Structural relaxation kinetics in FeSiB amorphous alloys

C. ANTONIONE*, M. BARICCO‡, G. RIONTINO*
*Istituto di Chimica Generale ed Inorganica, Facoltà di Farmacia, Via P. Giuria 9, 10125 Torino, Italy
‡Istituto Elettrotecnico Nazionale "G. Ferraris", Corso M. d'Azeglio 42, 10125 Torino, Italy

Structural relaxation kinetics in the FeSiB amorphous systems are studied on the basis of the activation energy spectrum model, through electrical resistivity variation measurements. The silicon content slightly modifies the features of the spectra, and a quite homogeneous distribution in energies for the processes leading to relaxation is obtained. Thermal stability against structural relaxation and crystallization is discussed.

1. Introduction

Amorphous FeSiB is one of the first and most widely studied metallic systems for magnetic applications. Owing to the very low power lossses and the very high permeability, this system is still of great interest. Several authors have discussed the influence of compositions and structure on the magnetic properties of this system; the importance of the preparation conditions [1] and thermal treatments [2, 3] have been singled out. The aim of this paper is to show the influence of silicon content on the thermal stability against structural relaxation and crystallization in a series of FeSiB amorphous alloys by means of electrical resistance measurements. The influence of composition on relaxation kinetics is discussed on the basis of a model recently proposed by Gibbs *et al.* [4].

2. Experimental procedure

A series of amorphous alloys having composition $Fe_{81}Si_xB_{19-x}$ ($3 \leqslant x \leqslant 10$ at.%) was prepared by a single-roller melt-spinning technique in air at a wheel speed of 6000 r.p.m. Typical dimensions of the ribbons were 2 mm in width and 30 μm in thickness. Different thermal treatments (under isothermal conditions and at constant heating rate) were performed under a purified argon atmosphere. For the isothermal treatments the annealing temperature was reached in a preheated furnace in about 1000 sec and maintained constant within ± 1 K.

The sample amorphousness was checked by means of a Philips X-ray diffractometer both before and after the thermal treatments.

The electrical resistance measurements were performed on samples typically 3 cm long by means of a four-probe d.c. digital ohmmeter with spring-loaded tungsten contacts. The sample temperature was monitored by a thermocouple 1 mm distant from the sample.

3. Results and discussion

3.1. Thermal stability

In Fig. 1 the electrical resistivity variations $\Delta\varrho/\varrho_0 \approx$

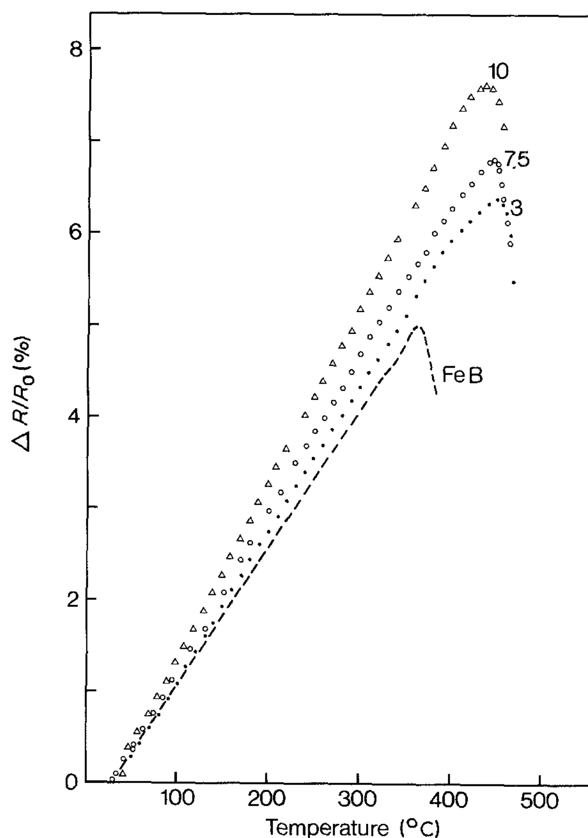

Figure 1 Electrical resistance (ER) variations, with respect to the room temperature value, for $Fe_{81-x}B_{19}Si_x$ amorphous alloys as functions of linearly increasing temperature. The silicon content (at.%) is indicated. Data for $Fe_{81}B_{19}$ amorphous master alloy are also reported (from [5]).

