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Nano-crystallisation and magnetic softening in Fe–B binary alloys induced by ultra-rapid heating

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Abstract
Magnetically soft nanostructures are known to be prepared by the primary crystallisation of Fe-based amorphous precursors containing Cu and/or Nb. These nonmagnetic additives are essential for accelerated nucleation and retarded crystal growth during crystallisation. However, it has recently been found that none of these additives are necessary for the preparation of similar nanostructures when ultra-rapid annealing (URA) is employed. As a result, a magnetically soft nanostructure with exceptionally high Fe contents is realized in a simple Fe–B binary system. An obvious question is the mechanism of the nanostructural formation in such a simple system. To answer this question, the crystallisation behaviour of amorphous precursors was investigated by means of in situ resistivity measurements with heating rates up to ~100 K s⁻¹. The primary crystallisation temperature (T_p) in Fe₈₆B₁₄ is increased at least by ~100 K under URA. This brings T_p to the vicinity of the glass transition (T_g) predicted by Egami’s zeroth-order approximation, suggesting that an enhanced nucleation rate near T_g due to the contribution of homogeneous nucleation could be responsible for the nanostructural formation in Fe₈₆B₁₄. Contrarily, the effect of URA is absent from Fe₈₀B₁₄Nb₆, and a magnetically soft nanostructure is realized by conventional annealing because the crystallisation reaction in this alloy takes place above T_g even with a low heating rate of ~1 K s⁻¹. URA offers new possibilities for enhancing the saturation magnetization in nanocrystalline soft magnetic alloys through reductions of the amount of nonmagnetic additives.

Keywords: grain size, random anisotropy, glass transition, coercivity, nucleation

(Some figures may appear in colour only in the online journal)

1. Introduction
One of the most successful examples of utilizing the crystallisation of amorphous alloys in technological applications is the Fe-based nanocrystalline soft magnetic alloys [1] prepared from melt-spun amorphous precursors. The first example of alloy development in this class of soft magnetic materials was reported by Yoshizawa et al [2] in 1988, which was followed by the development of many new alloys prepared similarly by the nano-crystallisation of melt-spun amorphous precursors [3–6]. The effect of the magnetocrystalline anisotropy (K₁) in these alloys is exchange-averaged and magnetic softening occurs simply by nanoscale grain refinement. These alloys have attracted much attention from the viewpoint of fundamental magnetism [1, 7–11].

Since the exchange-softening effect takes place where the grain size (D) is smaller than the natural exchange length (Lₐₓ = 30 – 40 nm in Fe-based alloys) [1], the nanostructural
formation upon the crystallisation of amorphous precursors is a primary condition in the alloy development. To realize nano-crystallisation, the vast majority of alloys developed to date contain a considerable amount of additives such as Nb [2, 3], Cu [2–6], and P [6]. Among these additives, the roles played by Cu and Nb were studied extensively; Cu is known to enhance heterogeneous nucleation [12] while Nb is believed to inhibit the crystal growth process [13] during nano-crystallisation in Fe-based alloys. These additives have been known to be effective in refining microstructures even in nanocomposite magnets [14]. Hence, it has been a common perception that a certain amount of nonmagnetic additives in addition to glass-forming elements is essential to realize magnetically soft nanostructures in Fe-based alloy ribbons. Consequently, their Fe content and saturation magnetization remain lower than those of Si steels.

A possible approach to realizing nanoscale microstructures with a reduced amount of nonmagnetic additives is rapid annealing. In the 1990s we reported that the mean grain size in nanocrystalline Fe–Zr–B alloys after primary crystallisation is reduced by 30% upon increasing the heating rate from 0.042 K s$^{-1}$ to 3.3 K s$^{-1}$ [15]. Recently, ultra-high heating rates up to 10$^5$ K s$^{-1}$ have been realized by a range of advanced materials processing and thermal analysis techniques [16–18]. Among these approaches, using a pair of preheated Cu blocks for annealing [17] is ideal because this technique could prevent a detrimental overheating effect due to crystallisation$^4$.

