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Structural relaxation in FeNiCrPB amorphous alloys by joint isothermal and tempering measurements of the electrical resistivity

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Primak's analysis of kinetic processes distributed in activation energy has been applied to discuss electrical resistivity measurements performed on two FeNiCrPB amorphous alloys. The structural relaxation has been studied both in isothermal and in tempering conditions. From a comparison of the kinetic analysis of these different measurements, the attack frequency of the activated processes has been computed and turns out to be $10^9\,\mathrm{sec}^{-1}$. Reversible and irreversible phenomena have been observed and studied separately. In these amorphous alloys, a higher Cr content leads to a higher thermal stability against structural relaxation, whereas the kinetic behaviour seems to be quite similar.

1. Introduction

Several attempts have been carried out in the last years to draw a phenomenological description of the structural relaxation processes in metallic glasses. Although many experimental data have been obtained, both from direct analysis of the evolution of the structure and from indirect analysis of the change of different physical properties, a complete description of the microscopic mechanisms of structural relaxation is still lacking.

In order to get a more accurate picture of such processes, several models have been proposed, some of which give a kinetic description of the changes of various structure-dependent properties [1]. Some research groups have worked on amorphous alloys with similar compositions, looking at different properties and showing the differences between the predictions of various models. In some cases [2], a sharp separation between reversible and irreversible processes is supposed, the first ones being associated with a chemical short range ordering and the second ones with a topological short range ordering, whereas in other cases [3] this distinction is less clear and the existence of a set of processes distributed in activation energy is assumed.

One of the most popular approaches exploits the Activation Energy Spectrum (AES) model (and successive modifications), proposed by Gibbs *et al.* [3–5] and based on a picture of the relaxation processes in terms of two-level systems, and on Primak's analysis of processes distributed in activation energy [6]. Such a model has been applied to several property changes associated to some type of atomic rearrangements, like electrical resistivity [7], coercive field [8], length [9], Young's modulus [10], creep [11], elastic properties [12] and enthalpy of relaxation [13].

In some cases, the existence of correlations between different property changes has been pointed out (for instance between length changes and Young's modulus [14]), whereas in other cases different properties do not show any correlation (for instance, electrical resistivity and Young's modulus [15]). By comparing the behaviour of different macroscopic properties affected by the relaxation process, it could be possible to draw some phenomenological hypotheses of the microscopic relaxation mechanisms.

On the other hand, the kinetic analysis of the changes of a single property could provide a good tool for the analysis of the population distribution of the various two-level systems (TLS), a starting point for a phenomenological description of the relaxation processes. The hypothesis of complete independency of different processes is the main limit of Primak's approach, which considers only their number in a given energy interval and not their type. Recently, an improved version of the AES model, with an exact treatment of the kinetic equations, has been proposed by Hygate and Gibbs [4]. To explain the reversible variations of a property, they suppose the existence of a correlation between barrier heights and the energy splittings of the TLS for the reversible processes, and associate the macroscopic variables with TLS parameters. A different behaviour seems to characterize the irreversible processes, where such a correlation is not present [5].

The aim of this work is to perform a kinetic analysis of the electrical resistivity variations in two FeNiCrPB amorphous alloys with different Cr content. Usually, for structural relaxation studies, only isothermal measurements are considered. In the present case, starting from Primak's analysis [6], we consider the

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data of both isothermal and tempering experiments in order to derive the initial activation energy spectrum for the considered property. From the comparison of the spectra obtained in both ways, the influence of the different parameters used in the model is pointed out. The effect of Cr on the structural relaxation of these alloys will also be briefly discussed.

2. Description of Primak's method

Let us consider a generic property related to a set of independent, activated processes distributed in activation energy. According to Primak [6], the initial spectrum of the available changes of this property can be obtained both from isothermal and tempering measurements. The change ΔP of the property P can be considered either as a function of time t, at a fixed temperature T, or as a function of the temperature, at a constant heating rate V_s.

In either case, time and temperature can be associated with a value of the activation energy, by means of one of the following equations

$$E_0 = kT \ln(\nu_0 t), \text{ in isothermal conditions} \quad (1a)$$

$$E_0 = (kT/b)[\ln(\nu_0 T/V_s) - a], \text{ in tempering conditions} \quad (1b)$$

where ν_0 is the attack frequency and a and b are suitable numerical parameters, discussed later in detail.

