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ABSTRACT
Nanocrystalline soft magnetic materials are known to be prepared by primary crystallization of Fe-based amorphous precursors. Since the crystallization reaction is exothermic, the amorphous precursor may experience a temporary rise in its temperature relative to its surroundings during the process of nanocrystallization. Given that typical latent heat of primary crystallization (∼100 kJ/kg), this temperature rise may exceed hundreds of degrees if not adequately controlled and thus, lead to the formation of unwanted magnetically hard compounds. This effect is generally small for isolated ribbons annealed with a moderate heating rate. However, the recent adoption of high heating rates and short annealing times has caused the self-heating effect to become relevant even for small sample sizes. In this work, the effect of self-heating on the microstructure and magnetic properties of nanocrystalline Fe86B14 is investigated. It is found that magnetically hard Fe-B compounds cannot be avoided when annealing under vacuum in an infrared furnace with a heating rate ≥3 K/s due to the self-heating effect. However, the high thermal conductivity of the copper blocks used by the ultra-rapid annealing process can successfully prevent a self-heating induced temperature rise during annealing, avoiding unwanted compound formation. Finite Element Analysis is also used for predicting the extent of self-heating during infrared annealing.

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I. INTRODUCTION
Nanocrystalline soft magnetic materials are produced by the crystallization of amorphous precursors. It is well known that during crystallization the release of latent heat acts to raise the temperature of a material above that of its surroundings. If this self-heating effect raises the temperature of an amorphous precursor above the onset temperature of unwanted magnetically hard phases, such as Fe2B or Fe5B in an Fe-B based alloy system, magnetic softness will be lost. The self-heating effect is given to be well understood by those working with large magnetic cores, which have a low specific surface area, as is common for commercial scale production. However, there has been little discussion of the self-heating effect in academic literature. This is likely due to the high specific surface area and small batch sizes of samples that are annealed at research scale. Recently, it has been shown that through increasing the heating rate and reducing the annealing time the microstructure and magnetic softness of some nanocrystalline alloys can be significantly improved. The use of high heating rates and short annealing times has led to the self-heating effect now becoming relevant even at research scale. For example, it was reported that a moderately sized magnetic core (19 mm OD, 15 mm ID, 5 mm thickness) of Fe86.8Cu1.0Mo0.2Si4B14 was required to be pre-annealed in order to obtain primary crystalline grains prior to a final annealing process so as to prevent the precipitation of Fe-B compounds due to self-heating.
In this study, the effect of self-heating during nanocrystallization on the microstructure and magnetic properties of Fe$_{86}$B$_{14}$ is investigated. The maximum heating rate which can be used during annealing of a single ribbon sample under vacuum without inducing magnetically hard compounds is explored using a conventional infrared (IR) annealing furnace. The self-heating effect is also explored for an ultra-rapid annealing process where pre-heated copper blocks are utilized. Lastly, Finite Element Analysis (FEA) is employed to estimate the extent of self-heating expected during IR annealing.

II. MATERIAL AND METHODS

A precursor amorphous ribbon with a nominal composition of Fe$_{86}$B$_{14}$ was produced by melt spinning (planar flow casting method) in an Ar atmosphere. A ribbon thickness of 15 μm was obtained with a width of 12.8 mm. Crystallization onset temperature and latent heat of crystallization was estimated by Differential Thermal Analysis (DTA) using a Perkin Elmer DTA7 calibrated with a 5N Al standard. Annealing was conducted using an Ulvac MILR-5000 infrared furnace under reduced pressure of less than 10$^{-3}$ Pa, with samples located inside a 10 μm Cu foil packet placed approximately 5 mm away from the temperature controller’s thermocouple. Ultra-rapid annealing was conducted in an Ar atmosphere with ribbons placed inside 10 μm thickness Cu foil packets. These packets were then compressed between two pre-heated Cu blocks (150 mm long, 50 mm wide) for 0.5 s with a force of 950 N using a pneumatic cylinder and an automated timing mechanism. A detailed description of the rapid annealing setup and heating rate estimation can be found elsewhere.

X-ray diffraction (XRD) patterns were acquired with a Bruker D8 diffractometer using a Co Kα source. Coercivity was estimated using a Riken BHS-40 DC hysteresis loop tracer. All measurements were conducted at 295 K. FEA was conducted using Ansys Workbench (V19.2) software package with the transient thermal analysis system working in conjunction with external data handling scripts written in Interactive Data Language (IDL).