$R/R_0 = (R_T - R_{RT})/R_{RT}$ (R_{RT} being the resistance value at room temperature) of the samples examined are shown as functions of linearly increasing temperature ($2\,\mathrm{K\,min^{-1}}$). For comparison, previously obtained results [5] are reported for the amorphous master alloy $Fe_{81}B_{19}$. The crystallization temperature T_x, evidenced by an abrupt decrease of $\Delta R/R_0$, is higher in the silicon-containing samples with respect to FeB, reaching the maximum value for the sample-

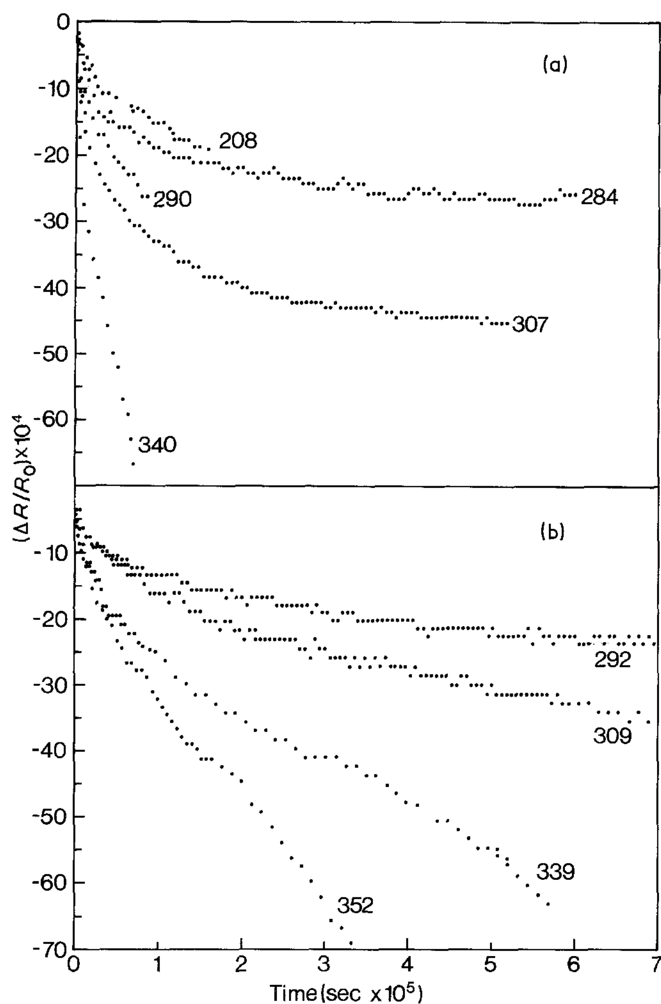

Figure 2 ER variations in isothermal conditions, with respect to zero time of annealing, for amorphous alloys (a) $Fe_{71}B_{19}Si_{10}$ and (b) $Fe_{78}B_{19}Si_3$ as functions of annealing time. The annealing temperatures (° C) are indicated.

containing 3 at.% Si (denoted Si 3) in agreement with previous results obtained with different techniques and in different experimental conditions [6]. In any case, an almost linear trend of the resistivity up to crystallization is observable. This is indicative of no appreciable chemical ordering during relaxation, as conversely suggested for other FeB-based amorphous alloys [5, 7, 8] in which a downward bending at intermediate temperatures has been pointed out.

