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Citation: Applied Physics Letters **70**, 1709 (1997); doi: 10.1063/1.118677
View online: http://dx.doi.org/10.1063/1.118677
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/70/13?ver=pdfcov
Published by the AIP Publishing

Relaxation process of Fe(CuNb)SiB amorphous alloys investigated by dynamical calorimetry

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(Received 28 October 1996; accepted for publication 29 January 1997)

Differential scanning calorimetry and dynamic differential scanning calorimetry were used to analyze the relaxation process of Fe(CuNb)SiB amorphous alloys. The Curie temperature (T_C) evolution of the amorphous phase during relaxation as a function of heating rate, time and pre-annealing temperature were measured. Two distinct relaxation processes are observed, consequent with topological and chemical short range order changes. © *1997 American Institute of Physics.* [S0003-6951(97)04313-1]

Since the discovery of the excellent soft magnetic properties of nanocrystallized Fe(CuNb)SiB amorphous alloys (FINEMET),[1] much effort has been devoted to investigating the nanocrystalline structure, the magnetic properties, the addition effect, etc. The kinetics of the nanocrystallization process is well established, but the relaxation phenomena before the crystallization as well as their action to induce nucleation have not been analyzed enough. During relaxation, short range order (SRO) changes occur in the amorphous phase. For instance, both the magnetic permeability and T_C change their values.[2,3] In this letter, a systematic analysis of the amorphous phase T_C evolution during relaxation and its physical interpretation in terms of SRO is attempted, as resulting from differential scanning calorimetry (DSC) and dynamic differential scanning calorimetry (DDSC) measurements.

Amorphous $Fe_{73.5}Cu_1Nb_3Si_{22.5-x}B_x$ ($x=5$, 8, and 12) ribbons with 15 mm width and about 20 μm thickness were produced by the planar flow casting method. The experiments were carried out on a Perkin-Elmer DSC-7. The DDSC measurements are provided as a facility in the same equipment. The common temperature program is superimposed with a dynamic temperature change.[4] The specific dynamic regime was as follows: repeatedly heat up 2 °C at a rate 8 °C/min and cool down 1 °C at a rate −4 °C/min, in the temperature range from 300 to 350 °C. By this technique the complex heat capacity was measured, $C_P=C'_P+iC''_P$. The real part, C'_P, named ''storage heat capacity,'' is the response of the material to store and release energy (reversible change); and the imaginary part, C''_P, named ''loss heat capacity,'' is the tendency of the material to dissipate energy (nonreversible change).[5] Therefore, the quantity C'_P gives the change of heat capacity during relaxation without any dissipative response. On the other hand, C'_P is more sensitive to the structural changes during the relaxation process than the overall heat capacity measured by standard DSC.

The DSC heating curves of the amorphous samples show clearly a relaxation process in a temperature range between T_C and the first crystallization peak. The amplified heat flow versus temperature for sample A ($x=5$) is presented in Fig. 1; several DSC curves are included to show the influence of heating rate in the measurement. The relaxation process appears as a very wide exothermic peak which shifts to higher temperatures with increasing heating rate, as expected in an activated process. The average activation energy of the relaxation process was estimated by the Kissinger method (shown in Fig. 2). The values of the amorphous samples analyzed are in the range of 1.6–1.9 eV, rather insensitive to the chemical composition. These values are lower than the nanocrystallization activation energy of Fe(Si) (3.8–4.4).[6] Because the relaxation process occurs in a large temperature range, the peak is flat to some extent, and therefore there is a large inaccuracy in the activation energy values measured.

The T_C value of the amorphous phase increases as it relaxes and depends on heating rate (see Fig. 1) because relaxation also occurs below T_C. For sample B ($x=8$) the results of T_C versus heating rate are plotted in Fig. 3. The T_C values exponentially decrease (consider the error) with the heating rate, since relaxation already occurred when the sample was heated up. With slow heating rate, more relaxation takes place during the heating, therefore the high heating rate asymptotical value may be considered as the T_C of the initial amorphous without relaxation.

