Non-equilibrium materials design: a case study of nanostructured soft magnets for cryogenic applications

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Abstract

Nanocrystalline soft magnetic materials are the latest and most promising of the soft magnetic materials that were developed at the end of the 20th century. They have since been studied extensively, and various alloy compositions have been developed and optimized for ambient and extreme (cryogenic and elevated temperature) applications. Their advantage lies in the unique combination of fine microstructure, crystal structure and composition, which can be achieved by rapid solidification and subsequent controlled annealing. In this article, we discuss the requirements and the challenges of the alloy designing these alloys and how it affects the crystal structure, microstructure and eventually the magnetic performance of new alloys designed for use at temperatures below 150 K in applications as varied as cryo-power electronics and magnetic shielding. The results from our latest studied alloy series are mentioned as an example.

Keywords: alloy design, nanocrystalline soft magnets, crystal structure, magnetic properties
Introduction

A remarkable improvement in the energy efficiency of soft magnetic materials has been achieved over the past century, primarily due to the discovery of better materials (e.g. Si-steels, amorphous, and nanocrystalline alloys), improved processing (including rolling techniques and rapid solidification) and better understanding of the underlying physics of applications (especially magnetic anisotropies and domain switching dynamics). This improvement is manifested by the progressive reduction of core losses in soft magnetic materials over the past 125 years (figure 1). Core losses in soft magnetic materials are the primary figure of merit for applications because they are a measure of the energy lost per switching cycle. Over the first half of the 20th century, core losses of electrical steels (i.e. Fe–Si alloys) were reduced by an order of magnitude by reducing the thickness of laminations, increasing the diameter of Fe–Si grains, and tailoring their crystallographic texture, resulting in better control of magnetic switching in these alloys [1]. Despite these advances, electrical steels used in power transformation and conditioning applications cause losses that equal 5–10% of the electric power generated in developed countries [2].

Seeking alternative materials with lower core losses resulted in the development of rapidly solidified amorphous alloys (e.g. Fe–Si–B) in the 1970s [3, 4]. Due to their high metalloid content (which makes vitrification possible), they possess higher resistivity, enabling their use at higher switching frequencies. The diluted Fe content, however, results in lower saturation magnetization. Attempts to increase the saturation magnetization through partial crystallization of the alloys failed because the grains that formed during the crystallization process were efficient domain wall pinning sites. Even short annealing times at crystallization temperatures as low as 330 °C resulted in grains nearly 100 nm in diameter, a size that interacts most strongly with domain walls (see figure 1(b)) [5]. At the earliest stages of annealing, the grain size might be made small enough to limit interaction with the domain walls, but the number of grains was not sufficient to make a significant impact on the saturation magnetization. In 1988, extensive nucleation was achieved in a modified metallic glass, allowing the formation of a nanocomposite soft magnetic alloy with grains less than 20 nm in diameter and crystallite volume fractions approaching 80% [6]. These alloys consisted of 96% Fe–Si–B (conventional metallic glass) with 1 at% Cu to provide nucleation sites for (Fe,Si) magnetic grains, and 3 at% Nb to limit the grain growth. The result had phenomenally low core losses (see figure 1(a)) and this small deviation in alloy design opened a whole new field of soft magnetic materials research and development.

For the past 25 years, nanostructured soft magnetic materials have been formed using a two-step process of rapid solidification followed by isothermal annealing [7]. The promise of nanocrystalline grains embedded in an amorphous matrix had long eluded the amorphous alloy research community due to two factors. First, when annealing temperatures sufficient to crystallize the alloys were reached, growth occurred rapidly leading to a small volume fraction of large crystalline grains. Second, few nucleation sites were active in the sample at these temperatures, preventing the formation of nanostructured materials. The combined additions of small amounts of a nucleation agent (e.g. Cu) and a grain growth inhibitor (e.g. Nb) resulted in a uniform nanocomposite material with grain sizes of less than 10 nm diameter and with an intergranular amorphous matrix about 2–3 nm in width. Since the development of these alloys in the late 1980s [6], several classes of these alloys have been developed with excellent performance for many magnetic applications [8–10]. The size and weight advantages of using
these materials in high frequency power converters (20 kHz, 2–3 MW) has been demonstrated, resulting in a size reduction of ~98% and loss reduction of ~90% compared to similar technology using Si-steel at 60 Hz [11]. While in large volumes, the costs of the nanocrystalline materials may be as low as 5 $ kg\(^{-1}\) (much greater than the ~2 $ kg\(^{-1}\) for Si-steels), the total materials cost for the application would be significantly lower due to its reduced size [12, 13].

