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Effects of pre-annealing or pre-cold-working treatments on the structural evolution of $Fe_{78}B_{13}Si_9$ amorphous alloys

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The effects of pre-annealing or pre-cold-working treatments on the structural modifications occurring during the heating of an $Fe_{78}B_{13}Si_9$ amorphous alloy are reported. Structural relaxation and crystallization stages were investigated with the help of internal friction measurements, Mössbauer spectroscopy and transmission electron microscopy. It is shown that pre-annealing involves atomic reorganizations, the effects of which are more obvious on the relaxation stage than on the crystallization one. Moreover, pre-cold-working implies atomic disturbances which modify the structural relaxation as well as the crystallization stage. The results are explained on the basis of the atomic structure of the amorphous alloy, consisting of atoms clusters, the characteristics of which are responsible for the observed phenomena.

1. Introduction

The material studied was a ferromagnetic amorphous alloy, chemical composition Fe 78%, B 13%, Si 9% (weight percentages). In a previous work [1], the structural evolution of such a metallic glass was followed as a function of temperature. The experimental technique used internal friction measurements performed at low frequency (1 Hz) with temperatures ranging from room temperature to 600 °C. Various stages were determined in the processes governing the return to structural stability of this material. According to internal friction measurements reported in Fig. 1, we note that four stages can be detected in the internal friction spectra of as-quenched $Fe_{78}B_{13}Si_9$ amorphous alloys. The first stage (20–260 °C), called "incubation", was characterized by no significant internal friction evolution. Between 260 and 450 °C, the internal friction spectrum exhibited a maximum which was attributed to "structural relaxation" and which constituted the second stage. The third stage (450–500 °C) was difficult to explain but was assumed to be associated with the ferro to paramagnetic transition or, possibly, with pre-crystallization phenomena. Finally, above 500 °C, the fourth stage corresponded to successive crystallization processes, each one giving rise to an internal friction maximum.

Of these four stages, two can be unambiguously explained: the second, where structural relaxation occurs, associated with a wide internal friction maximum, and the fourth, characterized by two internal friction maxima, each corresponding to a crystallization stage [2].

The structural relaxation can be defined as a homogeneous structural reorganization, the material undergoing only small short range atomic rearrangements, while crystallization will correspond to a heterogeneous return to stability in the sense that crystallized and amorphous phases will coexist until crystallization ends. The aim of the present study was to

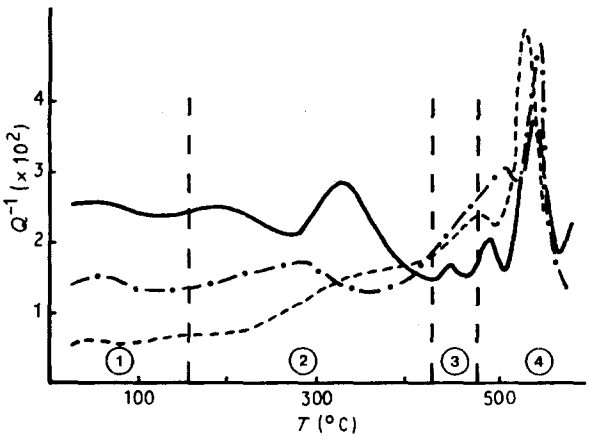

Figure 1 Schematic illustration of internal friction evolution as a function of temperature: (–·–) as-quenched, (– – –) pre-annealed, (—) pre-cold-worked state. 1, 2, 3, 4 are the successive stages termed, respectively, incubation, structural relaxation, pre-crystallization and crystallization.

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determine the possible influence of thermomechanical treatments on the progress of these two evolution stages. The treatments were carried out on the as-quenched alloy in order to modify the initial structural state before determining the further effect of temperature on the evolution of the material.

2. Results and discussion

In order to modify the structural state resulting from as-quenched conditions, preliminary heating treatments were first performed. This experiment was suggested by the observed effect of thermal cycles on the evolution of internal friction.