Most recently, we have employed this ultra-rapid annealing (URA) technique and demonstrated [19, 20] that a magnetically soft microstructure with a grain size of 18 nm can be prepared in simple Fe$_{80}$B$_{14}$ and Fe$_{80}$B$_{14}$Si$_2$ alloys. As a result, a high saturation magnetization ($J_s$) of 1.9 T along with a low coercivity ($H_c$) of 4.6 A m$^{-1}$ are realized. This $J_s$ value is comparable to that of Si steels whereas the $H_c$ value is an order of magnitude smaller, thus demonstrating the high potential of URA in nanocrystalline soft magnetic materials.

An obvious question here is the mechanism of nanostructural formation induced in a simple Fe–B–based alloy free of Cu and/or Nb. We have investigated [21] the effect of URA on the microstructural and magnetic properties in nanocrystalline Fe–Nb–B alloys, which are well-studied soft magnetic alloys (Nanoperm) originally developed in the 1990s [3, 22]. The nanostructure in this ternary system in the original work was obtained by conventional annealing, and a high permeability of $\sim 10^6$ was limited to Nb contents between 5 and 7 at% [15]. Lowering the Nb content below 4 at% resulted in a coarsening of the nanocrystallites, and thus sets a lower limit on the Nb content. However, this lower limit is suppressed to zero when URA is employed. This behaviour is ideal for investigating the nanostructural formation mechanism because the sensitivity of the grain size to the heating rate during annealing varies systematically with Nb content. To investigate the

$^4$Provided that the crystallization reaction takes place under an adiabatic condition, $\Delta H$ of crystallisation in typical amorphous Fe–B alloys ($\sim 10$ kJ mol$^{-1}$) could result in a temperature increase of a few 100 K, which is more than enough for triggering the formation of magnetically hard compounds via the secondary crystallisation reaction.

2. Experimental procedures

Amorphous alloys with compositions of Fe$_{80}$B$_{14}$ and Fe$_{100-x}$B$_x$Nb$_x$ ($x = 0, 1, 2, 3, 4, 5,$ and 6) were prepared by a single-roller melt spinner in an Ar atmosphere. Samples were characterised by x-ray diffraction and differential thermal analysis (DTA). Transmission electron microscopy (TEM) was carried out on an FEI Tecnai-T20 TEM operated at 200 kV. The mean grain size ($D$) was estimated from the $(110)_{bcc}$ reflection by using Scherrer’s formula. The optical broadening effect was subtracted quadratically from the line width for the grain size estimation. The saturation magnetic polarization ($J_s$) and the coercivity ($H_c$) were measured on a vibrating-sample magnetometer and a dc $B$–$H$ tracer, respectively.

In figure 1(a) we show a schematic diagram of the experimental setup employed for ultra-rapid heating. The two pure-Cu blocks were heated to an annealing temperature, and ribbon samples were inserted between the two blocks. The bottom Cu block was mounted on a gas actuator cylinder by which the top surface of the bottom block was raised to the level of the bottom surface of the top block. The temperature change in the sample was measured using a thermocouple with a diameter of 25 µm, which was spot-welded into a melt-spun ribbon. The ribbon sample was wrapped in a Cu foil with a thickness of 20 µm. The change in temperature during heating by the Cu blocks is shown in figure 1(b) along with the gradient of the temperature profile, i.e. the heating rate ($\alpha$). The average heating rate between 600 and 800 K obtained by a linear regression is $1.39 \times 10^4$ K s$^{-1}$. It is worth mentioning here that the average heating rate measured depends on the heat capacity of the thermocouple. Lower average heating rates of $9.2 \times 10^3$ K s$^{-1}$ and $1.3 \times 10^3$ K s$^{-1}$ were obtained for the same temperature range when the diameter of the thermocouple was increased to 0.1 mm and 2.0 mm, respectively. In the present report, the heating rate quoted was measured using a K-type thermocouple with a diameter of 0.1 mm, except where otherwise stated. Lower average heating rates of 22 and $2.3 \times 10^2$ K s$^{-1}$ were also realized by placing an extra layer of Cu foil with a thickness of 0.1 mm and alumina fibre matting in addition to the 20 µm thick Cu foil. A conventional infrared furnace operated under a reduced pressure ($<10^{-2}$ Pa) was used for annealing at a rate of 1.67 K s$^{-1}$.