Recent work in our group at the Naval Research Laboratory, and more recently at Case Western Reserve University, has been on the design of new soft magnetic alloys for application in extreme environments. Much of this work is application driven, for service temperatures between ambient and 200 °C for shipboard power applications [14, 15] and at cryogenic temperatures for use in superconducting motor applications [16]. The alloys described in this study were specifically designed for cryogenic applications including magnetic shielding and cryo-power electronics. In the former application, high permeability is a necessity and the latter low core losses are the principal figure of merit. This manuscript describes the alloy design principles we use to discover new alloys (containing Fe, Si, Al, Nb, Cu), featuring the design of cryogenic alloys as an example. The successful development of these alloys requires good glass formability (avoidance of nucleation/growth during quenching), abundant nucleation during annealing, restriction of grain growth, and understanding the partitioning of elements between phases during these processes. In the end, the partitioning and final microstructure dictate the magnetic properties of the resultant material. In many cases, the phase diagrams and results from the literature based on conventionally processed alloys are little help due to the non-equilibrium nature of the nanocomposite alloy processing. Where our alloy design tools fail us will also be discussed in terms of non-equilibrium phase development and unexpected compositional variations, which are largely unavoidable with the tools available today.

**Alloy design principles**

The alloy design principles for the Al/Si substitution was inspired by the work of Takahashi et al on single crystalline and polycrystalline Sendust alloy (7–11 wt% Si, 4–7 wt% Al, bal. Fe) [17, 18]. In their work, Takahashi et al examined the temperature dependence (−78–100 °C) of

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**Figure 1.** (a) Core loss as a function of time [3, 4]. (b) Grain size dependence of core loss for soft magnetic alloys (after Herzer) [10].
magnetocrystalline anisotropy $K_1$ and magnetostriction coefficients ($\lambda_{100}$, $\lambda_{111}$, $\lambda_{110}$) for Fe–Si–Al compositions close to the Sendust composition. They found that the temperature at which $K_1$ or $\lambda_s$ is zero depends sensitively on the Fe–Si–Al composition. Their results are summarized in figure 2. The desirable condition at any service temperature is to minimize the values of $K_1$ and $\lambda_s$ as they are contributors to hysteretic losses. This optimal condition shifts with temperature, requiring substitution of Fe with more Al and less Si as the temperature is lowered from 100 to $-78$ °C. The present study is interested in performance at cryogenic temperatures ($-196$ °C or 77 K). Using a linear extrapolation of the Takahashi et al data to the desired service temperature, we have identified Fe–Si–Al alloy compositions (black dots in figure 2(a)) with potentially near-zero values of $K_1$ and $\lambda_s$ for cryogenic applications.

Most magnetic materials have decreased $K_1$ as the temperature is raised to the Curie temperature. So, it is unusual that a near-zero $K_1$ value is identified at cryogenic temperatures when the Curie temperature is much higher than room temperature, as observed in the Fe–Si–Al alloys described here. The reason for the near-zero $K_1$ value is illustrated in figure 2(b), as the temperature is lowered, the $K_1$ indeed becomes larger, but it changes sign, resulting in a crossing of $K_1 = 0$ at a temperature (see arrows) that varies strongly with the composition of the alloy. Indeed, this feature of the Fe–Si–Al alloy system was exploited as a major factor in the alloy design. This is not a robust way to design an alloy, since small deviations in temperature

**Figure 2.** (a) Schematic diagram of the changes in magnetocrystalline anisotropy and magnetostriction as a function of Si and Al content in Fe–Si–Al alloys (after [17, 18]). The compositions of the (Fe,Si,Al) contents of our alloys are represented by black dots and the solid, straight, black line shows the trend in composition. The lines marked $-196$ °C are extrapolated from the original work from Takahashi. (b) Schematic diagram of the change in magnetocrystalline anisotropy with temperature for three compositions (A, B, C).
can have a large impact on coercivity (and therefore losses), but it is one way to make a very low coercivity alloy at cryogenic temperatures.