To analyze the evolution of the relaxation process, preannealing of the amorphous samples at some selected tem-

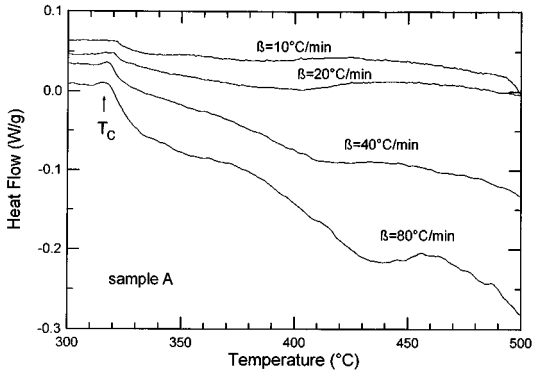

FIG. 1. The DSC curves obtained at different heating rate for sample A ($x=5$) in the temperature range where relaxation process appears.

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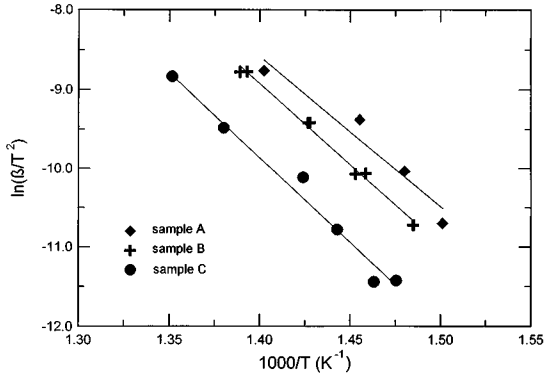

FIG. 2. A Kissinger plot of $\ln(\beta/T^2)$ vs $1/T$, where β is the heating rate and T is the relaxation peak position (β/T^2 in min^{-1} K^{-1} unit).

peratures, T_a, for 1 h were performed. Then, to check to which extent the relaxation process occurred during that pre-annealing, the T_C was measured again under continuous heating. The sequential DSC curves of the pre-annealed amorphous samples present a significant change of the profile extending in the whole temperature range where relaxation occurs, as shown in Fig. 4(a). The comparison of the DSC curve of amorphous sample with the DSC curves after pre-annealing indicates that at $T_a<450$ °C the relaxation is still operating after pre-annealing. However, when $T_a=450$ °C the relaxation was completed during the pre-annealing, but if $T_a=470$ °C the nucleation and growth of Fe(Si) is even promoted at a lower temperature than that observed without pre-annealing. Another important phenomenon presented in Fig. 4(a) is that the T_C of the pre-annealed amorphous phase increases with T_a, as plotted in Fig. 4(b). When $T_a=470$ °C the T_C shows a large increase resulting from some Fe(Si) nuclei formed during annealing. There are only a few Fe(Si) nuclei in the sample, even though the effect is clearly detected by the T_C value.

As is well known, the relaxation process is related to some atom rearrangement (chemical or topological SRO changes) indirectly observed as energy is released in DSC curves.[2,3] Owing to the fact that T_C depends on the average distance between magnetic atoms, the T_C increase can probably be explained as SRO changes where the Fe–Fe bond distance decreases, the Cu, Nb, and/or B atoms diffusing into the surroundings. The local structure in the Fe neighborhood has the tendency to transform towards ordered arrangement

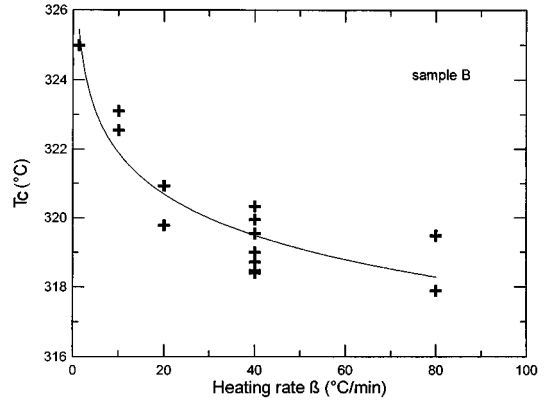

FIG. 3. T_C changes with the heating rate for sample B ($x=8$).