In any case, the activated contribution ΔP to the macroscopic changes of the property can be expressed by

$$\Delta P = \int_0^\infty p(E)\,\mathrm{d}E = \int_0^\infty p_0(E)\,\vartheta(E)\,\mathrm{d}E \quad (2)$$

where $p(E)$ is the density of the property changes, $p_0(E)$ is the initial spectrum of the available property changes and $\vartheta(E)$ is the characteristic annealing function, taking slightly different forms in isothermal and tempering treatments. The upper integration limit in Equation 2 can be substituted by the value of E_0 by approximating $\vartheta(E)$ to a step function

$$\Delta P = \int_0^{E_0} p_0(E)\,\mathrm{d}E \quad (3)$$

The values of the p_0 function can be obtained by the following equations

$$p_0(E) = \mathrm{d}\Delta P/\mathrm{d}E = (1/kT)\,\mathrm{d}\Delta P/\mathrm{d}\ln t = (t/kT)\,\mathrm{d}\Delta P/\mathrm{d}t, \quad (4a)$$

in isothermal conditions, and

$$p_0(E) = \mathrm{d}\Delta P/\mathrm{d}T(1/F_c(T)), \text{ with } F_c = (k/b)[\ln(\nu_0 T/V_s) - a + 1], \quad (4b)$$

in tempering conditions.

The density of the property changes $p_0(E)$ is related to the density of available activated processes $q_0(E)$, through the coupling factor $c(E)$

$$p_0(E) = c(E)\,q_0(E) \quad (5)$$

Since in this approach all relaxation processes are considered uncorrelated, the $q_0(E)$ value is just the number of all available processes having an activation energy in the range between E and $E + \mathrm{d}E$, without making any distinction among them. For this reason, the $c(E)$ value should be written as $\langle c(E) \rangle$, where the average is to be performed over all possible processes having activation energy in the range between E and $E + \mathrm{d}E$ [16].

Within this approach, every different physical property is characterized by a different value of $\langle c(E) \rangle$ and $p_0(E)$. However, $q_0(E)$ is assumed to be an intrinsic feature of a given amorphous material produced under given conditions. Notice that a particular relaxation process (described by $q_0(E)$ and taking place at a given energy) may affect different properties to different extents. Certain properties could also be virtually unaffected by that particular process. This does not mean that $q_0(E)$ is identically zero; it just means that $\langle c(E) \rangle$ is vanishingly small for the considered property.

In order to give a complete, even if phenomenological description of the relaxation processes, it would be necessary to know the $q_0(E)$ function, which however remains experimentally unaccessible. By comparing the $p_0(E)$ curves obtained for different properties in the same material, possible correlations may be found. It would be possible to establish, for instance, if there are physical properties which are affected in the same way in a particular energy range, i.e. have a similar $\langle c(E) \rangle$ function.

3. Experimental procedure

Amorphous alloys of composition $Fe_{44-x}Ni_{36}Cr_xP_{14}B_6$ ($x = 5$ and 10 at %) were prepared by melt spinning in air, starting from pure elements and Fe–B and Fe–P master alloys.

The relative electrical resistance variations (supposed equal to the relative electrical resistivity variations) were measured directly by the four-probe d.c. method with spring-loaded W contacts. The samples, about 4 cm long, were placed over a Macor holder and put inside a quartz tube with purified Ar atmosphere. During heat treatments, the temperature was controlled by a thermocouple placed near the sample.

The tempering experiments were performed at a constant heating rate of $0.66\,\mathrm{K\,sec^{-1}}$.

For isothermal experiments, the furnace was preheated at a temperature slightly higher than the one chosen for the annealing, in order to reach the measurement temperature in a time as short as possible. After stabilization of the temperature, the tube with the sample holder was inserted in the furnace and reached the isothermal conditions in about 1000 sec. X-ray diffractometry has been used to check the amorphousness of the ribbons, both in the as-prepared condition and after each anneal.

In a study of structural relaxation through isothermal experiments, the heating transient is a crucial parameter. In some kinetic studies on metallic glasses, the measurements have been carried out at fixed temperature after an annealing procedure, comparing the results with the ones obtained in the same conditions on untreated samples [17]. In this case, a faster heating of the sample may be attained. However, a measurement of the absolute value of the physical property is needed, instead of using the relative property variations. Such a fact obviously increases the experimental error.

The results obtained by means of the measurements described here are shown elsewhere [18, 19].