A fine-grained microstructure was desired for reduction of the effective magnetocrystalline anisotropy (as explained by the random anisotropy model [19]). It has been shown that excellent magnetic softness can be achieved for alloys consisting of two phases—a nanocrystalline phase with grain less than 15 nm and an amorphous intergranular matrix phase. To achieve this microstructure, rapid solidification processing is used to produce an amorphous alloy followed by isothermal annealing to form the desired microstructure. For this reason, additional constraints on the composition were necessary. Glass-forming elements including metalloids (e.g. Si and B) and early transition metals (e.g. Zr, Nb, and Hf) are necessary to provide stability to the amorphous precursor such that the alloy can be cooled from the melt faster than the atoms can rearrange themselves into equilibrium structures. Deep eutectics have been identified as the best regions for amorphous alloy formation due to the stability of the liquid phase to low temperatures. Other alloy design considerations include using atoms with distinctly different atomic radii and with large relative heats of mixing between components, both of which tend to widen the glass forming composition region [20].

When a fully amorphous alloy is successfully produced, the nanocomposite microstructure can only be produced if a large number of nuclei are present and if the growth of the crystallites is restricted. Previous work has shown that late transition metal elements (especially Cu and Au) segregate during the early stages of annealing, providing the nucleation sites necessary for development of the nanostructure. Early transition metals have been found to restrict the diffusion of the growing nanocrystalline grains allowing a refined grain size. For these reasons, the most successful alloys of the nanocomposite soft magnets formed by rapid solidification consist of many elements [7]. In addition to microstructure evolution concerns, consideration of the application may dictate additional constraints due to environmental, functional, and/or structural considerations. The compatibility of potential alloying additions can be influenced by considering previous work on similar alloy systems or trends in polycrystalline materials (e.g. the Slater–Pauling curve [21] for magnetization or Bethe–Slater curve [22] for exchange interactions), however these approaches are largely empirical.

Using these alloy design principles, several Fe$_{87-x}$Si$_x$Al$_x$Nb$_3$B$_9$Cu$_1$ compositions were chosen. The elements Fe, Si, and Al concentrations were selected based on the extrapolation of the data in figure 2, seeking compositions that minimize hysteretic losses ($K_1$ and $\lambda$, near-zero). Their solute ratios were chosen assuming that the desired crystallite composition matched the nominal composition of the alloy. The remaining elements, Nb, B, and Cu, were included to enable the desired microstructure to be formed. The non-equilibrium processing of the alloys necessarily adds a large degree of uncertainty to the outcome of such alloy design. The expected phases are not necessarily formed during annealing, the compositions of each phase are not easily predicted from the nominal composition of the alloy, and the properties of the alloy are strongly dependent on both of these conditions. The unfortunate result of this uncertainty is a rather inefficient empirical and iterative approach to alloy design.

This manuscript illustrates the alloy design for a new nanocomposite alloy with compositions near those of a commercially available (and well-studied) alloy composition (Fe$_{73.5}$Si$_{13.5}$B$_9$Nb$_3$Cu$_1$, a.k.a. Finemet). Despite the substantial prior work on this related alloy, several complicating factors were discovered during the development of the (Fe,Si,Al)-based alloy described here, resulting in the need for multiple iterations to identify the processing and composition ranges that result in the best performance.
Experimental procedure

Amorphous alloy ribbons with composition Fe$_{87-z}$Si$_z$Al$_x$Nb$_3$B$_9$Cu where (x, z) = (0,13.5), (2, 17), (3.5, 19), (5, 21.5), (6, 22), (6, 23.5), (7, 25), (7.25, 23.75), and (9, 26) were produced using a single roller melt-spinner at 50 m s$^{-1}$ and an orifice of 0.75 mm in a He environment. Samples with ribbon morphology were produced with a thickness of about 20 mm, width of 2 −3 mm, and lengths between a few centimeters and several meters. The as-spun ribbons were isothermally annealed at 475, 500, 525, 550 or 750 °C for 3.6 ks in an argon atmosphere and then quenched rapidly in water. The crystallization process was examined by differential thermal analysis using a TA Instruments SDT2960 with a heating rate of 0.333 K s$^{-1}$. The crystal structure of as-spun and annealed ribbons were examined by a Philips APD 3520 x-ray diffractometer (XRD) and a Scintag X-1 using Cu Kα radiation. From the XRD patterns we calculated the lattice constants of the crystalline phase (by fitting the diffraction peaks and using the cos$^2 \theta$/sin \( \theta \) method) and the grain size (using the Scherrer equation) [23].