III. RESULTS AND DISCUSSION

A two stage crystallization process has been observed by DTA (0.67 K/s) for amorphous Fe$_{86}$B$_{14}$. As is well established, the primary crystallization of magnetically soft bcc-Fe was seen to be followed by the formation of magnetically hard Fe-B compounds. The first ($T_{c1}$) and second ($T_{c2}$) crystallization onset temperatures were seen to be 666 K and 760 K respectively. The latent heat of crystallization released by primary ($\Delta H_1$) and secondary ($\Delta H_2$) crystallization was estimated at 120 kJ/kg and 88 kJ/kg respectively. The size of $\Delta H_1$ is comparable to that measured for other nanocrystalline alloys such as Fe$_{82}$Co$_{10}$Si$_6$B$_{12}$P$_3$Cu$_{0.6}$ (88 to 110 kJ/kg), Fe$_{83}$Nb$_3$Si$_4$B$_{12}$ (75 kJ/kg) and Fe$_{89}$Co$_{10}$Nb$_3$B$_{16}$ (130 kJ/kg). The first ($T_{c1}$) and second ($T_{c2}$) crystallization onset temperatures were seen to be 666 K and 760 K respectively. The latent heat of crystallization released by primary ($\Delta H_1$) and secondary ($\Delta H_2$) crystallization was estimated at 120 kJ/kg and 88 kJ/kg respectively. The size of $\Delta H_1$ is comparable to that measured for other nanocrystalline alloys such as Fe$_{82}$Co$_{10}$Si$_6$B$_{12}$P$_3$Cu$_{0.6}$ (88 to 110 kJ/kg), Fe$_{83}$Nb$_3$Si$_4$B$_{12}$ (75 kJ/kg) and Fe$_{89}$Co$_{10}$Nb$_3$B$_{16}$ (130 kJ/kg).

Figure 1a displays the coercivity ($H_c$) of Fe$_{86}$B$_{14}$ after annealing under reduced pressure in an IR furnace with heating rates of 0.3, 1, 3 and 10 K/s. Note that the temperatures listed is the set point of the furnace. Figure 1b displays the lowest $H_c$ obtained after the onset of primary crystallization with respect to heating rate for samples annealed by IR furnace under reduced pressure and by copper block ultra-rapid annealing.

Figure 2 displays XRD patterns acquired from the samples annealed at selected temperatures (IR furnace set point) with heating rates of a) 0.3 K/s, b) 1 K/s, c) 3 K/s and d) 10 K/s.

From Figs. 1a and 2 it is seen that a similar trend is established for heating rates of 0.3 and 1 K/s. At lower annealing temperatures, $H_c$ is less than 10 A/m and an amorphous microstructure is maintained. At intermediate annealing temperatures $H_c$ increases to between 100 and 300 A/m and a bcc-Fe phase is observed along with a residual amorphous phase. Note that poor magnetic softness is expected after primary crystallization for Fe-B alloys annealed at these heating rates as the resultant grain size is larger than the exchange length. At the highest annealing temperatures, $H_c$ abruptly increases to more than 1000 A/m and magnetically hard Fe-B compounds are observed. This progression of $H_c$ and microstructure with annealing temperature is seen to be different for the higher heating rates of 3 and 10 K/s. For these higher heating rates $H_c$ is seen to sharply increase from less than 10 A/m to more than 1000 A/m over a narrow temperature range of 10 K. Furthermore, it can be seen from Fig. 2c and 2d that the structure of the as-cast ribbon now
transitions from an amorphous phase to bcc-Fe + Fe-B compound phases, with no indication of an intermediate bcc-Fe and residual amorphous microstructure.

The microstructural progression observed by XRD in Fig. 2 can be summarized as the following:

- For heating rate ≤ 1 K/s: **Amorphous → Amorphous** + bcc-Fe → bcc-Fe + Fe-B compounds,
- For heating rate ≥ 3 K/s: **Amorphous → bcc-Fe + Fe-B compounds**,

where amorphous* is the B enriched residual amorphous phase seen after the onset of bcc-Fe.

The microstructural progression of amorphous Fe86B14 is well understood and is known to follow that seen for heating rates ≤ 1 K/s in Fig. 2. Therefore, the ribbons annealed with heating rates ≥ 3 K/s must also transition through an amorphous* + bcc-Fe microstructure prior to the formation of Fe-B compounds. As this is not seen for heating rates ≥ 3 K/s, it is suggested that the latent heat released during crystallization is sufficient to raise the ribbon temperature above the secondary crystallization onset temperature once primary crystallization of bcc-Fe begins.

From Fig. 1b it is seen that for heating rates beyond 3 K/s $H_C$ increases above 1000 A/m for the IR annealed samples. Alternatively, samples annealed using an ultra-rapid annealing method can experience heating rates five orders of magnitude higher than that of the IR annealing method while still maintaining magnetic softness. As previously described elsewhere, the use of ultra-rapid annealing also leads to a highly refined microstructure and this is the cause of the reduction in $H_C$ shown in Fig. 1b.

Figure 3a displays the measured temperature, as opposed to the furnace set point, of an as-cast and a pre-annealed ribbon as they were heated in an IR furnace under reduced pressure. The pre-annealed ribbon had already undergone both primary and secondary crystallization. The temperatures of the ribbons were monitored (120 Hz sample rate) by a secondary, 20 μm thermocouple, placed in direct contact with the ribbon. The as-cast ribbon is seen to undergo a rapid increase in its temperature at approximately 692 K which is not observed for the pre-annealed ribbon. This increase in the temperature of the ribbon is attributed to the release of latent heat during crystallization as it is not observed by the pre-annealed ribbon.