2.1. Influence of thermal cycles on the structural relaxation stage

As mentioned previously, the structural relaxation stage occurs between 260 and 450 °C, therefore the structural evolution of the material during thermal cycles performed in this temperature range was studied. The structural modifications detected by internal friction measurements are shown in Fig. 2a. In this figure, note that the internal friction level decreases progressively as a function of the number of cycles. This decrease leads to the disappearance of the wide internal friction maximum associated with the structural relaxation. The rate of this evolution is illustrated in Fig. 2b where the internal friction values, measured at 350 °C, are reported as a function of the corresponding cumulative heating time. This curve shows that, by extrapolation, the structural stability would be reached after long annealing times. This effect is studied in later experiments.

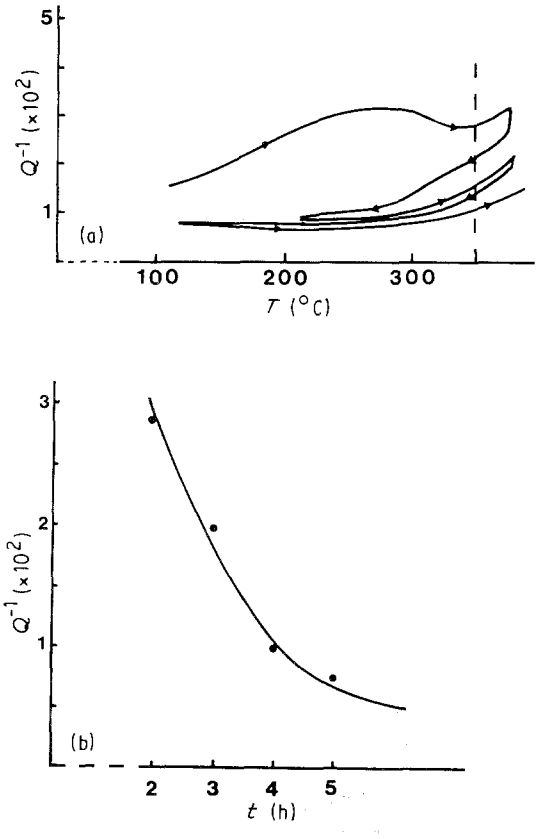

Figure 2 (a) Effect of heating cycles on the internal friction level between 100 and 400 °C. (b) Evolution of the internal friction level measured at 350 °C, (---) in (a), as a function of a cumulative heating time.

2.2. Influence of pre-annealing treatments on the structural relaxation stage

To ensure that the structural stability of the material corresponding to the temperature of the chosen thermal treatment is reached, long-term annealings were performed on the as-quenched material. After these pre-annealing treatments, the internal friction spectra evolution (Fig. 3) provides evidence of a modification of the atomic organization because of a decrease of the internal friction level. This behaviour is somewhat similar to that resulting from thermal cycling effects, as described previously. These preliminary heating treatments imply a "recovery" process involving either elastic stress accommodation or chemical coordination rearrangements [1]. In order to shed light on the occurrence of these phenomena, Mössbauer spectroscopy experiments were performed on the as-quenched material and on the recovered alloy after a pre-annealing treatment. The Mössbauer spectrum shown in Fig. 4 is observed to be the same when as-quenched and pre-annealed samples are compared. Conversely to internal friction experiments, Mössbauer spectroscopy seems to indicate that no significant atomic modifications are induced by such an annealing treatment, at least in the neighbouring Fe atoms. This result is confirmed by the curve in Fig. 5 and the data in Table I, where H is the mean hyperfine field, σ the standard deviation, A_1, A_2, A_3, are the relative intensities of the absorption lines (increasing velocity) in the elementary sextuplet. A_2 would be equal to 4, 0 or 2 for the direction of the hyperfine field relative to the γ-rays, perpendicular, parallel or at random, respectively.