Atom probe tomography (APT) was performed using a Cameca local electrode atom probe (LEAP) system [24]. Needle-shaped samples were prepared directly from annealed ribbons of each composition using standard focused ion beam milling techniques [25]. Field evaporation of the sample was performed with either voltage pulsing or laser pulsing (one sample for each method per composition) under vacuums better than 10$^{-10}$ torr at a specimen temperature of 80 K. The pulsed laser system used a UV laser with a wavelength of 355 nm. Both techniques used a 200 kHz pulse repetition rate and less than 10 ps pulse duration. Voltage pulsing resulted in smaller data sets (<500 k atoms per sample) with good mass resolution, while laser pulsing provided large data sets (5−20 M atoms per sample) with limited mass resolution. Analysis of the data was performed using the Camica Integrated Visual and Analysis Software allowing the determination of grain compositions using proximity histograms and isoconcentration surfaces.

The magnetic hysteresis loops and thermomagnetic measurements were measured using an ADE Model 4HF and a Lakeshore cryotronics model 7410 vibrating sample magnetometer. The hysteresis loops of the samples annealed at 550 °C were measured at temperatures between 77 and 300 K and with applied fields up to 1.592 MA m$^{-1}$. In order to measure the extremely small coercivity values observed in our samples, the VSM allowed us to use a 16 A m$^{-1}$ field increment near zero field and the data points were interpolated to zero to determine the coercivity. In addition, each piece was measured five to ten times and an average value was obtained. Thermomagnetic measurements were conducted under an applied field of 318.4 kA m$^{-1}$ from 25 to 500 °C.

Results and discussion

The crystallization behavior of the as-spun alloys occurs in at least two steps (see [26] for details). During primary crystallization (i.e. devitrification of the first crystalline phase), ferromagnetic nanocrystallites form within the amorphous matrix, resulting in improved magnetic properties. Crystallization at higher temperatures destroys this fine grained microstructure resulting in deteriorated properties. The equilibrium phase diagram suggests that a cubic phase with D0$_3$ ordered phase (BiF$_3$ crystal structure) will form during primary crystallization for the (Fe$_{87}$-zSi$_z$Al$_x$) content of our alloys. Indeed, this D0$_3$ phase is typically observed for the Finemet composition, (Fe$_{0.855}$Si$_{0.155}$)$_{87}$Nb$_3$B$_9$Cu$_1$, which is similar to the
alloys described in this study (i.e. (Fe,Si,Al)_{87}Nb_{3}B_{9}Cu_{1}) [7]. Because these alloys are produced by non-equilibrium methods, however, other competing phases are possible, including ones that are not observed at this composition in equilibrium. The other potential primary crystalline phases found on the Fe-rich side of the (Fe,Si,Al) phase diagram include the cubic phases with A2 (body centered cubic–BCC) and B2 (CsCl crystal structure) crystal structure. These competing phases can be distinguished by powder x-ray diffraction methods. Ordered arrangement of the Si and Al atoms in the B2 and D0₃ crystallites exhibits additional diffraction peaks (superlattice reflections) compared to the solid solution (e.g. in the A2 phase). These differences are illustrated in more detail in [7].