For samples with 3 and 10 wt % Si (Si 3, Si 10) isothermal measurements were performed at temperatures lower than T_x. In Fig. 2 the electrical resistivity variation is shown as a function of time at different annealing temperatures. In this case, $\Delta R/R_0$ is equal to $[R(t) - R(t_0)]/R(t_0)$ where t_0 is the time at which isothermal conditions are attained. At all the temperatures considered, the electrical resistivity shows a decreasing trend which is mainly associated with the decrease of free volume introduced by quenching [9, 10]. The decrease is enhanced, in the same range of temperatures, by a higher silicon content, as can be seen in Fig. 3 in which the value of $\Delta R/R_0$ at 15 000 sec

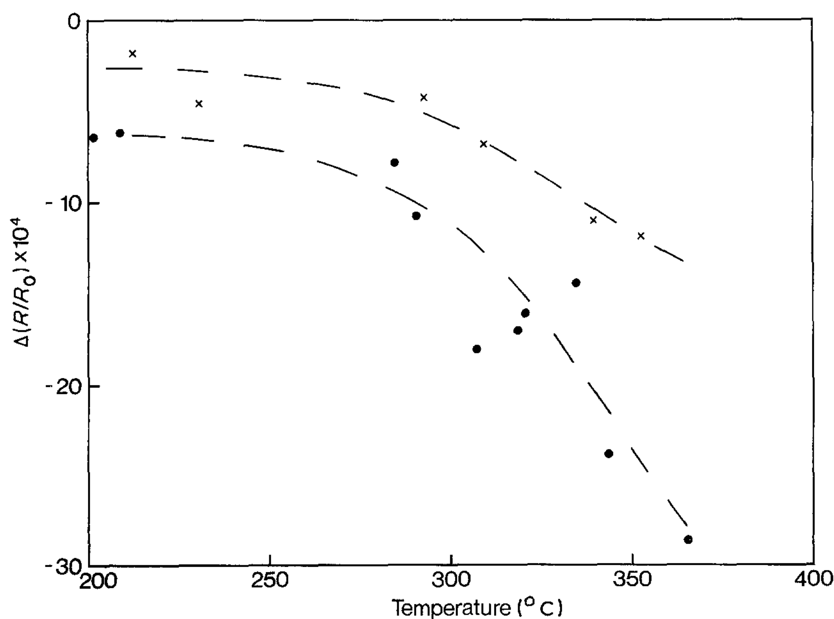

Figure 3 ER variation values taken at 15 000 sec from the initial time of annealing for amorphous alloys (×) Si 3 and (●) Si 10, as functions of annealing temperatures.

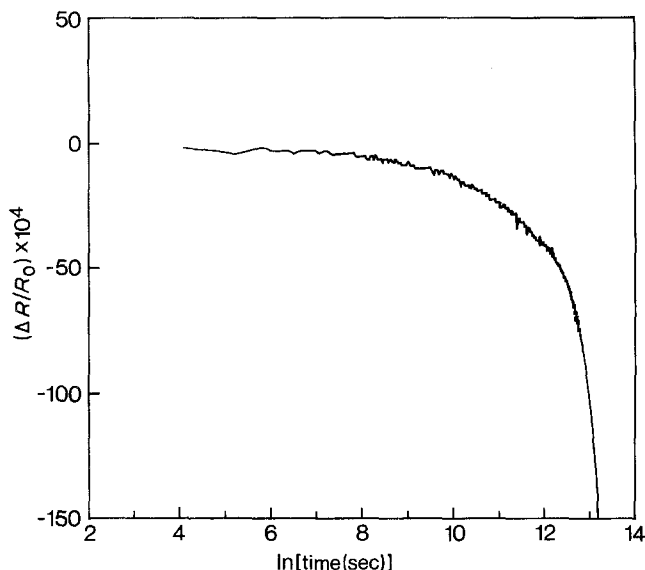

Figure 4 ER variations as functions of ln (time), for amorphous $Fe_{78}B_{19}Si_3$ isothermally annealed at 352° C.

is plotted against the annealing temperature. The resulting minor effect on the resistivity change by an addition of 3 at.% Si compared with 10 at.% indicates a higher stability against structural relaxation processes for the first alloy.

In some cases, the annealing was carried out for more than 5×10^5 sec (about 6 days) in order to check the behaviour of the material for crystallization under isothermal conditions. The downward bending of the curves in these cases is clearly due to the start of crystallization processes, as confirmed by X-ray diffractometry.