4. Data analysis

4.1. Isothermal experiments

Following the AES model, a plot of the property change as a function of the activation energy E_0 obtained from Equation 1a allows one to unify the variations measured at different temperatures in one curve (the master curve [7]), representing the relative change of the property at each considered energy value. In principle, it should be possible to obtain the same curve with a single measurement, performed at a fixed temperature, but for a time long enough to scan the entire energy range of interest.

We consider the electrical resistivity variations as the difference between the resistance of the sample in annealing conditions and the resistance value at room temperature, normalized to the room temperature value

$$\frac{\Delta R}{R_{\mathrm{rt}}} = \frac{R(T, t) - R_{\mathrm{rt}}}{R_{\mathrm{rt}}} \qquad (6)$$

Under the assumption that the heating of the sample to the annealing temperature is fast enough to avoid any relevant relaxation processes, only the change of the electrical resistivity during the isothermal annealing was considered, neglecting the data obtained during the initial rise. A temperature-dependent value has been subtracted from the electrical resistivity variations observed in isothermal conditions, in order to put into evidence only the activated part of the observed changes ($\Delta P = \Delta R/R_{\mathrm{rt}}$ reduced). Such a value is connected with the Debye–Waller effect and with any other unactivated contributions to the resistivity at each annealing temperature. Usually [7, 15], a linear temperature dependence is assumed for such a value, analogous with crystalline alloys. Also in this case, linear coefficients have been obtained by measuring the resistivity of the as-quenched samples in the first 70 K above room temperature, both during heating up to the temperature of isothermal annealing and in tempering experiments at a constant heating rate. No relaxation phenomena are supposed to take place in the considered temperature range. This approach is the same suggested by Fogarassy *et al.* [15], whereas in paper [7] a fully relaxed sample is taken into account. We obtained linear coefficient values of 0.00587 and 0.00167 K^{-1}, respectively, for the amorphous alloys with 5 and 10% Cr content.

The master curves for the two samples are shown in Figs 1 and 2. The mismatch of different segments of the curve can be related to

(1) a partial inhomogeneity among samples used in different isothermal anneals;

(2) a wrong choice of the linear coefficient, leading one to either over- or under-estimate the intrinsic contribution at different temperatures and

(3) too long a temperature transient before isothermal treatment of samples, resulting in the occurrence of relevant relaxation phenomena in non-isothermal conditions and, as a consequence, in a comparison of samples with different initial conditions.

The $p_0(E)$ curve is obtained by differentiating the master curve with respect to E_0, according to Equation 4a. Each segment of the master curve is differentiated separately in this way and the y-axis shifts of the master curve have no influence on the subsequent calculations. The results are shown in Figs 3 and 4, for the alloys containing 5 and 10% Cr, respectively. Each segment of the master curve and of the $p_0(E)$ curve has been interpolated and smoothed, in order to reduce the scattering generated by numerical differentiation. According to the current views [5], the attack frequency has been initially chosen to be of the order $10^{12}\,\mathrm{sec}^{-1}$, i.e. the Debye frequency for single atom jumps. We will show later that such a value has to be modified to some extent to better explain the present results.

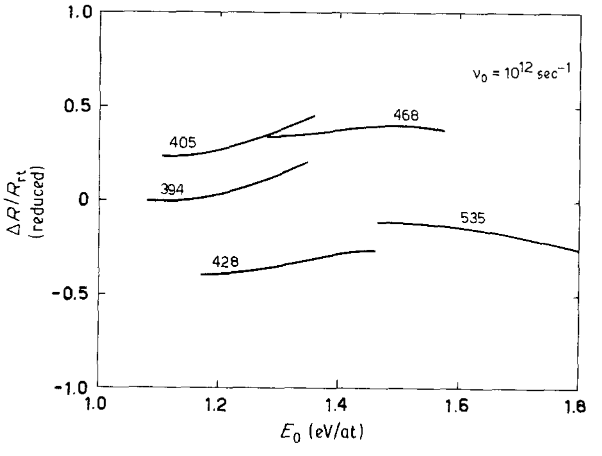

Figure 1 Reduced variations of the electrical resistivity against activation energy for the $\mathrm{Fe_{39}Ni_{36}Cr_5P_{14}B_6}$ amorphous alloy. The temperature of each isothermal treatment is indicated in K.