Close examination of the x-ray diffraction patterns obtained from ribbons annealed at temperatures exceeding the primary crystallization temperature (but not secondary crystallization) reveals a variation in the observed crystal structure for a given alloy composition. This is illustrated in the alloy containing 7.25% Al (see figure 3), where three different crystalline phases are observed depending on the annealing temperature over a temperature range of about 75 °C. Similar results are observed for the other compositions in this study. At the lowest annealing temperatures (475 and 500 °C), a solid solution with A2 structure is observed due to the presence of only the fundamental Bragg reflections (see figure 3 at 475 °C), indicating that
the Fe, Si, and Al are interchangeable in the structure. At the highest annealing temperatures (525 and 550 °C), reflections from the D03 phase are observed, indicating a large degree of atomic ordering and an approach to the equilibrium crystal structure expected for this nominal alloy composition. The D03 phase is identified by the presence of at least the (111) and (200) diffraction peaks, near 25–35° two theta (see figure 3, 550 °C). At intermediate temperatures, reflections from the B2 phase are observed, as indicated by the presence of the (200) superlattice reflection (again labeled with reference to the D03 structure), but absence of the (111) superlattice reflection. The amounts of various phases can be deduced by the relative intensity variation of the peaks. In the case of the sample in figure 3, a combination of A2 and B2 phases is observed in the sample annealed at 500 °C and B2 and D03 phases are found in the sample annealed at 525 °C. This variation in observed crystal structure with annealing condition is generally observed for all the compositions studied, with greater variety of phases over larger ranges of annealing temperature observed for samples containing more Al. The fact that the degree of atomic order is complex in these alloys can have a substantial impact on the observed properties and limits the predictive nature of our alloy design!

Our alloy design was based on specific desired Fe–Si–Al ratios in the ferromagnetic crystallites (figure 2), and determining these compositions in the final alloys is essential for understanding (and improving upon) the observed magnetic properties. Measuring the change in lattice parameter with composition (and annealing condition) can help to identify the composition of the crystalline phase in alloys with less complexity (using Vegard’s law [23] for instance). This approach fails for several reasons in these nanocrystalline alloys. First, the small size of the grains causes Scherrer broadening [23] in the diffraction peaks, which reduces their intensity and gives larger error during analysis. Secondly, all of the samples experiencing only primary crystallization have a majority two-phase microstructure [26], each phase with distinctly different composition (due to the preferential segregation of elements during annealing). Finally, even in alloys without the complication of order–disorder transformations a dilution of the lattice parameter is observed which has been attributed to dissolution of large early transition metal atoms and/or stress effects from the ~1–2% density difference between the nanocrystallites and the parent amorphous phase [27, 28]. Combined, these effects preclude the use of XRD for compositional analysis. Energy dispersive x-ray techniques in the transmission electron microscope have proven equally challenging due to the fine grain size and the resultant problems with producing thin foils having single grains in the through-thickness, thereby isolating contributions from each phase in the microstructure. For these reasons, we have employed APT for compositional analysis of the alloys’ constituent phases. In concert with transmission electron microscopy (see [16, 26] for details), these complementary techniques provide invaluable information about the microstructure, distribution of phases, and composition of our nanocomposite samples (for example, see [29]).

The APT reconstructions shown in figure 4 illustrate the segregation of elements in the three phases illustrated in the schematic figure 5, namely: (1) primary crystallites, (2) copper nucleants, and (3) residual amorphous matrix. Analysis of these reconstructions shows strong partitioning of B and Nb to the amorphous matrix phase and slight partitioning of the Fe and Si to the nanocrystalline phase. This behavior is expected based on prior APT studies on (Fe,Si)-based nanocrystalline alloys [30, 31]. The strong segregation of Al to the Cu-rich precipitates (see figure 4) was, however, unanticipated. The Cu-rich precipitates are only about half Cu, containing about 40% Al, and 5–6% Si. Some uncertainty in the labeling of Al atoms occurs due to the charge-to-mass ratio similarity between Al$^{27}$ and Fe$^{54}$. This significantly changes the
concentration of Al, and to a lesser extent Si, in the magnetic phases in our sample and results in
a strong deviation from the nominal composition of the alloy and departure from our intended
alloy design. Warren et al observed similar partitioning of Al and Fe to the Cu-rich clusters in a
Fe\textsubscript{71.5}Si\textsubscript{13.5}Al\textsubscript{2}Nb\textsubscript{3}B\textsubscript{9}Cu\textsubscript{1} alloy annealed at 480 and 520 °C [32].