3.2. Kinetic analysis of structural relaxation

The structural relaxation phenomena have been analysed on the basis of the activation energy spectrum (AES) model [4]. In this model, the total change of a physical property P due to thermally activated and uncorrelated processes may be expressed by

$$\Delta P = p_0(E, T)\, E_0 \qquad E_0 = kT \ln (\nu_0 t)$$

where p_0 is the total available property change in the activation energy range from E to $E + dE$, k the Boltzmann constant, T and t the annealing temperature and time, respectively, ν_0 a frequency factor of the order of the Debye frequency ($10^{12}\,sec^{-1}$). The number of available processes, $q(E)$ is related to the property change by a coupling factor $c(E)$, leading to $p_0(E) = c(E)\, q(E)$. By assuming that p_0 is constant in the range of analysed E in each isothermal experiment, the property change due to structural relaxation would be proportional to ln t.

If we consider the plot of $\Delta R/R_0$ relative to the longest isothermal treatments as a function of ln t, a deviation from linear behaviour is in effect observable for the Si 3 sample, as shown in Fig. 4. In the last part of the curve, this is due to the start of the crystallization phenomena that lead to a higher variation of the examined property. Before that, the departure from linearity is due to the energy dependence of p_0; for the shortest annealing times, the explored energy range is not sufficient to show this dependence, considering that p_0 is usually admitted to be a very broad function [4].

A plot of the rate of the resistivity change $d(\Delta R)/d(\ln t)$ against annealing temperature is shown in Fig. 5 for Si 3 and Si 10 alloys. As can be seen, the different

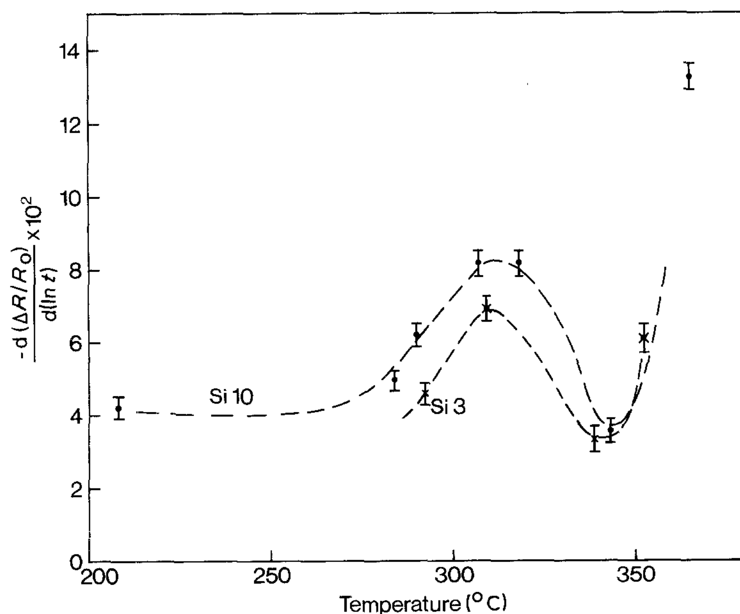

Figure 5 ln (time) derivative of ER variations as a function of annealing temperatures for Si 3 and Si 10 amorphous alloys.

