also occupy (B) sublattice with 8 Fe atoms as NN. The D sublattice is occupied by Si atoms with 8 Fe atoms as NN. Fe atoms occupying the B sublattice have only Fe atoms as NN compared to 4 Si atoms as NN at (A,C) sublattice. Hence, the magnetic moment of Fe atom is lower for (A,C) sublattice compared to B sublattice. When Si concentration decreases, Fe atoms substitute the Si atoms at the D sublattice. Hence, the magnetic moment of Fe atoms at (A,C) sublattice increases due to decrease in number of Si atoms as NN.

In the case of furnace annealed sample, 20 at. % Si corresponds to an average of 3.2 Si atoms and 12.8 Fe atoms in a supercell. Similarly, for laser annealed sample, 15 at. % Si corresponds to an average of 2.4 Si atoms and 13.6 Fe atoms per supercell. Hence, when 5 supercells are considered, they contain a total of 80 atoms. The furnace annealed sample has (16 Si, 64 Fe) whereas (12 Si, 68 Fe) atoms are present in the laser annealed sample. It has been reported that the magnetic moment of Fe decreases linearly with increase in number of Si atoms as NN.³⁵ The magnetic moment of Fe atoms as a function of Si NN has been calculated for each supercell configuration and an average magnetic moment per supercell was obtained. The obtained magnetic moment value was

normalized with respect to the average mass of the super cell to obtain saturation magnetization (Table II). The calculated values are in close agreement with experimental observations (Table II) indicating a low volume fraction of Fe_2B phase as only $\text{Fe}(\text{Si})$ phase was considered for theoretical calculation. This result is in agreement with the XRD analysis (Figure 3(a)).

In the present work, the processing conditions employed result in incomplete partitioning of silicon in the $\alpha\text{-Fe}$ phase due to rapid quenching during laser annealing. The $\alpha\text{-Fe}(\text{Si})$ phase contains about 15 at. % of silicon in the laser-annealed sample (Figures 6(e) and 7(e)), as indicated by the proximity histograms created from the atom probe reconstruction. Thus, due to less partitioning of silicon in laser-annealed sample, the magnetic moment of iron atoms is larger than conventional furnace-annealed samples (Table I). This can rationalize the increase in saturation magnetization observed in case of the laser-annealed sample. In addition, crystallization within the region between the consecutive laser tracks can be attributed to increasing temperature (Figure 9(b)) close to the primary crystallization temperature (>780 K)(Figure 3(b)), which also contributes to the increment of saturation magnetization (Figure 9).

The TEM micrographs clearly indicate that the precipitate density is quite high for laser-annealed samples (Figures 4(a)–4(d)) compared to furnace-annealed samples (Figures 5(a) and 5(b)). Significant crystallization is observed for the laser-annealed sample as indicated by the TEM diffraction patterns (Figures 4(a) and 4(c)) although the processing time involved (1.2 ms) in laser annealing is many orders of magnitude shorter than conventional annealing (1 h). This is indicative of high nucleation rate for laser-annealing compared to furnace-annealing. The nucleation rate is governed by both thermodynamic and kinetic factors. During laser annealing, the temperature of annealing is considerably higher (>950 K) than furnace annealing (823 K), as evident from the thermal model (Figure 9). Furthermore, diffusion in amorphous materials is governed by the amount of available free volume. During furnace annealing, diffusion as well as annihilation of free volume (relaxation) takes place

FIG. 10. (a) Hysteresis curves (b) schematic showing temperature dependence of nucleation and growth rate.

TABLE II. Comparison of magnetization values.

Process	Supercells configuration	Nearest neighbor configuration	Magnetic moment (μ)	Average moment per cell (μ)	Normalized magnetic moment (emu/gm)	Experimental value
Furnace annealing 20at% Si	4 cells with 13Fe 3Si	5 Fe atoms with 0 Si atoms as NN	11	22.064	153.341	155
		13 Fe atoms with 3 Si atoms as NN	12			
	1 cell with 12Fe and 4 Si	4 Fe atoms with 0 Si atoms as NN	8.8			
		12 Fe atoms with 4 Si atoms as NN	9.52			
Laser annealing 15 at. % Si	2 cells with 13Fe 3Si	5 Fe atoms with 0 Si atoms as NN	11	25.76	173.98	175
		13 Fe atoms with 3 Si atoms as NN	12			
	3 cell with 14Fe and 2 Si	6 Fe atoms with 0 Si atoms as NN	13.2			
		8 Fe atoms with 2 Si atoms as NN	14.4			

simultaneously. In contrast, laser annealing involves rapid heating rates and generation of localized thermal stresses that in turn increases the amount of available free volume.²⁹ Thus, diffusion during laser annealing is enhanced compared to furnace annealing. In addition, the precipitate size in a microstructure depends on both nucleation rate as well as growth rate. During crystallization, the temperature (T_{Imax}) at which maximum nucleation rate occurs is observed at intermediate temperatures between T_m (melting temperature) and T_g (glass transition) as shown in the schematic (Figure 10(b)). This is attributed to lower thermodynamic driving force at very high temperatures and lower atomic mobility for lower temperatures¹⁹ (Figure 10(b)). In contrast, the temperature at which the maximum growth rate (T_{Umax}) occurs is above maximum nucleation rate temperature (T_{Imax}) and just below melting temperature (T_m) (Figure 10(b)). Thus in laser annealing, the nucleation rate is much higher relative to the growth rate where as in furnace annealing, the nucleation rate is lower compared to growth rate as shown in the schematic (Figure 10(b)).