The electrical resistivity of the ribbon samples during the heating process by the Cu blocks was measured by a four-probe method. Both the annealing and resistivity measurements using the Cu blocks were carried out in an Ar atmosphere. Figure 1(c) schematically shows the configuration of this resistivity measurement. A strip 160 mm long with a width of 1 mm and a thickness of 15 µm was used, and the sample was wrapped by a polyimide tape to insulate it electrically from Cu. The time resolution of the data acquisition was
0.5 ms. The temperature change was also estimated by using a pure Pt ribbon where the temperature dependence of electrical resistivity was known. The error of temperature during heating was determined by the difference between this estimate and the measurement by the thermocouple.

3. Results and discussion

3.1. Effect of heating rate on the grain size and magnetic softness

The crystallisation behaviour of amorphous $\text{Fe}_{100-x}\text{B}_{14}\text{Nb}_x$ ($x = 0–6$) has been well studied [23, 24], and it is known that all the alloys show a two-stage crystallisation behaviour described by the following sequence: amorphous $\rightarrow$ bcc-Fe + residual amorphous $\rightarrow$ bcc-Fe + compounds. During the primary crystallisation reaction, the solute atoms are rejected from the bcc-Fe precipitates, and hence, the amorphous matrix is enriched with solute. The partial equilibrium between the primary bcc-Fe phase and the residual amorphous phase is maintained during primary crystallisation, and the crystal growth becomes diffusion-controlled [11]. The metastability of the bcc-Fe/amorphous two-phase microstructure is lost at the second stage of crystallisation, leading to the formation of magnetically hard compounds [11]. Hence, maintaining this metastable equilibrium is an essential condition for realizing a magnetically soft microstructure. In figure 2 we show the
change in the coercivity as a function of annealing temperature for the Fe100-xB14 alloy (x = 0, 4, and 6) alloys. The precursor amorphous ribbons were annealed at α = 1.7, 22, 2.3 × 10^2, and 9.2 × 10^3 K s^-1. The onset of primary crystallisation estimated by DTA at α = 0.67 K s^-1 is indicated in each figure by an arrow. It is commonly seen for all the alloys that the Hc of the samples annealed above the onset of primary crystallisation shows large values in relatively low annealing temperatures (T_a). This magnetic hardening effect is well known in alloy systems where the Curie temperature of the residual amorphous matrix is low and the intergranular exchange coupling is limited [25]. Upon increasing the volume fraction of the bcc-Fe grains at a higher T_a range, the intergranular coupling is strengthened and the exchange softening is promoted, leading to a gradual decrease in Hc. However, this is followed by an abrupt increase in Hc at the highest end of T_a due to the formation of magnetically hard compounds at the second stage of crystallisation. It is also seen that the T_a at which the lowest Hc value is obtained for each heating rate, hereafter referred to as the optimum annealing temperature, shows a tendency to increase with increasing heating rate, thus reflecting the effect of heating rate on the crystallisation kinetics. The Hc after optimum annealing for both the Fe86B14 and Fe82B14Nb4 alloys is reduced dramatically from ~100 A m^-1 to a few A m^-1 upon increasing α from 1.7 to 9.2 × 10^3 K s^-1. However, this dramatic softening effect is absent from the Fe80B14Nb6 alloy because a small Hc < 10 A m^-1 is realized even by conventional annealing.

In figure 3 we show the change in the mean grain size (D) estimated from x-ray diffraction as a function of heating rate during annealing for the Fe100-xB14 alloy (x = 0, 4, and 6) alloys. These D values were obtained from the samples annealed at the optimum annealing temperature. The results at the lowest heating rate 8.3 × 10^{-2} K s^{-1} are from our previous report [23]. The mean grain size after primary crystallisation in the Fe86B14 and Fe82B14Nb4 alloys is reduced dramatically by increasing heating rate whereas such a grain refinement effect is absent from the Fe80B14Nb6 alloy. The microstructures of the Fe86B14, Fe82B14Nb4, and Fe80B14Nb6 alloys after annealing were also confirmed by TEM. In figure 4 we show the bright-field transmission electron micrographs obtained from (a) Fe86B14 annealed at 673 K with a heating rate (α) of 1.7 K s^{-1}, (b) Fe86B14 annealed at 773 K with α = 9.2 × 10^3 K s^{-1}, (c) Fe80B14Nb4 annealed at 898 K with α = 1.7 K s^{-1}, and (d) Fe80B14Nb6 annealed at 963 K with α = 9.2 × 10^3 K s^{-1}. A dramatic microstructural refinement is confirmed for both the Fe86B14 and Fe82B14Nb4 alloys by increasing the heating rate, but little change in D is seen for Fe80B14Nb6; this is consistent with the results in figure 3. Since the well-known exchange-softening effect takes place when the grain size becomes lower than L_{ex} (30–40 nm) and the coercivity is proportional to the sixth power of the grain size for D < L_{ex} [1, 2], the dramatic magnetic softening in figures 2(a) and (b) are well understood by the grain refinement effect induced by rapid annealing. The absence of the softening effect by URA in the Fe86B14 alloy is also consistent with the lack of the grain refinement effect in this alloy.

