Enhancement of soft magnetic properties by nanocrystallization in modified cast iron

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Abstract

A cast iron composition has been modified by additions of Al, B, Y and Cu to the Fe–C master alloy in order to achieve glass forming ability as well as good magnetic properties. Amorphous ribbons were synthesized by rapidly quenching at 10⁶ K/s and the devitrification process was controlled by varying the Y and Cu contents so as to achieve a composite structure of bcc Fe nanocrystals in an amorphous matrix. An improvement of saturation magnetization was observed by annealing the as-quenched ribbons. However, coercivity does not necessarily improve upon annealing, and therefore, the annealing should be judiciously scheduled. Effect of minor impurities in cast iron on the coercivity and saturation of these alloys was found to be insignificant.

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1. Introduction

In the past two decades, considerable research has been dedicated to the development of ferromagnetic amorphous alloys [1]. These alloys have short-range structural order, but still possess a long-range magnetic order. Due to the random atomic arrangement the short-range local magnetocrystalline anisotropies are averaged to zero over large atomic distances. An exchange coupling among the local moments exists and causes the long-range magnetic ordering. Once magnetocrystalline anisotropy is set to zero, the processing can be adjusted so as to minimize shape and stress anisotropies and obtain a truly soft-magnetic component.

In some alloys, further enhancement is possible with the introduction of nanocrystals in the pre-existing amorphous matrix [2]. By keeping the size of the crystals smaller than the ferromagnetic exchange length, the randomly distributed anisotropies of the homogeneously distributed nanocrystals continue to average out. In Finemet [2], this two-phase composite structure leads to compensation of magnetostriction (between crystalline and amorphous phases) and reduced magnetoelastic energy, thereby giving coercivity ($H_c$) values that are even lower than the as-quenched amorphous alloy. In this case, the optimal annealing treatment is designed to balance volume percentage of nanocrystals to achieve minimum coercivity. Furthermore, the nanocrystals are strongly exchange coupled leading to higher magnetization saturation.

In the present work, these ideas have been applied to a modified Fe-based alloy that was synthesized from a commercially available cast iron. The effects of Al, B, Y and Cu addition to a Fe–C (cast iron) alloy for forming an amorphous alloy composition with good soft magnetic properties was investigated. The effect of annealing on the magnetic behavior was also studied.

2. Experiment

A commercial grade cast iron (FC25) of analyzed composition Fe₈₁.₈₃C₁₂.₉₀Si₃.₆₄Mn₀.₇₄P₀.₀₅S₀.₁₂Cr₀.₁₁Cu₀.₆₁ (concentration expressed in atomic percentages) was used as a Fe–C master alloy. This result in trace elements including Mn, P, S and Cr (treated as impurities).
For the synthesis of the Fe–(Al,C,B,Si)–(Y,Cu) alloys, the Fe, C, Si and Cu are already present in the cast iron, while the remaining components that are added (viz. Al, B, Y, additional Fe and Cu) are of 99.99% purity. Ingots of desired composition were arc melted in an argon atmosphere and a homogeneous composition was achieved. It will be shown that impurities from the commercial cast iron do not significantly affect the soft-magnetic behavior.

The ingots were then induction melted in a quartz tube and argon atmosphere and injected onto a copper wheel rotating at 40 m/s (single roll melt spinning). In this way, a rapid quenching at $10^5$ K/s was achieved, necessary to form amorphous ribbons of about 3 mm width and 20 µm thickness.

Differential Scanning Calorimetry (DSC) (Diamond, Perkin Elmers, USA) was done to study the thermal properties and determine the glass transition temperature, $T_g$, crystallization temperature, $T_x$ and thereby estimate an optimal annealing temperature, $T_a$. The ribbons were annealed at this temperature in a vacuum furnace.

The magnetic properties namely, saturation magnetization ($M_s$) and coercivity ($H_c$) was determined using a Vibrating Sample Magnetometer (VSM) (VSM-5, TOEI, Japan).

3. Results and discussion

As mentioned earlier, an amorphous structure leads to some unique magnetic properties that can be understood based on the absence of long-range order. However, even in the absence of LRO in amorphous alloys, the local atomic arrangement can often result in short-range order (SRO) that is representative of the equilibrium crystal structure [3]. Thus, there exists a randomly directed local magnetocrystalline anisotropy, which averages to zero over longer distances. Further, the local moments associated with the SRO are assumed to be exchange coupled [3,4]. The competing forces of local anisotropy, that tends to randomly orient the moments and the exchange interaction that tends to align the moments leads to a critical magnetic correlation length that is nearly 20 µm in 3d-base amorphous alloys [4]. Thus, nano-sized crystals that are nucleated within the magnetic correlation length are exchange coupled and continue to have their moments aligned.