The apparent disagreement between internal friction and Mössbauer spectroscopy evolution can be explained by considering that internal friction changes are governed by elastic effects produced by the relief of internal stresses resulting from the quenching process. Such a phenomenon implies little modification in the respective positions of atoms but, in order to keep the

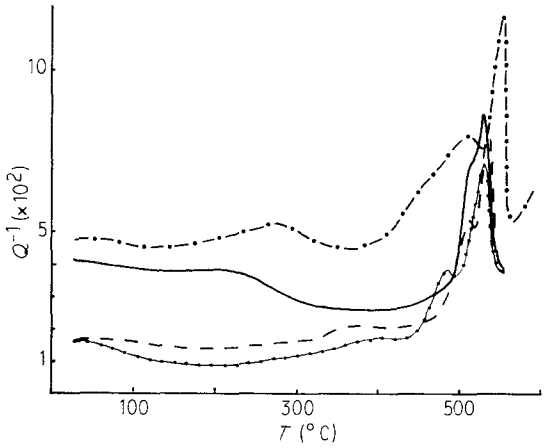

Figure 3 Effect of pre-annealing treatment on the internal friction spectra: (-·-) as-quenched, (—) 4 h, (-··-) 6 h, (– – –) 7 h pre-annealed sample at 350 °C.

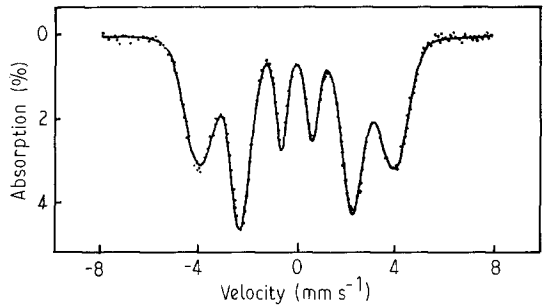

Figure 4 Mössbauer spectrum of a 3 h pre-annealed sample at 315 °C. This spectrum is exactly superimposable with that for the as-quenched specimen. The full curve corresponds to the fitted spectrum using a computer program by Dubois *et al.* [9].

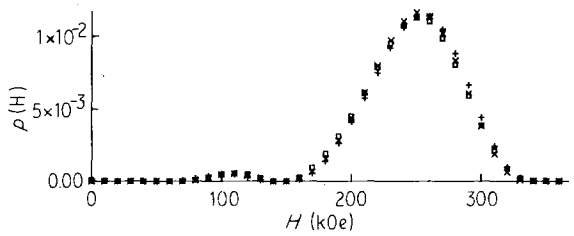

Figure 5 Hyperfine field distributions for $Fe_{78}B_{13}Si_9$ samples (□) as-quenched, (+) pre-annealed, (×) pre-cold-worked.

TABLE I Hyperfine parameters of $Fe_{78}B_{13}Si_9$ materials

	H (kOe)	σ (kOe)	$A_1:A_2:A_3$
As-quenched	244	39	3:2.82:1
Pre-annealed	248	38	3:2.85:1
Pre-cold-worked	245	37	3:2.61:1

neighbouring Fe atoms unchanged, accordingly to Mössbauer results, the atomic disturbances must affect only the relative positions of atoms other than Fe. Consequently, we propose a structure made of atomic clusters, centred on Fe atoms, keeping their configuration unchanged, during pre-annealing, but having the possibility to modify their relative orientations, as illustrated in the scheme of Fig. 6. Moreover, it must be borne in mind that internal friction is a dynamic method, so the phenomena detected by this technique must be related to instantaneous atomic modifications induced by the oscillating stress produced by the pendulum movement. Changes in the local symmetry of atomic clusters can lead to the diffusion of atoms as it is observed in the Snoek's or Zener's effect of crystalline materials.