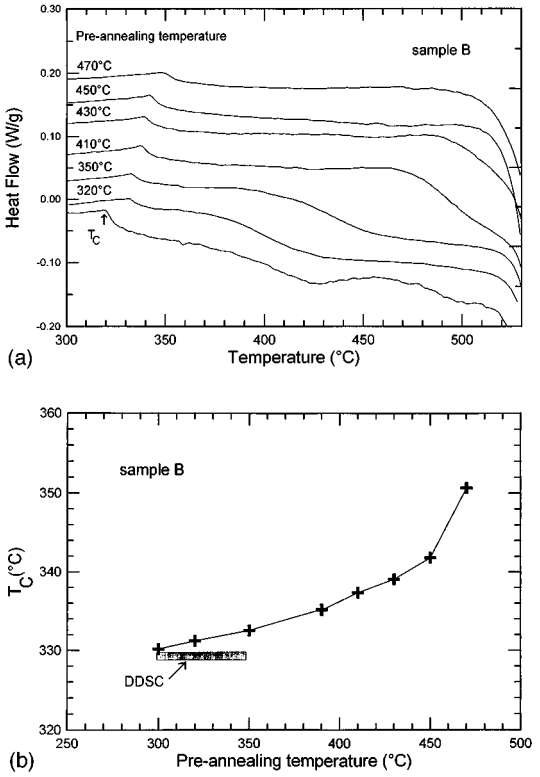

FIG. 4. (a) The DSC curves of sample B ($x=8$) after pre-annealing for 1 h at several temperaturs. (b) T_C changes of pre-annealed sample B as a function of pre-annealing temperature.

like bcc or DO_3, becoming embryos of the Fe(Si) phase as corroborated by Mössbauer analysis.[7,8]

To investigate the time dependence of relaxation *in situ* measurements of the T_C evolution by annealing in the temperature range of 300–350 °C were carried out by DDSC. The real value of T_C appears in these measurements as the peak of heat capacity C_P' without any effect of dissipative C_P''. In Figs. 5(a) and 5(b) we present by C_P' of samples B and C ($x=12$), respectively. It is clear that T_C increases with annealing time. As shown in Fig. 6, in the first few hours the relaxation process proceeds rapidly, then it becomes slow. The shape of T_C versus annealing time cannot be fitted by only one exponential function. Two relaxation times, τ_1 and τ_2 are necessary for each sample. That is

$$T_C(t)=T_0+\sum_{i=1}^{2}\Delta T_i\left[1-\exp\left(-\frac{t}{\tau}\right)\right],$$

where the T_0 is the T_C value of the initial amorphous without relaxation, ΔT_i is the T_C change due to i relaxation process, and τ_i is its characteristic decay time. In our analysis, both ΔT_i and τ_i are assumed constant in the temperature range explored.

Best fitted values are: $T_0=318.1$ °C (B) and 313.0 °C (C), which are in agreement with the DSC continuous heating results; these data show that the T_0 of amorphous depends on the initial chemical composition. The characteristic decay time τ_1 for both samples B and C is close to 0.45 ± 0.03 h, the characteristic decay time τ_2 value is 5.5 h (B), and 6.6 h (C). The values of ΔT_1 are 11.2 °C (B) and 11.9 °C (C), and are very similar. The quantity ΔT_2 has nearly the same