Both thermodynamic and kinetic factors favor faster diffusion for increased nucleation density. This increase in nucleation density results in the overlap of diffusion fields, resulting in soft impingement and as a consequence, finer crystallite size is achieved. In multi-pass laser annealing, considerable amount of re-heating takes place (Figure 9(b)) during subsequent laser passes, resulting in further growth and nucleation of new precipitates. This results in a wide size distribution of precipitates (~ 25 – 200 nm) (Figures 4(a)–4(d)) across the laser track with a mean precipitate size of 70 nm. The precipitate size has a very strong influence on the magnetic properties like coercivity.

The coercivity is strongly influenced by the grain size (D), it has a D^6 relationship till the threshold size (ferromagnetic exchange length) and changes to $1/D$ for grain sizes greater than the ferromagnetic exchange length.⁷ It is reported by many researchers that the precipitate size within the ferromagnetic exchange length (typically ~ 30 nm) has zero anisotropy based on the random anisotropy model.⁸ In the present case, larger precipitates (with size more than the ferromagnetic exchange length) possess significant magneto-crystalline anisotropy and hence contribute to the increase in coercivity. Furthermore, the presence of Fe_2B also contributes to coercivity due to higher magnetocrystalline anisotropy. In addition to coercivity, as mentioned earlier, the remnant magnetization (moment at $B = 0$) remains

the same (~ 65 emu/gm) for both furnace and laser annealed samples, as indicated by the arrow in the hysteresis plot (Figure 10). It has been reported³⁷ that formation of Fe_2B is the major contributing factor for increase in remanence due to higher magnetocrystalline anisotropy value (430 kJ/m^3)³⁷ compared to $\text{Fe}(\text{Si})$ (8 kJ/m^3). Thus, a small amount of Fe_2B result in substantial increment in remanent magnetization. Hence, it is speculated that the volume fraction of Fe_2B phase to be same in both furnace and laser annealing. Although remanent magnetization remains same, the M_r/M_s value for laser annealed is less (0.37) compared to furnace annealed (0.42) sample indicating better softmagnetic behavior for the former case. This is attributed to higher M_s (Table I) value of laser annealed sample due to less Si partition as explained earlier.

Furthermore, it has been previously proven by Lorentz microscopy that the presence of iron borides acts as domain wall pinning centers, thereby strongly increasing coercivity.³⁸ During the formation of primary $\alpha\text{-Fe}(\text{Si})$ crystallite dendrites in furnace annealed sample, boron is rejected into the amorphous matrix due to very low solubility of boron in the $\alpha\text{-Fe}(\text{Si})$ phase.³⁹ This results in the enrichment of boron at the interface between the crystalline dendrite and amorphous matrix, resulting in the pinning of domain walls during magnetization. This explains the high coercivity for furnace-annealed samples. As annealing progresses, more boron gets enriched into the amorphous phase and finally results in the formation of Fe_2B . Furthermore, as pointed out earlier, furnace-annealed samples developed a dendritic microstructure, whereas the crystallites in the laser-annealed samples exhibited equiaxed morphology. This could be due to less partitioning of silicon, the partitioning has an influence on the interface stability. Thus, shape anisotropy factors may further increase the coercivity of the furnace-annealed samples. Hence, the increase in coercivity of furnace annealed samples can be explained based on Fe_2B formation, crystallite size and morphology and the increase in saturation magnetization for laser annealed samples can be attributed to less partitioning of Si.

Future work will be aimed at designing efficient heat transfer strategies during laser-annealing to obtain a finer grain size and retain a lower coercivity with substantial increases in the saturation magnetization. The present work demonstrates that laser processing can also be utilized to generate patterned nano-structures by direct laser irradiation without using masks. It is clearly indicative from the current work that shape of the laser beam plays a crucial role in

altering the microstructure at a very fine scale (Figures 3(b)–3(d)). This phenomenon can be extended to generate variety of patterned nano-structures by shaping the laser beam according to the requirement.

V. CONCLUSIONS

In conclusion, laser annealing resulted in significant crystallization of amorphous ribbons and enhanced saturation magnetization compared to the as received ribbon as well as furnace-annealed samples. The XRD and TEM based analyses revealed the formation of the BCC α -Fe(Si) and Fe₂B phase in both laser and furnace annealed samples. Silicon partitioning into α -Fe phase for furnace annealed sample was higher (~20 at. %) compared to that in laser annealed samples (~15 at. %). The peak temperatures achieved during laser processing, both within the laser track as well as in between these tracks, exceeds the crystallization temperature, as predicted by our heat transfer model. The enhancement in magnetic properties in the case of the laser-annealed samples can be attributed to a finer grain or crystallite size as well as less silicon partitioning into the α -Fe(Si) crystallites.

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