2.3. Influence of pre-cold-working treatments on the structural relaxation stage

A modification of the as-quenched structure was performed by a cold-working treatment consisting of scratching the two faces of our amorphous alloy ribbons with the help of abrasive paper. The internal friction spectrum corresponding to such a cold-worked state (Fig. 1) exhibits important modifications

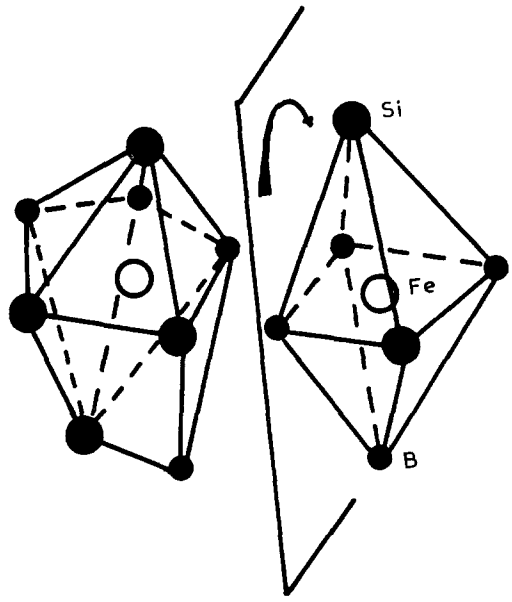

Figure 6 Strictly hypothetical scheme of atomic configurations showing the possibility of cluster rotations changing the relative positions of atoms such as Si and B, but retaining unchanged the neighbouring Fe atoms.

relating to the results obtained on as-quenched samples. In particular, we note that cold-working increases the initial internal friction background level and enhances the internal friction maximum associated with the structural relaxation stage. The modification of the incubation stage, in as-quenched samples, indicates that atomic disturbance is brought about by cold-working. According to the previous results, care must be taken to define precisely what type of atomic modification is involved. Mössbauer spectroscopy experiments were performed on the cold-worked specimen. The Mössbauer spectrum relative to the mechanically disturbed amorphous structure is somewhat changed for the as-quenched state. The observed changes (Fig. 5 and Table I) are just a slight decrease of the relative intensity of the second and fifth lines. This accounts for perturbations in the spin texture of the material, involving a new distribution of atomic clusters constituting the amorphous structure. More precisely, this structural reorganization implies relative rotations between atomic clusters including Fe atoms, the neighbourhood of which is unchanged during this process, as illustrated in Fig. 6.

Changes in the texture will consist of the re-orientation of atomic clusters constituting the amorphous material and will lead to a modification of the internal friction maximum profile associated with the structural relaxation. It has been reported [3–5] that this maximum is able to account for a relaxation time distribution corresponding to the respective responses of the various atomic configurations of clusters to mechanical stimulations resulting from the internal friction experiment. Consequently, if we assume that the spin texture modification implies preferential cluster orientation, such a phenomenon will lead to a reduction in the range of relaxation times and to an increase in the contribution of these privileged clusters to the internal friction level. This explains why, in the

case of a cold-worked sample, the observed internal friction maximum associated with structural relaxation appears less wide and higher than in the case of the as-quenched material.

2.4. Effect of pre-annealing or pre-cold-working on the crystallization stage

The internal friction maxima, observed during the fourth stage of the spectra in Fig. 1, were connected with successive stages of crystallization [1, 2, 6, 7]. In the case of our alloys, the maxima were respectively associated with the appearance of Fe_2B and αFe, at low temperatures and Fe_3B and (Fe, Si) [1, 2] at higher temperatures, as observed in FeB and FeSiB alloys [8–10].

If we compare the profile of the internal friction maxima obtained, with an as-quenched sample and with a pre-annealed specimen (Fig. 7), no significant modification of these maxima is observed after a pre-annealing treatment. This is valid whatever the length of the pre-annealing treatment, provided that the annealing is performed in the temperature range of structural relaxation. Such a phenomenon was observed in the crystallization of $Cu_{60}Zr_{40}$ alloy [11].