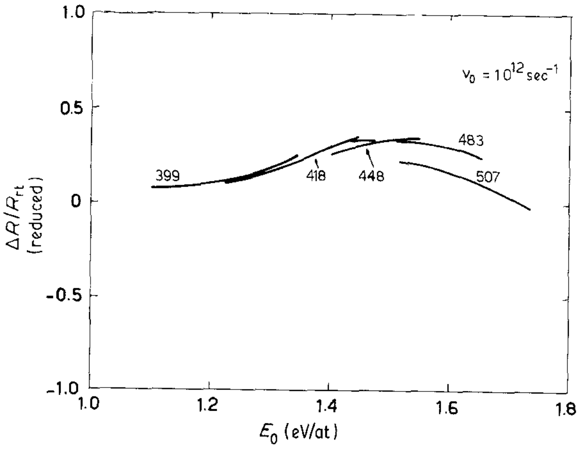

Figure 2 Reduced variations of the electrical resistivity against activation energy for the $\mathrm{Fe_{34}Ni_{36}Cr_{10}P_{14}B_6}$ amorphous alloy. The temperature of each isothermal treatment is indicated in K.

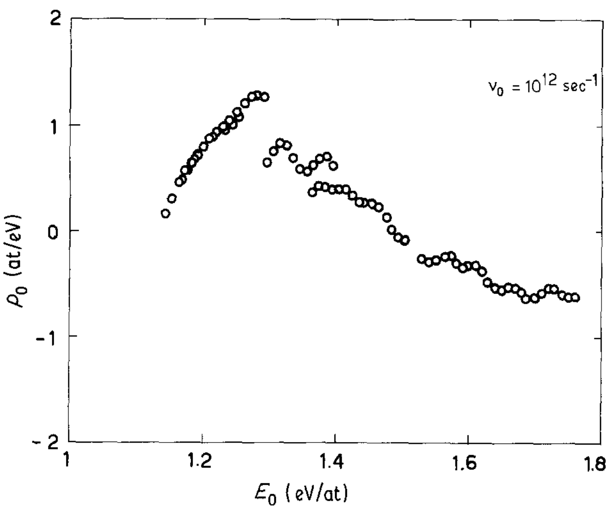

Figure 3 Initial activation energy spectrum obtained from isothermal measurements for the $Fe_{39}Ni_{36}Cr_5P_{14}B_6$ amorphous alloy. Attack frequency = 10^{12} sec^{-1}.

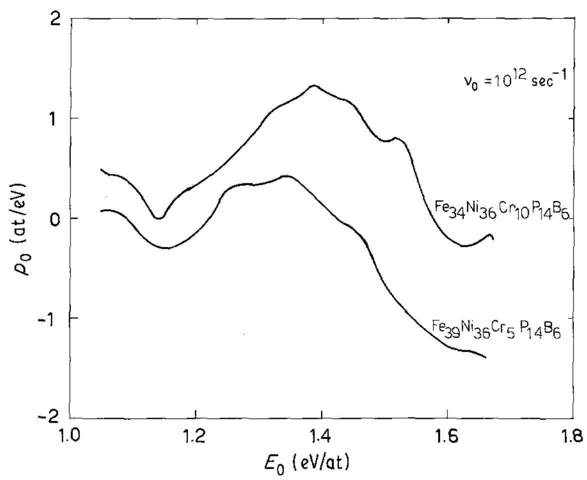

Figure 5 Initial activation energy spectra obtained from tempering measurements at a constant heating rate of 0.66 K sec^{-1}. Attack frequency = 10^{12} sec^{-1}.

4.2. Tempering experiments

The $p_0(E)$ curve can also be obtained, in tempering conditions, from the derivative of the property change with respect to the temperature (Equation 4b). Each temperature value is then associated to an energy by Equation 1b. The a and b values appearing in Equations 1b and 4b have been obtained by Primak's linearization [6] of the function $y + \ln(y + 2)$, where $y = E_0/kT$, in the energy range between 0.5 and 2.5 eV/at, i.e., typical values for the considered relaxation phenomena. These parameters turn out to be $a = 2.463$ and $b = 1.033$, in agreement with the values suggested by Primak [6]. In tempering conditions, the relationship between temperature and energy, obtained from Equation 1b, is quite linear, and depends on the v_0 and V_s values.

Here again, the same linear coefficient described previously has been subtracted from the experimental data. This correction leads to the subtraction of a constant value from the derivative $d\Delta P/dT$. It is worth noting that any different choice of the linear coefficient will be simply reflected in a shift of the $p_0(E)$ curve along the y-axis, without affecting its shape.