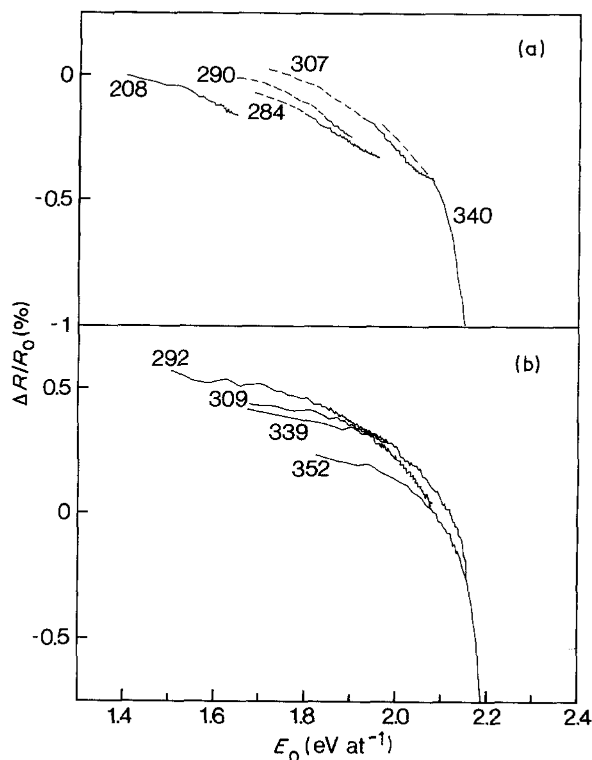

Figure 6 ER variations for (a) Si 10 and (b) Si 3 alloys, as functions of $E_0 = kT \ln(\nu_0 t)$.

silicon content slightly modifies the rate of change, but not its temperature dependence. The non-linear trend of the rate, already found in other amorphous systems [11], confirms again that p_0 is not energy-independent.

Following the AES model, a "master curve" for the samples examined has been obtained by plotting the resistivity change under isothermal conditions as a function of $E_0 = kT \ln(\nu_0 t)$ (Fig. 6). To obtain this curve, a subtraction of the temperature coefficient for resistivity (TCR), independent of the relaxation phenomena, is necessary to eliminate all intrinsic effects. The dependence of resistivity on the linearly

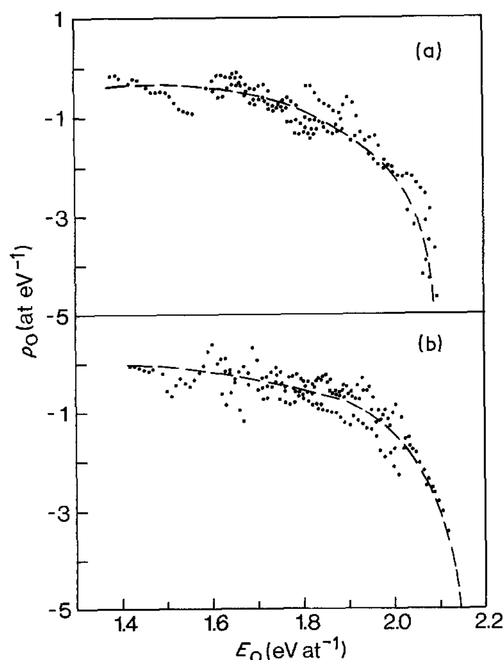

Figure 7 Initial spectra of activation energies for (a) $Fe_{71}B_{19}Si_{10}$ and (b) $Fe_{78}B_{19}Si_3$ amorphous alloys.

increasing temperature in the first 100 K starting from room temperature, as well as the resistivity dependence during the fast heating up to isothermal annealing, are considered, assuming that no appreciable relaxation phenomena take place in these conditions. Both methods lead to the same result, and we take a linear coefficient of $1.87 \times 10^{-2}\,K^{-1}$ for $Fe_{80}Si_{10}B_{10}$ and $1.68 \times 10^{-2}\,K^{-1}$ for $Fe_{80}Si_3B_{17}$.

The slight mismatch between the different segments of the master curve could be due either to composition inhomogeneities of the samples used for the different isothermal treatments or to an improper choice of the TCR subtraction. Here again, a fast decrease in the last part of the curve is clearly observable, due to the incipient crystallization of the samples.

In the case of isothermal treatments at the highest temperatures, all the relaxation phenomena occur during the heating up to the annealing temperature, and only crystallization effects can be detected thereafter. This confirms the importance of a fast reaching of the isothermal conditions to evaluate the incidence of the fastest processes in structural relaxation, as pointed out by different authors [11, 12].