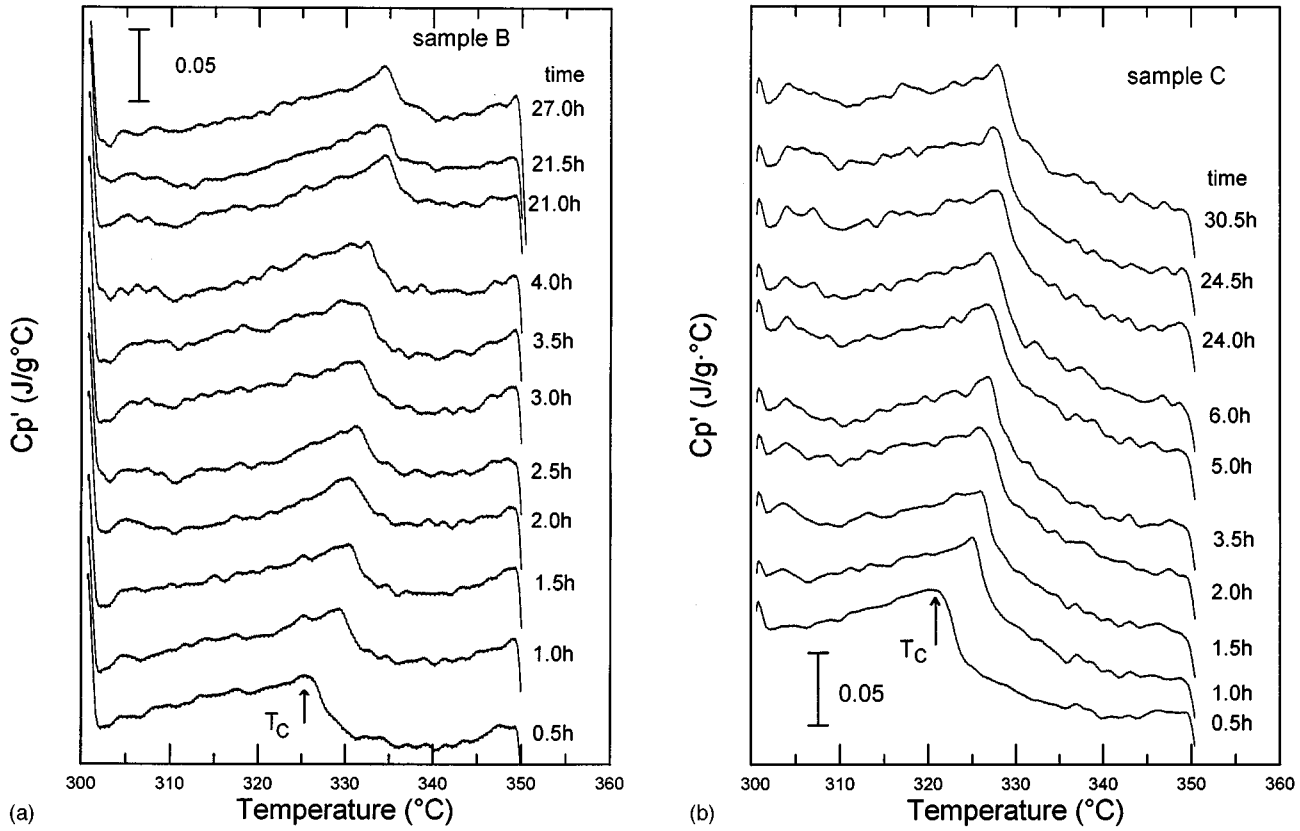

FIG. 5. The evolution of the DDSC curve with annealing time for sample B ($x=8$) (a) and sample C ($x=12$) (b).

value, 5.16 ± 0.01 °C, for both samples. It means that independent of the composition, two different relaxation processes influence the T_C value.

The rapid relaxation process (named 1) is probably the response to the topological rearrangement in some local regions, acting relatively fast at the measured temperature. The slow relaxation process (named 2) could account for the chemical SRO tendency which needs enhanced atomic mobility not available at these relatively low temperatures, but promoting nuclei formation at higher temperatures. The T_C is more sensitive to the topological SRO changes than to the chemical SRO ones, since ΔT_1 is about twice of ΔT_2. That is, shortening the Fe–Fe bond distance significantly affects T_C. However, once some embryos appear, large changes of T_C will come out [see Fig. 4(b)].

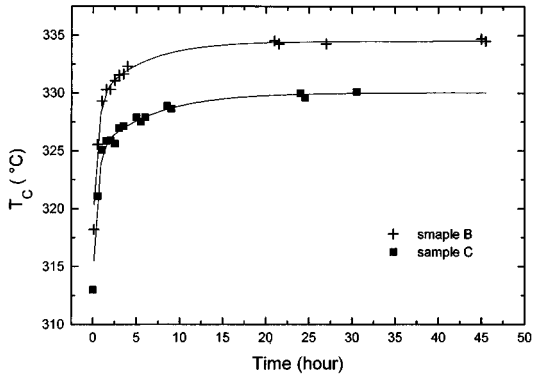

FIG. 6. T_C as function of annealing time of samples B ($x=8$) and C ($x=12$).

From the systematic analysis of the relaxation on some FINEMET amorphous alloys, as resulting from the heat treatment monitored by DSC and DDSC experiments, it is shown that most of the relaxation heat is released in the temperature interval between T_C and the onset of nanocrystallization, with a mean activation energy of 1.75 ± 0.15 eV.

From the storage heat capacity, the *in situ* measurement by DDSC in the temperature range of 300–350 °C shows the T_C enhancement with the annealing time. It was found that there are two distinct relaxation processes with characteristic decay times $\tau_1=0.45\pm0.03$ h and $\tau_2=6\pm0.5$ h, which are suggested to be caused by topological and chemical SRO changes, respectively.

Financial support from CIRIT by Project No. 1995SGR-00514 is acknowledged.

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