However, if we consider the internal friction spectra corresponding to the as-quenched and pre-cold-worked states (Fig. 8), noticeable differences appear in the profiles of internal friction maxima related to the

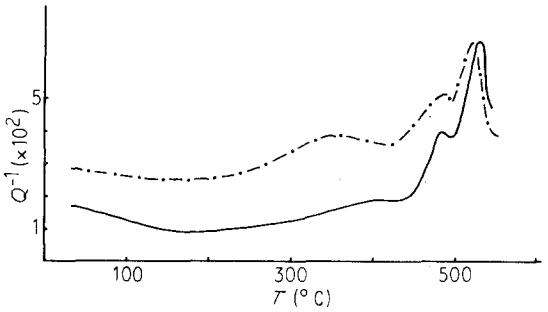

Figure 7 Effect of pre-annealing on the crystallization stage. In the as-quenched state, a small shift is observed in the temperature maxima but the heights of the maxima are unchanged when the internal friction background is substracted.

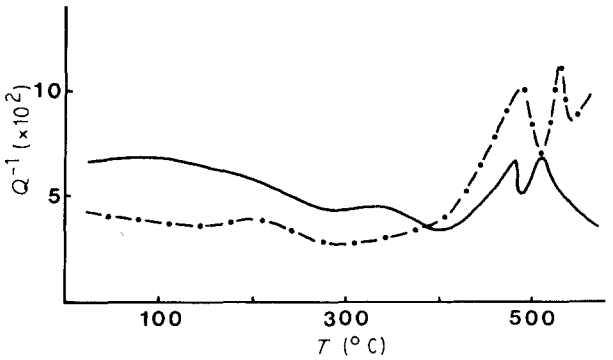

Figure 8 Effect of a pre-cold-working treatment on the internal friction maxima associated with the crystallization stages. An important decrease in these maxima is observed for the pre-cold-worked sample.

crystallization stages. More precisely, we note that for the cold-worked sample, the temperatures of the maxima are shifted, but principally, the heights of these maxima are clearly decreased compared to the as-quenched state. Additional structural studies carried out with the help of TEM (Fig. 9) have shown that the compounds resulting from the crystallization processes, are the same whatever is the initial structural state, i.e. as-quenched or cold-worked. In other terms the chemical decomposition of the amorphous phase is unmodified by the effects of cold-working. Mössbauer spectroscopy performed on the crystallized state showed that the chemical nature of the primary phase which appears in the early stage of crystallization, is a solid solution of Si in Fe rather than pure Fe (Fig. 10).

According to these observations, the reason why crystallization stages are disturbed by pre-cold-working must be related to physical parameters, and the most obvious one would result from the changes previously observed in the spin texture. Indeed, if we assume that such a phenomenon could imply a modification of the texture of atomic clusters, then it will induce effects on nucleation sites. For a pre-cold-worked sample, and under the effect of temperature, the gathering of nearest atomic clusters of approximately the same configurations and orientations could lead to nuclei reaching a critical size earlier in temperature than in as-quenched specimens. This explains why the positions of the internal friction maxima associated with crystallization, are shifted towards lower temperatures.

Explanations for the decrease in the maxima height are more complicated. During early stages of crystallization the amorphous phase transforms into a cc(Fe, Si) solid solution, the specific relaxation strength of which is high (i.e. high damping) leading to an increase in internal friction. On the other hand, it can be easily understood that Fe_2B and Fe_3B have low relaxation strengths. Indeed, in such compounds the nature of the chemical bond is more covalent than metallic, and leads to a rigid network where the atomic displacements, being slight, imply a low internal friction background. Consequently, when Fe_3B (or Fe_2B) nucleates, the internal friction will decrease and an internal friction maximum will result from the competitive effects of (Fe, Si) matrix evolution and Fe_3B (or Fe_2B) precipitation. On the basis of these considerations, the effect of cold-working on the height of the internal friction maxima associated with crystallization must be due to a modification of the nucleation processes of Fe_3B and Fe_2B, changing the relative amounts of the (Fe, Si) matrix and Fe_3B or Fe_2B precipitates.