In purely amorphous structure, the local anisotropy determines the exchange length. However, in a composite (amorphous + nanocrystalline) structure, it is the average anisotropy and not the local anisotropy that determines the exchange length. This follows from the fact that the moment variation is primarily due to the moment on nanocrystals and not due to the intervening amorphous matrix [5]. The result is the expansion in scale of the exchange interactions in the composite structure compared to the purely amorphous structure. In order to maintain randomness of anisotropy it is necessary to obtain sufficient number of nanocrystals so that the inter-particle distance is less than the exchange length.

The contribution of magnetoelastic anisotropy is significant in a composite structure since the crystalline and amorphous regions have opposing magnetostrictive strains [6]. This is not necessarily a disadvantage, since it offers the opportunity to tailor the magnetostricition to desired values by adjusting the volume fraction and size of the nanocrystals through appropriate heat treatment [7].

Therefore, annealing an amorphous alloy is a dynamic process on the atomic scale. As Fe rich nanocrystals are formed, the amorphous matrix is enriched in metalloid content thereby lowering its Curie’s temperature ($T_c$), and weakening the interaction between the Fe rich crystallites. The magnetostricition is composition dependent and varies throughout the process. Thus, although Al, B, Si and C are primarily added as glass-formers, their presence has important consequences on the magnetic behavior. The volume fraction of the crystallites determines the randomness as well as the magnetostricitive strains. In order to achieve the optimum magnetic properties, the size and the volume fraction of the nanocrystals as well as the composition of the intervening amorphous matrix must be controlled by a judicious selection of composition and heat treatment.

This has been attempted in the present work using the Fe$_{71.6}$Al$_{6.8}$C$_{5.7}$B$_{13.5}$Si$_{1.6}$Cu$_{0.3}$ (remaining 0.5 at.% consists of Mn (0.3%), P (0.1%), Cr (0.05%) and S (0.05%))$^1$ as the base alloy. The DSC of amorphous Fe$_{71.6}$Al$_{6.8}$C$_{5.7}$B$_{13.5}$Si$_{1.6}$Cu$_{0.3}$ (Fig. 1(a)) shows that this alloy devitrifies by formation of two distinct phases, characterized by the peaks at 804 and 839 K, respectively. Through X-ray diffraction of samples (Fig. 2) annealed at these peaks, the phases were identified as α-Fe (space group Im$ar{3}$m, $a = 0.288$ nm) (first peak) and a complex (C,B)$_6$Fe$_{23}$ ($Fm\overline{3}m$, $a = 1.0686$ nm) phase (second peak), respectively. Thus, the α-Fe grains are first nucleated in the amorphous matrix, leading to depletion of Fe in the matrix. At higher temperature, the driving force is sufficient to form the complex (C,B)$_6$Fe$_{23}$ phase which contains around 116 atoms with a large lattice parameter of 10.686 Å [8]. It is interesting to note that this structure contains features of the metastable icosahedral structure [9]. However, only the α-Fe nanocrystals lead to enhancement of soft magnetic properties through the mechanisms already described and study of the (C,B)$_6$Fe$_{23}$ phase is beyond the scope of this paper.

It was found that addition of small amounts (up to 2 at.%) of Y completely suppressed the bcc Fe phase, and the amorphous Fe$_{68.4}$Al$_{17.9}$C$_{5.3}$B$_{13.5}$Y$_{1.0}$Si$_{1.4}$Cu$_{0.3}$ directly devitrified to the (C,B)$_6$Fe$_{23}$ complex phase (Fig. 1(b)). Further, addition of Y and up to 1.3 at.% Cu resulted in a shallow α-Fe peak followed by a distinct (C,B)$_6$Fe$_{23}$ peak (Fig. 1(c)).

$^1$ All the compositions mentioned hereafter contain Mn, P, Cr and S as impurities.
The temperature difference between the peaks primary and secondary peaks is increased, since the (C,B)\_6Fe\_23 phase formation needs higher activation energy in the presence of Y and Cu. Thus, by varying the Y and Cu content, it is possible to control the crystallization kinetics in these alloys.

From the DSC, it is seen that if annealing is carried out at a temperature below the onset of crystallization of the $\alpha$-Fe, but above the glass transition temperature, $\alpha$-Fe grains will be nucleated. These grains will have a slow growth rate as indicated by the shallow peak that we attribute to the presence of Y. This provides a sufficient process window to enable a control on the $\alpha$-Fe nanocrystal size. Thus, the annealing temperature was empirically chosen to be $0.95T_{\text{onset}}$.