Figure 3b displays the temperature of two as-cast ribbons which were ultra-rapidly annealed between pre-heated copper blocks while their temperature was again monitored (1 kHz sample rate) by a 20 μm thermocouple placed in contact with the ribbons. One of the two ribbons was placed in direct contact with the copper blocks...
The presence of this peak at 720 K for the insulated ribbon and not for the exposed ribbon suggests that, despite the significantly higher heating rate experienced by the exposed ribbon, the latent heat due to crystallization is rapidly conducted away by the copper blocks and so no partial temperature rise is observed. The high thermal conductivity, the high thermal mass and the intimate contact of the copper blocks may act to provide a path for heat to flow into, and away from the ribbons being annealed. It is likely that for the insulated ribbon the latent heat due to crystallization could not be removed as rapidly which caused the ribbon temperature to rise faster than the trend, leading to the peak observed.

The process of self-heating in an IR furnace under reduced pressure has been simulated using FEA with a transient thermal analysis system. A 20 µm Fe₈₆B₁₄ ribbon with an specific heat of 507 J/kg/K, a length of 120 mm and a width of 13 mm was considered with an initial temperature of 303 K. The ribbon was assumed to be isolated in a perfect vacuum such that radiation is the only form of heat transfer to or from the sample. All surfaces of the ribbon were considered to have a surface emissivity of 0.1. The primary and secondary crystallization onsets (Tₓ₁ and Tₓ₂) of Fe₈₆B₁₄ at 10 K/s were estimated based on our previous in-situ resistivity measurement of amorphous Fe₈₆B₁₄ during rapid heating. The crystallization process of Fe₈₆B₁₄ is simulated by a step-by-step approach with a time period of 0.3 s per step and each step is assumed to be isothermal. The fraction of phase transformation completed in each isothermal step (ΔV₁) was calculated by the JMAK kinetic model which is defined by

\[ V_t = 1 - \exp\left(-K \times t^n\right), \]  

where the rate constant \( K \) is described by

\[ K = \exp\left(\frac{-31.8 \times 10^3}{T + 41}\right) \]

The Avrami exponent \( n = 1.5 \) to 2) and the constants in Eq. (2) were determined experimentally by a series of in-situ resistivity measurements at temperatures between 693 and 733 K for amorphous Fe₈₆B₁₄. For each step, the \( \Delta V_t \) was calculated based on Eq. (1) and then the heat generation rate by primary crystallization is generated. This heat generation rate was then input into the FEA software as a thermal load to calculate the temperature of the ribbon for subsequent simulation step.

Figure 4 displays the simulated temperature profile of an amorphous Fe₈₆B₁₄ ribbon obtained by FEA.

The heat transfer between the ribbon and the heating source of the furnace is simulated by a ‘radiation to ambient’ thermal load where the ambient temperature (dashed line) initially increases from 303 K to 733 K by 10 K/s and is then fixed at 733 K. As the ribbon has a thermal mass there is a delay in the increase of the average ribbon temperature compared to the ambient temperature (IR source) as shown by the solid line in Fig. 4. Primary crystallization begins when the ribbon temperature reaches 700 K. The average ribbon temperature shows a sharp increase at the onset of primary crystallization and exceeds the secondary crystallization onset temperature of 796 K. This sharp increase in ribbon temperature at 796 K is attributed to the latent heat of primary crystallization. As the predicted heat dissipation rate by radiation is slower than the heat generation rate by crystallization, a self-heating effect is seen. The rise
The simulated temperature profile of as-cast Fe$_{86}$B$_{14}$ during IR annealing as estimated using FEA.

in ribbon temperature is seen to exceed $T_{x2}$ and so it is expected that magnetically hard Fe-B compounds would be formed, degrading magnetic softness. The rapid temperature rise due to crystallization is followed by a decrease in temperature as the heat is radiated away to ambient and coincides with the completion of primary crystallization. This FEA simulation agrees with the experimental results as it suggests that an as-cast Fe$_{86}$B$_{14}$ ribbon annealed under vacuum with a heating rate of 10 K/s will experience a temperature rise sufficient to induce the secondary crystallization reaction due to self-heating.

In conclusion, the precipitation of magnetically hard Fe-B compounds could not be avoided during infrared lamp annealing of isolated Fe$_{86}$B$_{14}$ ribbons under vacuum with a heating rate $\geq$ 3 K/s due to the self-heating effect. However, self-heating is seen to be effectively suppressed in the ultra-rapid annealing process by using pre-heated Cu blocks due the high rate of heat removal made possible by this technique.

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The authors declare no competing financial interest.

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