According to these results, after crystallization, a pre-cold-worked sample must exhibit higher amounts of Fe_3B or Fe_2B than in an initially as-quenched specimen. In order to verify such a dependence, X-ray diffraction studies and TEM observations may shed some light. The first TEM results presented in Fig. 11 are not stimulating; we note a very fine grain size and a somewhat heterogeneous micro-structure (mean diameter of particles 50–60 nm). Heterogeneity in grain

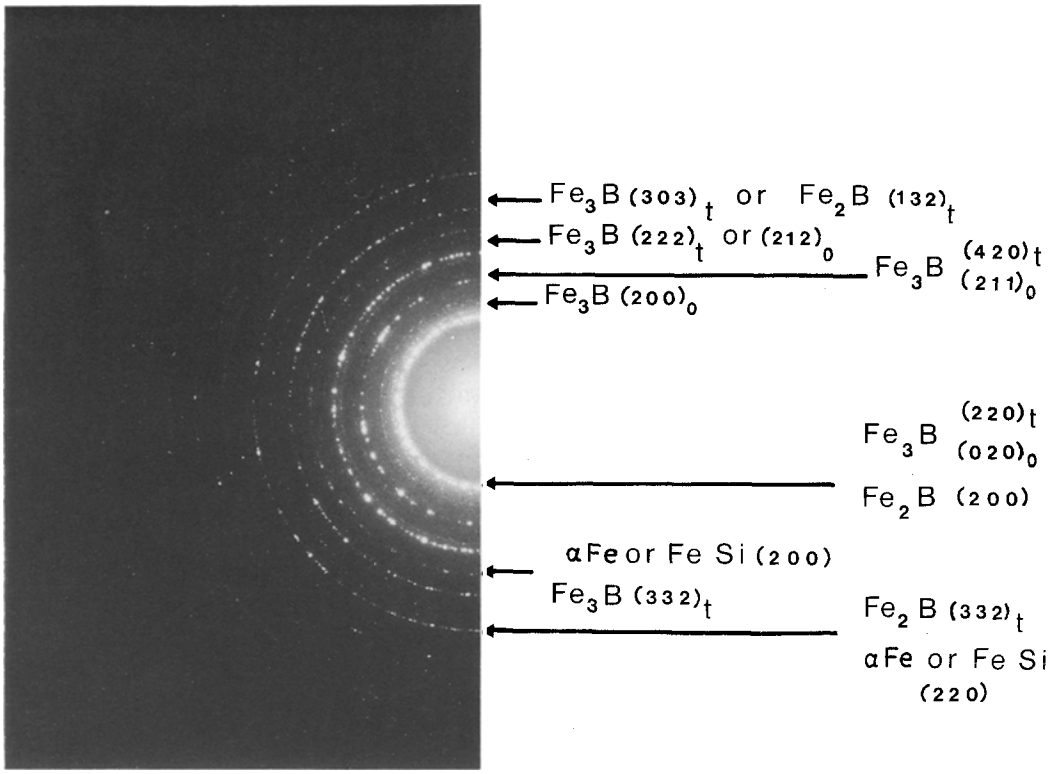

Figure 9 Identification of crystallization compounds by TEM diffraction. Various interpenetrations of diffraction rings can be seen. o, Orthorhombic; t, tetragonal.

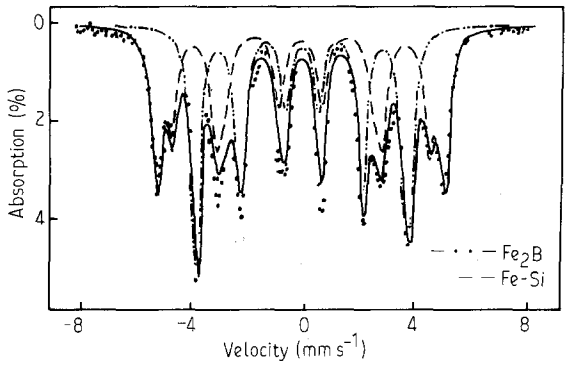

Figure 10 Mössbauer spectrum corresponding to a crystallized state, the second crystallization stage being complete. This spectrum is interpreted on the basis of Fe_2B and Fe–Si solid solution parameters.