The derivative of the master curves with respect to E_0, giving the initial spectrum of the activation energies, is reported in Fig. 7 for Si 3 and Si 10 samples. Two types of deduction can be made from the trend so obtained. The nearly constant value of p_0 for both samples, before crystallization starts, indicates firstly that the activated processes contributing to the resistivity change are uniformly distributed in energy and that, assuming a similar value of the coupling factor $c(E)$ at each activation energy considered, for the Si 10 samples the number of such processes in each range between E and $E + \mathrm{d}E$ is higher than for the Si 3 sample. The structureless character of the spectra indicates that quite homogeneous types of process contribute to relaxation, like free volume reduction, differently from what happens in more complex amorphous alloys [13], for which different chemical affinities between the component atoms may be hypothesized to act.

The p_0 value due to crystallization occurs at about $2\,\mathrm{eV\,at.}^{-1}$ for both samples. A slightly higher value can be obtained for Si 3 alloy, confirming its higher stability as previously singled out. These values are in agreement with the activation energies for crystallization obtained in different ways on amorphous alloys with similar compositions [3, 14].

4. Concluding remarks

From isothermal and tempering measurements of the electrical resistivity variations in FeBSi amorphous alloys, the same effect of the silicon content has been shown on structural relaxation and crystallization: for the lowest silicon content, a higher stability is observed.

Structural relaxation phenomena show, in Si 3 and Si 10 samples, a slightly different rate but a similar temperature dependence.

The AES model has been used to analyse the relaxation data, demonstrating a dependence of p_0 on the energy.

A master curve has been obtained for both the alloys, showing a similar behaviour. The trend of the initial spectrum of activation energies suggest that the processes contributing to structural relaxation are of the same type, uniformly distributed in energy.

References

1. F. E. LUBORSKY, J. J. BECKER, J. L. WALTER and H. H. LIEBERMANN, *IEEE Trans, Magn.* **Mag-15** (1979) 1146.
2. A. ZALUSKA and H. MATYJA, in Proceedings of 4th International Conference on Rapidly Quenched Metals, Vol. 1, edited by T. Masumoto and K. Suzuki (Japan Institute of Metals, Sendai, 1982) p. 683.
3. S. SURINACH, M. D. BARO and N. CLAVAGUERA, in Proceedings of 5th International Conference on Rapidly Quenched Metals, Vol. 1, edited by S. Steeb and H. Warlimont (North-Holland, Amsterdam, 1985) p. 323.
4. M. R. J. GIBBS, J. E. EVETTS and A. J. LEAKE, *J. Mater. Sci.* **18** (1983) 278.
5. G. RIONTINO and F. MARINO, *Scripta Metall.* **18** (1984) 13.
6. C. ANTONIONE, L. BATTEZZATI, G. COCCO and F. MARINO, *Z. Metallkde* **75** (1984) 715.
7. P. ALLIA, D. ANDREONE, R. SATO TURTELLI, F. VINAI and G. RIONTINO, *J. Appl. Phys.* **53** (1982) 8798.
8. G. RIONTINO, M. BARICCO and F. MARINO, *Scripta Metall.* **20** (1986) 1011.
9. A. van den BEUKEL, *ibid.* **20** (1986) 783.
10. B. FOGARASSY, A. BOHONYEY, A. CZIRAKI, I. SZABO, L. GRANASY, A. LOVAS and I. BAKONYI, *J. Physique. Coll.* **C8** (1985) C8-473.
11. E. WOLDT and J. A. LEAKE, in Proceedings of 5th International Conference on Rapidly Quenched Metals, Vol. 1. edited by S. Steeb and H. Warlimont, (North-Holland, Amsterdam, 1985) p. 687.
12. H. R. SINNING, L. LEONARDSSON and R. W. CAHN, *Int. J. Rapid Solidification* **1** (1985–85) 175.
13. G. RIONTINO and M. BARICCO,*Phil. Mag. A* in press.
14. J. WOLNY, J. M. DUBOIS and Y. SOLTYS, in Proceedings of 5th International Conference on Rapidly Quenched Metals, Vol. 1, edited by S. Steeb and H. Warlimont (North-Holland, Amsterdam, 1985) p. 307.

Received 10 July
and accepted 12 November 1987