Using a model for the solute segregation first proposed by Herzer [33] on Fe–Si–Nb–B–Cu alloys, we added the effect of substitution of Al to be consistent with the APT analysis. Of all

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Atoms within a \textasciitilde10 nm thick slice, cut perpendicular to the analysis direction, from an APT analysis volume of 69 nm in diameter and 277 nm long containing 22.5 M atoms of a Fe\textsubscript{65.5}Si\textsubscript{16.5}Al\textsubscript{3}Nb\textsubscript{3}B\textsubscript{9}Cu\textsubscript{1} alloy annealed at 550 °C for 3.6 ks. The data were obtained by laser pulsing.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Schematic diagram of the microstructure evolution of the nanocrystalline soft magnetic alloy Fe\textsubscript{73.5}Si\textsubscript{13.5}B\textsubscript{9}Nb\textsubscript{3}Cu\textsubscript{1}.}
\end{figure}
alloying elements, Si was found to most strongly segregate to the crystalline phase, so a minimum threshold of 16 at% Si was used to delineate the nanocrystalline regions from the amorphous and Cu-rich precipitate phases. The shape and size of the resulting thresholded regions were comparable to the shape and size of grains determined by TEM (compare figure 4 to [26]), suggesting that the threshold was taken at an appropriate level. From this observation, the following equation was used to estimate the composition of the crystalline and amorphous phases:

\[
(1 - v_{\text{Cu}}) \left[ v_{\text{cr}} \left\{ \text{Fe}_{1-x}\text{Si}_{z-x}\text{Al}_x \right\} + (1 - v_{\text{cr}}) \left\{ \left( \text{Fe}_{1-a}\text{Nb}_{a}\right) \text{B} \right\} \right] + v_{\text{Cu}} \left\{ \text{Cu}_{0.35}\text{Al}_{0.39}\text{Si}_{0.06} \right\}
\]

where, \(v_{\text{cr}}\) and \(v_{\text{Cu}}\) are the volume fractions of crystalline and Cu-rich phases respectively, \(x\) is the Al content, \(z\) is the Si + Al content, and \(a = n^{-1}(\lambda_{\text{Nb}}/\lambda_{\text{B}})\). From this analysis, the average composition of thresholded regions was determined and used in the analysis of intrinsic magnetic properties for the crystalline phase.

The Curie temperature of the alloys were identified from thermomagnetic measurements using a vibrating sample magnetometer. In these alloys, the Curie temperature of the amorphous phase is much lower than that of the crystalline phase, allowing for an accurate independent measure of the crystalline phase Curie temperature, since the amorphous phase at such elevated temperatures is paramagnetic. A summary of the results is presented in figure 6, where data from the series of alloys we produced in this study (circles) are compared with data from the literature (squares), where crystalline compositions were estimated from lattice parameters. The Al/Si ratio of the crystalline phase (from the composition model) is marked for alloys containing both Si and Al in the nanocomposite alloys. The Curie temperatures of binary (Fe,Si) and (Fe,Al) alloys are also shown, indicated by dashed and solid lines, respectively. The trend of reduction in crystalline phase Curie temperature with increased amounts of Si + Al is
obvious, however the subtle change in slope is consistent with the Al/Si ratio for the crystalline phase (keeping in mind that Al has a strong enthalpy of mixing with Cu during the early stages of crystallization).

Remarkably, the Curie temperature of binary alloys (shown in figure 6) has not been reported to have a strong dependence on the degree of order. However, this is not the case for the coercivity of the nanocomposite alloys described in this paper. Coercivity ($H_c$) is an extrinsic magnetic property which is strongly influenced by the magnetocrystalline anisotropy ($K_1$) and magnetostriction ($\lambda$) present for the phases in the nanocomposite and it affects the hysteretic losses of these materials. The random anisotropy model has been successfully applied to nanocrystalline alloys, with a resultant reduction in coercivity with grain size ($D$):

$$H_c = p \frac{K_1D^6}{\mu_0M_S A}$$

where $A$ is the exchange stiffness, a constant that is near $10^{-11}$ J m$^{-1}$ for Fe–Si–Al based alloys (largely independent of composition) and $p$ is a proportionality constant near 0.5. The magnetocrystalline anisotropy is quite sensitive to composition and crystal structure.