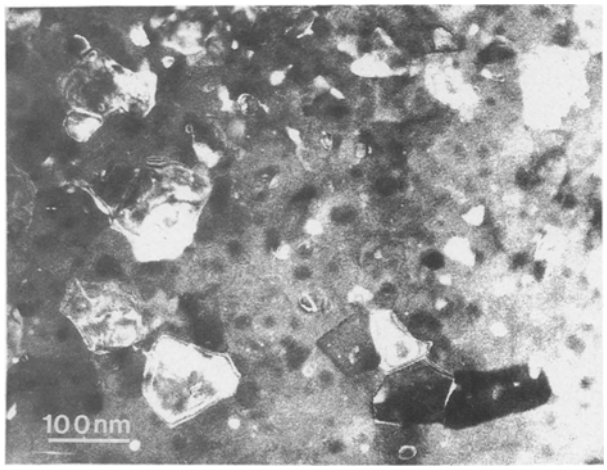

Figure 11 Transmission electron micrograph showing the heterogeneity of the crystallization grain size.

size favours a multi-stepped crystallization process but it is difficult to determine the chemical nature of each crystal (Fe, Si solid solution, Fe_3B or Fe_2B) because of the limited dimensions of the "selected-area" diaphragms used in TEM. Consequently, further study will compare the evolution of electron diffraction rings observed on as-quenched and pre-cold-worked samples annealed in the crystallization temperature range.

3. Conclusion

Preliminary annealing or cold-working treatments have been performed on as-quenched amorphous FeSiB alloys in order to study the possible effects of these treatments on the further structural modifications occurring as a function of temperature between room temperature and 600 °C. Structural relaxation and crystallization stages were specially investigated.

An as-quenched alloy exhibits an internal friction maximum associated with the structural relaxation stage. It was shown that this maximum was progressively reduced to zero as a function of annealing treatments and the average internal friction was decreased over the whole temperature range. This accounted for atomic reorganizations giving rise to anelastic effects.

Mössbauer spectroscopy showed no obvious modifications between an as-quenched and a pre-annealed sample in the structural relaxation range. It was deduced that the atomic reorganization revealed by internal friction experiments must keep the atomic neighbouring Fe atoms unchanged. From these results, a structure composed of clusters centred on Fe atoms was proposed for the as-quenched or annealed

alloys. The pre-annealing modified only the relative positions of clusters.

For the crystallization stage, it was observed that pre-annealing did not lead to any significant modifications in the profile of internal friction maxima associated with this phenomenon. The crystallization was explained on the basis of potential nuclei consisting of various atoms clusters. The effect of annealing was shown to be inefficient in modifying the cluster repartition of as-quenched samples. Thus the crystallization process appeared to be unchanged, whatever is the structural state, i.e. as-quenched or annealed. This was shown by internal friction measurements.

After a pre-cold-working treatment, the internal friction maximum, associated with the structural relaxation, was observed to be greatly modified relative to that corresponding to the as-quenched specimen. This was explained on the basis of a modification of the relaxation time distribution spectrum associated with the atomic cluster distribution, deduced from Mössbauer spectroscopy results showing a change in the spin texture.

The effect of cold-working on the crystallization stages was a clear modification of the profile of the internal friction maxima associated with these stages. This has been concluded to be a consequence of the previous effect revealed on the structural relaxation.

Modified nucleation was assumed to take place during crystallization of a pre-cold-worked sample. Such a structural state would involve effects on the nucleation processes leading to changes in the relative amounts of matrix (Fe, Si solid solution) and precipitates (Fe_3B or Fe_2B) compared to an initially as-quenched sample. Nevertheless, such an assumption must be verified by TEM studies.

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