In both figures 3 and 4, it is evident that the grain size of conventionally annealed Fe86B14 is larger than that of
the Nb-free Fe86B14 alloy, indicating that the well-known effect of Nb on inhibiting the grain growth process is limited in Fe83B14Nb4. A simple reason for this inverse effect of Nb addition on the grain size could be the crystallisation temperature. The crystallisation onset ($T_{x1}$) in Fe–B alloys is known to be enhanced by reducing the average 3d electron concentration, and thus, $T_{x1}$ is increased dramatically by additions of early transition metals such as Nb. As a result, the optimum annealing temperature at $\alpha = 1.7 \text{ K s}^{-1}$ is also raised significantly from 673 K to 823 K by the addition of 4 at% Nb. This temperature increase (150 K) corresponds to a few 100-fold increase in diffusivity, given the typical activation enthalpy of diffusion for transition metals in Fe-based amorphous alloys (~2 eV) [26]. Thus, the benefit of Nb addition on limiting the crystal growth rate is likely lost by the enhanced $T_{x1}$. The well-established argument on the mechanism of Nb addition on the nucleation frequency must be the governing factor in the grain size refinement starts to take place at $\alpha \sim 100 \text{ K s}^{-1}$ in the Fe86B14 alloy. Hence, conventional thermal analysis techniques are unable to trace the crystallisation process upon rapid annealing. Although ultra-fast heating scanning calorimetry has recently been developed [30], its availability is limited, and the heat capacity of the sample needs to be extremely small. An alternative approach to tracing the phase transformation in solids is the electrical resistivity method [31–33]. Unlike DTA/DSC, the resistivity method does not rely on the enthalpy change associated with crystallisation, and thus, the crystallisation process may be investigated in situ while the sample is annealed using the

Figure 5. Bright-field cross-sectional TEM images for ultra-rapidly annealed Fe87B13 acquired from (a) the free surface and (b) roll-chilled sides.
preheated Cu blocks. The temperature dependence of the electrical resistivity for amorphous Fe$_{86}$B$_{14}$ was measured using a conventional infrared furnace at $\alpha = 8.3 \times 10^{-2}$ K s$^{-1}$. Figure 7 shows the result along with a DTA curve obtained with the same heating rate. The resistivity ($\rho$) was normalized by the value at room temperature ($\rho_{RT}$), and the temperature derivative of $\rho/\rho_{RT}$ is also shown. Two abrupt decreases are evident on the $\rho/\rho_{RT}$ curve, and its derivative exhibits two negative peaks where the primary and secondary crystallisation exotherms are seen on the DTA curve. This shows that the resistivity is sensitive enough to trace the crystallisation reactions in Fe$_{86}$B$_{14}$. The discrepancy between the peak temperatures in these two methods is within 6 K.

The resistivity of amorphous Fe$_{86}$B$_{14}$ was also measured at higher heating rates up to 95 K s$^{-1}$ by using the preheated Cu blocks. The heating rate for each resistivity measurement was defined by the rate at the onset of primary crystallisation while the error was determined by the variation of $\alpha$ during the crystallisation reaction. Owing to the requirement of an electrically insulating layer between the sample and the Cu foil, the heating rates are considerably lower than the highest rate realized by the Cu blocks. Figure 8 shows the temperature dependence of the normalized resistivity and its temperature derivative for amorphous Fe$_{86}$B$_{14}$. The results presented in figure 7 for $\alpha = 8.3 \times 10^{-2}$ K s$^{-1}$ are also included for comparison. Two-stage crystallisation reactions are evident on each resistivity curve, and the onset of crystallisation shows a clear tendency to increase upon increasing the heating rate.