As demonstrated in figure 3, the structure of the nanocrystalline grains that form is strongly dependent on annealing temperature, with D03, A2, or B2 structures possible. In (Fe,Si)-based nanocrystalline alloys, the D03 phase provides the smallest coercivity and the best magnetic performance and the same is true for the (Fe,Si,Al)-based alloys in the present study. The A2 phase tends to provide a moderate coercivity, however the D03 phase exhibits the lowest coercivity. Despite having smaller grain diameters on average, samples containing the B2 phase always show much higher coercivity (see figure 7). Figure 7 summarizes our findings of crystal structure, coercivity, saturation magnetization, and grain size as a function of annealing temperature and Al content. The coercivity values are presented in A m$^{-1}$, magnetization in Am$^2$ kg$^{-1}$ and grain size in nm.

As the purpose for this work was the development of new soft magnetic materials for cryogenic applications, figure 8 presents results for the application service temperatures of interest (between 100 and 150 K). We measured each sample five to ten times to get an average value of coercivity with small error bars. The smallest value of coercivity was observed for Fe$_{63.25}$Si$_{16.5}$Al$_{7.25}$B$_9$Cu$_1$ at both 100 and 150 K. The estimated composition of the nanocrystallites using the composition model for 75% crystalline phase is Fe$_{69.4}$Si$_{21.9}$Al$_{8.7}$ for this alloy. This value is remarkably close to the extrapolated value from figure 2(a), although it is richer in Si than the estimate. The sometimes strong variation of coercivity with temperature is attributed to the sometimes strong variation of magnetocrystalline anisotropy with temperature. Figure 2(b) illustrates the variation of the near-zero value of magnetocrystalline anisotropy for various compositions (marked in figure 2(a)) and temperature. The rate at which the magnetocrystalline anisotropy varies through zero and the temperature where this occurs are both important to the variation of coercivity with temperature. The saturation magnetization varies in a more predictable and expected way (figure 8(b)). As more Si and Al are substituted for Fe, the Curie temperature drops and the saturation magnetization also drops. At 100 and 150 K, the magnetization is noticeably higher as a result of less thermal fluctuations at these temperatures. For reference in our previous work [16], the coercivity and saturation magnetization for Finemet (Fe$_{73.5}$Si$_{13.5}$Nb$_3$B$_9$Cu$_1$) are 139.5 Am$^2$ kg$^{-1}$ and 0.52 A m$^{-1}$ at RT [16] and 156.6 Am$^2$ kg$^{-1}$ and 0.92 A m$^{-1}$ at 150 K, respectively.
Figure 7. Diagram showing the coercivity (inset values) and grain size (dashed contours) variation of (Fe,Si,Al)\(_{87}\)Nb\(_3\)B\(_9\)Cu\(_1\) alloys with varying Al content and annealing temperature (3.6 ks). The sample with 0 at% Al has the composition Fe\(_{73.5}\)Si\(_{13.5}\)Nb\(_3\)B\(_9\)Cu\(_1\) (Finemet composition).

Figure 8. (a) Coercivity as a function of Si + Al content for Fe\(_{72-x-y}\)Si\(_{15+x}\)Al\(_x\)Nb\(_3\)B\(_9\)Cu\(_1\) alloys annealed at 550 °C for 3.6 ks and measured at 100, 150, and 295 K. (b) Saturation magnetization as a function of Si + Al content measured at 100, 150, and 295 K. The inset shows a typical hysteresis loop for these samples (coercivity too small to see on this scale).
In equilibrium, all of the alloys shown in figure 7 would have the D0₃ structure (among minority Fe₂B, Fe₃B, etc) due to the composition being near the 3:1 ratio of Fe:Si+Al). The non-equilibrium processing that enables the nanocomposite microstructure to form in these alloys also enables the formation of non-equilibrium primary crystallites. With a better fundamental, predictive capability provided by improved thermodynamic databases, not only would we know when these phases are likely to form, but we would also be able to design non-equilibrium phases into the alloys. This may be especially important to the development of advanced permanent magnet materials where stable phases with improved performance have been elusive despite extensive searches for new phases with better performance than rare earth transition metal based compounds [36, 37].

Conclusions and outlook

A design cycle for nanocomposite magnetic alloy development has been shown to have difficult predictability. With improved predictive tools, including better thermodynamic databases for CALPHAD-type approaches involving novel alloy systems, and property databases for identification of compositions of interest, the design cycle will be less empirical and more predictable, resulting in greater success rates and higher percentages of success for alloy design experiments.

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