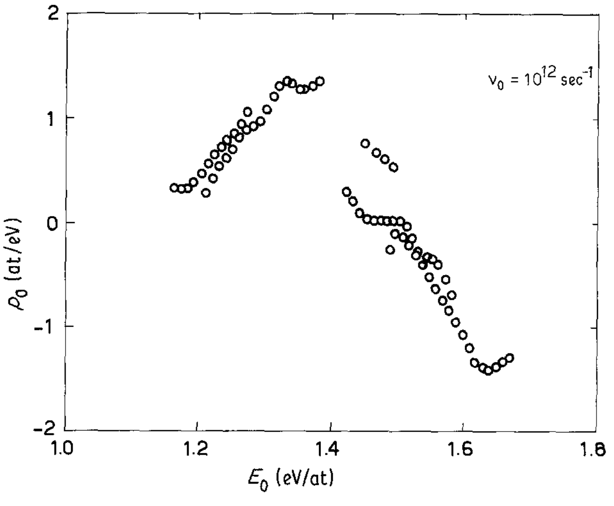

Figure 4 Initial activation energy spectrum obtained from isothermal measurements for the $Fe_{34}Ni_{36}Cr_{10}P_{14}B_6$ amorphous alloy. Attack frequency = 10^{12} sec^{-1}.

According to Equation 4b, the derivative of the property change with respect to the temperature must be multiplied by the $F_c(T)$ factor. The $p_0(E)$ curves obtained in this way with $v_0 = 10^{12}$ sec^{-1} are shown in Fig. 5. Like in isothermal conditions, the calculation of the numerical derivative required several interpolation and smoothing routines.

5. Discussion

5.1. Attack frequency factor

A comparison of the $p_0(E)$ curves obtained by both methods, makes it possible to immediately verify that the considered range of activation energies is quite similar, and the general trends of the curves are comparable. A more accurate analysis can suggest the better value to choose for the v_0 parameter. The attack frequency factor is usually obtained from the analysis of cross-over effects, and different values have been suggested for it [16]. We define the v_0 value by direct comparison of the $p_0(E)$ curves obtained in both cases, looking for the best agreement between them. As a matter of fact, a change of the v_0 value has different effects on the shape of the $p_0(E)$ curves obtained in different ways. In fact, for the curves obtained from isothermal experiments, a change in v_0 results only in a shift along the energy axis, with a progressive spread of the curve (the higher the v_0 value, the broader the curve), without any change along the y-axis. On the other hand, the $p_0(E)$ curves obtained from tempering experiments are modified along both the x- and the y-axis by a change in v_0, owing to the presence of the function $F_c(T)$ in Equation 4b (the lower the v_0 value, the narrower and higher the $p_0(E)$ curve). For instance, the effects of a change of v_0 by several orders of magnitude on the $p_0(E)$ curves of $Fe_{34}Ni_{36}Cr_{10}P_{14}B_6$ obtained through isothermal and tempering measurements are shown in Figs 6 and 7 respectively.

It should be recalled that the choice of the value of the linear coefficient does not affect the shape of the $p_0(E)$ curves derived in isothermal conditions, while,