The effect of heating rate ($\alpha$) on the crystallisation temperature was analysed based on the following Kissinger method [33]:

$$\ln \left( \frac{\alpha}{T_p^2} \right) = - \frac{E_a}{k_B T_p} + \text{const.},$$  \hspace{1cm} (1)

where $T_p$ is the peak temperature where the maximum reaction rate is reached, $E_a$ is the apparent activation energy, and $k_B$ is Boltzmann’s constant. It is worth mentioning here that...
the negative peak temperature on the d(ρ/ρRT)/dT curve may not necessarily reflect the exact point of the maximum reaction rate because of the possible deviation from the ideality between the resistivity change and the fraction transformed. Rossiter [31] pointed out that the extent of the deviation depends highly on the morphology and the distribution of the precipitates. However, as demonstrated in figure 7, the deviation is within a few degrees for the Fe86B14 alloy. Using the peak temperatures observed on the d(ρ/ρRT)/dT curves, ln(α/α2) is plotted against 1/TP in figure 9. In this plot, the results obtained by DTA in a low α range between 5 × 10⁻² and 6.7 × 10⁻¹ K s⁻¹ are also included. Although the scattering of plots at the highest end of the heating rate tends to be larger due to the error of temperature measurements, the overall trend is described by equation (1). The apparent activation energy extracted from the Kissinger plot is 2.6 eV and 3.6 eV for the primary and secondary crystallisation processes, respectively. Given the activation energy for the tracer diffusion of 3d transition metals in amorphous alloys (1.5–2.5 eV) [26], these values appear to be slightly higher than those of diffusion. This is natural given the fact that the crystallisation process is governed by both the nucleation and crystal growth kinetics, which cannot be described by the single thermal activation process of atomic diffusion assumed in equation (1). Nevertheless, the heating rate dependence of the primary crystallisation temperature is confirmed to be described phenomenologically by the Kissinger model.

3.3. Mechanism of grain refinement by URA

The most significant aspect of the nanostructural formation by URA is that the usual nonmagnetic additives such as Nb and Cu are no longer essential for the formation of a magnetically soft nanostructure. It is well known that Cu in the nanocrystalline Fe–Si–B–Nb–Cu alloys forms clusters [12] prior to crystallisation. These Cu clusters with a high population density could become heterogeneous nucleation sites, or they could induce destabilized Fe-rich regions in the amorphous phase [17], leading to a significantly enhanced nucleation rate. The crystal growth rate in this alloy system is considered to be retarded by Nb addition [13]. Hence, the nanostructural formation in this traditional Fe–Si–B–Nb–Cu system is well understood by the combination of these two alloying effects. Similarly, the nanostructural formation in amorphous Fe87B13 and Fe86B14 upon URA must also be due to either an accelerated nucleation rate or a reduced crystal growth rate (or a combination of both). However, as discussed in the previous section, the latter is highly unlikely in the rapidly annealed alloys because of the significant increase in crystallisation temperature. Judging by the Kissinger plot in figure 9, the crystallisation temperature is raised by ~100 K in our URA (α up to 10⁴ K s⁻¹). This corresponds to an increase in diffusivity by two orders of magnitude in Fe-based amorphous alloys [26], and thus, a higher crystal growth rate is expected. Consequently, the grain refinement effect induced by URA must be attributed to an accelerated nucleation rate.