The TEM micrograph of the Fe$_{73}$Al$_{6.4}$C$_{5.6}$B$_{10.9}$Si$_{1.6}$Y$_{1.4}$Cu$_{0.8}$ ribbons annealed for 1 h at 738 K (Fig. 3) shows the presence of finely distributed nanocrystals of $\sim$25 nm average diameter in an amorphous matrix. The SAD pattern (Fig. 3(a)) shows that all the nanocrystals are of the $\alpha$-Fe phase.

The magnetic properties of as-quenched and annealed Fe$_{73}$Al$_{6.5}$C$_{5.6}$B$_{10.9}$Si$_{1.6}$Y$_{1.4}$Cu$_{0.8}$ ribbons are compared in Fig. 4. The $M_s$ of the as-quenched alloy is 146 emu/g. The annealing results in an increase of $M_s$ to 156 emu/g, due to stronger exchange interaction among the nanocrystals. The coercivity after annealing is 0.37 Oe, which is higher than that for the as-quenched alloy (0.14 Oe), indicating that the 25 nm average diameter is slightly large.

In order to study the effect of the impurities such as P, S, Mn and Cr, a ribbon of Fe$_{72}$Al$_{8}$C$_{6}$B$_{14}$ was prepared from 99.99% pure elements and its $M_s$ and $H_{ci}$ were found to be 155 emu/g and 0.39 Oe, respectively (Table 1). These properties are similar to those for Fe$_{71.6}$Al$_{6.8}$C$_{5.7}$B$_{13.5}$Si$_{1.6}$C$_{0.3}$ which has a $M_s$ of 153 emu/g and $H_{ci}$ of 0.37 Oe. Thus, the properties are similar for pure alloys and alloys prepared from commercial cast iron. The amount of impurities in cast iron is not sufficient to significantly affect the $M_s$. Further, the rapid quenching causes the impurities to remain in solution, thereby preserving the homogeneity of
Fig. 3. TEM image of Fe\textsubscript{73}Al\textsubscript{6.4}C\textsubscript{5.6}B\textsubscript{10.9}Si\textsubscript{1.6}Y\textsubscript{1.4}Cu\textsubscript{0.8} ribbons annealed for 1 h at 738 K (a) SAD pattern, (b) bright field and (c) dark field images of annealed samples. The average nanocrystal diameter is \( \sim 25 \) nm. The nanocrystals are all of the bcc Fe phase.

![TEM image](image_url)

**Table 1**

| Composition                  | As-quenched | Annealing conditions | Annealed |
|-----------------------------|-------------|----------------------|----------|
| \( M_s \) (emu/g)          | \( H_c \) (Oe) | \( T \) (K) | \( t \) (h) | \( M_s \) (emu/g) | \( H_c \) (Oe) |
| 1. \( \text{Fe}_{73}\text{Al}_{6.4}\text{C}_{5.6}\text{B}_{10.9}\text{Si}_{1.6}\text{Y}_{1.4}\text{Cu}_{0.8} \) | 146          | 738                  | 1        | 156             | 0.37          |
| 2. \( \text{Fe}_{71.6}\text{Al}_{6.8}\text{C}_{6}\text{B}_{13.5}\text{Si}_{1.4}\text{Cu}_{0.3} \) | 153          | –                    | –        | –               | –             |
| 3. \( \text{Fe}_{72}\text{Al}_{8}\text{C}_{6}\text{B}_{14} \) | 155          | –                    | –        | –               | –             |

\( M_s \) is found to increase upon annealing while impurities do not significantly affect these values.
the amorphous structure and not forming any pinning sites. The contribution of the included impurities from cast iron to coercivity is, therefore negligible.

Thus, simple modifications of the commercially available cast iron composition resulted in alloys whose properties can be tailored to desired values by annealing. These alloys inherently possess higher electrical resistivity due to additions such as B, C and Si, which reduce the core loss. The above mentioned advantages make these alloys suitable for applications in mass-production of transformer cores and electronic article surveillance devices [1].

4. Conclusions

The effect of up to 2 at.% Y and 1.3 at.% Cu on the devitrification of the alloy has been studied. Y is found to suppress the \( \alpha \)-Fe phase while Cu favors the nucleation of this phase. Thus, by choosing a temperature below the onset of \( \alpha \)-Fe and above the glass transition temperatures, a dispersion of \( \alpha \)-Fe nanocrystals in an amorphous matrix has been obtained, and corresponding enhancement of \( M_s \) was observed. However, coercivity did not necessarily improve upon annealing, and therefore, the annealing needs to be judiciously scheduled. Starting from a commercial alloy, it is possible to tailor the soft magnetic behavior of these alloys to achieve desired properties by varying the Y and Cu content and the annealing schedule.

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