The nucleation mechanisms in amorphous materials upon crystallisation have been studied extensively [27, 34, 35], and it is known that the homogeneous nucleation rate is highly temperature-dependent. The kinetics of homogeneous nucleation is limited below the glass transition temperature (Τg), and thus, heterogeneous nucleation starts to govern the nucleation kinetics well below Τg. Köster and Herold [27] pointed out that quenched-in nuclei or embryos insufficient in size at higher temperatures could become stable at lower temperatures, leading to nucleation. However, the nucleation frequency of heterogeneous nucleation in amorphous alloys is usually very limited unless additives such as Cu or Au are added. Hence, the population density of nuclei below Τg is small, and the microstructure after crystallisation tends to be coarse and inhomogeneous. Contrarily, the contribution of viscous flow to the atomic transport term of the nucleation kinetics becomes significant near Τg, and homogeneous nucleation starts to govern the nucleation frequency. These effects of temperature on the nucleation frequency have been confirmed experimentally for both primary and polymorphic crystallisation reactions in amorphous Fe–Ni–B alloys by Köster and Meinhardt [35]. They demonstrated that the volume density of crystals is enhanced by as large as two to three orders of magnitude by increasing the annealing temperature to above Τg. The maximum grain refinement effect observed in the present study is from about 70 nm to 20 nm. This corresponds to an increase in the crystal volume density by approximately two orders of magnitude, which is well within the change reported by Köster and Meinhardt. Thus, our experiment can be understood by the contribution of homogeneous nucleation near Τg.

Although the glass transition temperature is crucial for discussing the possible effect of homogeneous nucleation, it remains challenging to experimentally measure Τg for amorphous Fe87B13 and Fe86B14 alloys because the onset of crystallisation in these alloys is too low to reveal the glass transition behaviour by currently available techniques. However, a crude approximation may be possible when Τg is known for alloys.
with similar chemical compositions. Egami [36] suggested in his early work that $T_g$ in amorphous alloys is approximated by

$$T_g = \frac{1}{\alpha + D}$$

where $f^i$ and $f^m$ are the molar fraction and the melting point of the $i$th element in the alloy. Lu and Li [37] analysed the glass transition temperatures of more than two hundred Ca-, Cu-, rare earth-, Mg-, Ni-, Ti-, and Zr-based amorphous alloys in a great amount of literature. Their analyses agree with this zeroth-order approximation proposed by Egami, and the average $T_g$ is 0.385 for the aforementioned nonferrous alloys. As we discuss below, the glass transition is a kinetically governed process, and $T_g$ depends on the heating rate. Thus, Egami’s zeroth-order approximation ($T_g \approx 0.4 T_m$) should only stand under a conventional heating rate (~1 K s$^{-1}$).

To test this approximation in Fe metalloid-based amorphous alloys, the glass transition temperatures of amorphous Fe$_{86}$B$_{14}$Nb$_x$ ($x = 6$ and 8) alloys [24] along with those of amorphous (Fe, Co, Ni)-Si-B [38], (Fe, Co, Ni)-Si-B-Nb [39], and Fe-B-C-Si [40] alloys are plotted against their $T_m$ in figure 10. The $T_g$ measurements in these previous reports were performed at a heating rate of ~1 K s$^{-1}$. The proportionality constant in these Fe metalloid alloys is 0.405, with a standard error of 0.017; this is consistent with Egami’s prediction.

In figure 11 we show the onset of primary crystallisation ($T_{cr}$) for amorphous Fe$_{78}$B$_{14}$Nb$_x$ ($x = 0$–8) alloys obtained by the resistivity measurements ($\alpha \geq 3.6$ K s$^{-1}$) and DTA ($\alpha \leq 0.67$ K s$^{-1}$). In this figure, $0.405 \pm 0.017 T_m$ is shown along with the $T_g$ of $x = 6$ and 8 alloys estimated elsewhere from the temperature dependence of the specific heat ($C_p$) acquired at $\alpha = 1.3$ K s$^{-1}$ [24]. Due to the enhancement of $T_{cr}$ by Nb addition, $T_{cr}$ exceeds $T_g$ at around $x = 6$ even under a low heating rate of $8.3 \times 10^{-2}$ K s$^{-1}$. Hence, the contribution of viscous flow to the homogeneous nucleation kinetics must be significant even when annealed conventionally when Nb content is 6 at%: this is consistent with the fact that the effect of URA on the grain size is totally absent in the Fe$_{80}$B$_{14}$Nb$_x$ alloy (figure 6). Furthermore, $D \sim 10$ nm is realized regardless of heating rate.

Since glass transition is a kinetically governed process, $T_g$ is also increased along with $T_{cr}$ when the heating rate is increased. Thus, the effect of ultra-rapid heating on $T_g$ needs to be discussed in order to clarify the possibility of homogeneous nucleation in the nanocrystalline Fe$_{78}$B$_{14}$ alloy. The kinetics of glass transition in amorphous alloys has been studied from the viewpoint of fragility [41], and the effect of heating rate on $T_g$ was investigated for some metallic glasses. Since the glass transition process involves collective atomic transport, its apparent activation energy becomes much larger than that for a typical single atomic jump. Bruning and Samwer [42] pointed out that the apparent activation energy for $T_g$ is typically a factor of three larger than that for atomic diffusion. They also investigated the dependence of $T_g$ on heating rate for Pd- and La-based metallic glasses, and demonstrated that $T_g$ is described well by the following Vogel–Fulcher–Tammann (VFT) type expression:

$$T_g(\alpha) = T_g^0 + \frac{A}{\ln(B/\alpha)},$$

or equivalently

$$T_g(\alpha) = T_g^0 + \frac{D^* T_g^0}{\ln(B/\alpha)},$$

where $T_g^0$ is the asymptotic value of $T_g$ at $\alpha \to 0$. The parameters $A$ and $B$ have dimensions of K and K s$^{-1}$, respectively. The strength parameter $D^*$, defined by the ratio of $A$ to $T_g^0$, reflects the deviation of the temperature dependence of viscosity from the Arrhenius law. Some metallic glasses have been investigated based on this model, and both parameters $D^*$ and $B$ were extracted experimentally [42–45]. The extracted $D^*$ typically spans from 0.3 ± 0.05 [45] to 7 ± 2 [44] while $\ln B$ spans from 5 ± 6 [45] to 25 ± 20 [44]. The significant error for the latter parameter seems to be due to the large
pointed out that the contribution of viscous flow to the atomic transport term of the homogeneous nucleation kinetics commences at least 50 K below the experimentally observed $T_g$. Since the temperature difference between $T_g$ and $(T'_g)$ for amorphous Fe$_{86}$B$_{14}$ becomes $<50$ K at $\alpha > 10^2$ K s$^{-1}$, it is likely that the primary crystallisation reaction in this amorphous precursor proceeds with homogeneous nucleation when URA is employed. The mean grain size ($D$) after primary crystallisation for amorphous Fe$_{80}$B$_{14}$ (figure 6) clearly reflects this trend, and $D$ shows a decrease from 50 nm to 20 nm when $\alpha$ is increased from 1 K s$^{-1}$ to $10^2$ K s$^{-1}$. Consequently, the grain refinement effect induced by URA can be explained consistently by the accelerated homogeneous nucleation rate brought about by the viscous flow contribution near the glass transition temperature.

4. Conclusions

In order to understand the mechanism of nanostructural formation induced by URA in a simple Fe–B binary system, the effect of heating rate on the microstructural and magnetic properties after primary crystallisation have been investigated for amorphous Fe$_{100-x}$B$_x$Nb$_x$ ($x = 0–6$) alloys. The results obtained are summarized below:

(i) The grain size of Fe$_{100-x}$B$_x$Nb$_x$ ($x < 5$) after primary crystallisation was found to decrease dramatically from 50–70 nm to about 20 nm by increasing the heating rate from $8.3 \times 10^{-2}$ K s$^{-1}$ to $10^2$ K s$^{-1}$, resulting in a significant decrease in the coercivity. Contrarily, the effect of URA on grain refinement is absent from Fe$_{80}$B$_{14}$Nb$_6$, and a magnetically soft nanostructure is obtained even with a conventional heating rate of $\sim$1 K s$^{-1}$.

(ii) The glass transition behaviour is absent from amorphous Fe$_{86}$B$_{14}$ because the onset of crystallisation ($T_x$) is too low to reveal the glass transition temperature ($T_g$). However, $T_x$ is increased considerably by Nb addition, and it exceeds $T_g$ for $x > 5$. Hence, the nano-crystallisation in Fe$_{80}$B$_{14}$Nb$_6$ takes place with the contribution of viscous flow to the nucleation kinetics whereas such a contribution is limited in Fe$_{86}$B$_{14}$ when the amorphous precursor is annealed conventionally.

(iii) The onset of primary crystallisation in Fe$_{86}$B$_{14}$ is enhanced by at least $\sim$100 K when URA is employed, and it is predicted to be in the vicinity of $T_g$. Thus, the contribution of viscous flow to the homogeneous nucleation kinetics can be responsible for the nano-crystallisation in amorphous Fe–B alloys induced by URA.

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