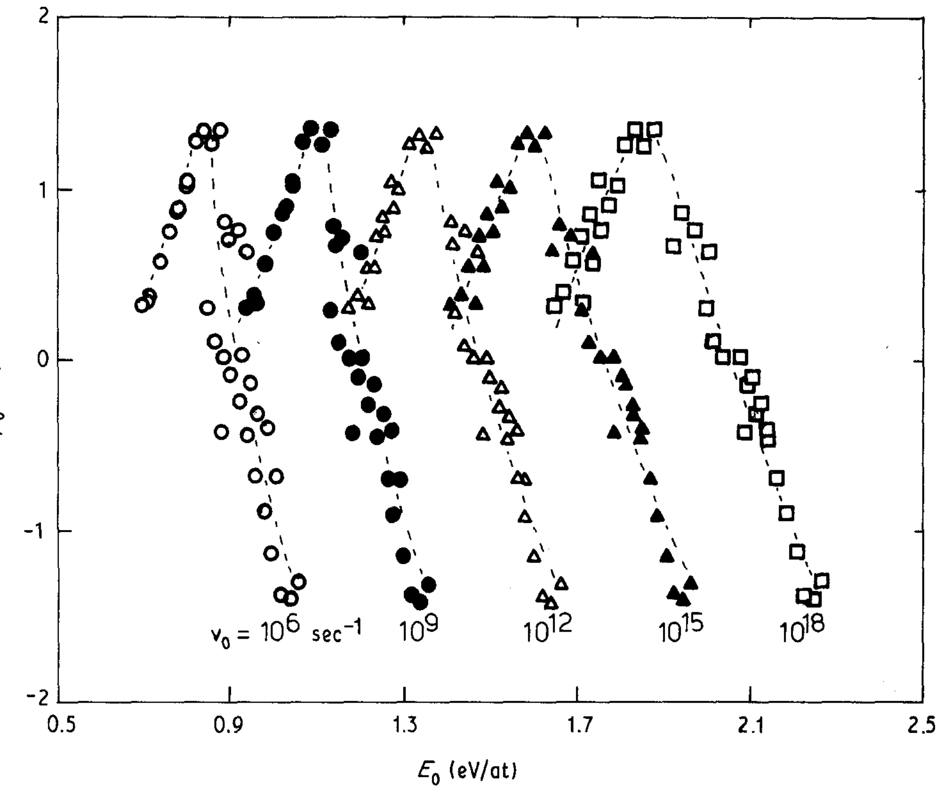

Figure 6 Effect of the change of the ν_0 value on the initial activation energy spectrum obtained in isothermal conditions for the $Fe_{34}Ni_{36}Cr_{10}P_{14}B_6$ amorphous alloy.

as mentioned before, the curves obtained from tempering measurements may be shifted of a constant quantity along the y-axis, owing to an incorrect estimate of the linear coefficient. For this reason, in order to compare these $p_0(E)$ curves with the ones obtained from isothermal measurements, a preliminary shift along the y-axis may sometimes be needed. After these adjustments, the best choice of ν_0 may be obtained by comparing (1) the values of the maxima of the $p_0(E)$ curves and (2) the values of energy at which $p_0(E)$ is zero. The best value for ν_0 turns out to be 10^9 sec^{-1} for both considered amorphous alloys, in agreement with

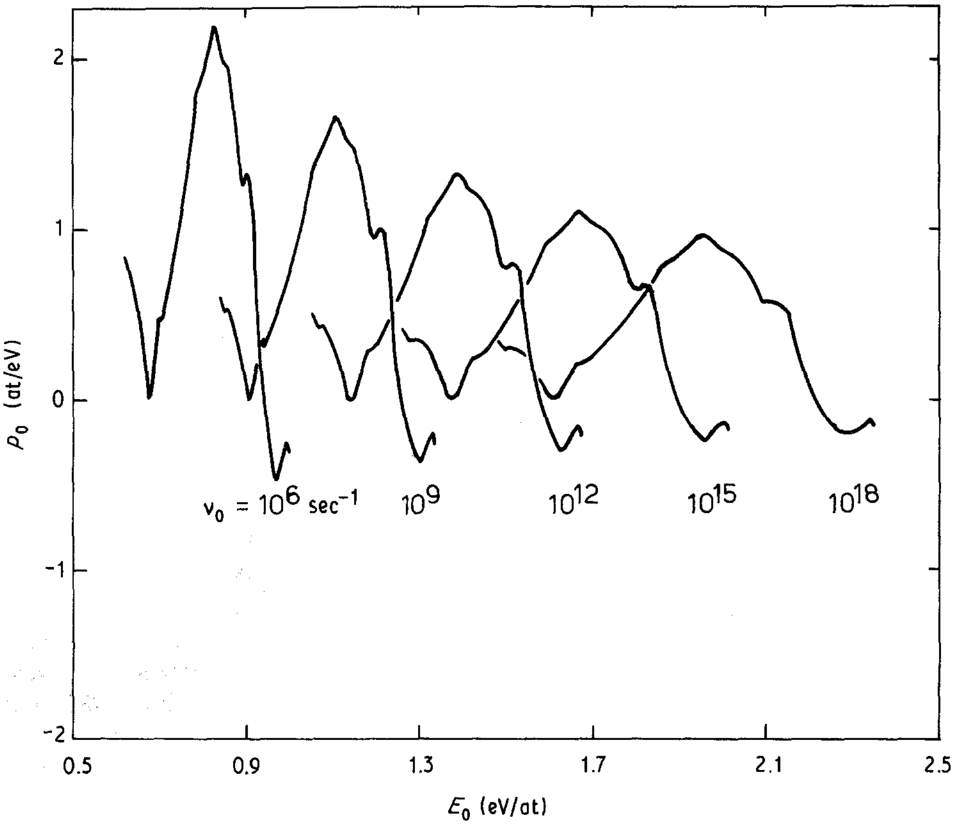

Figure 7 Effect of the change of the ν_0 value on the initial activation energy spectrum obtained in tempering conditions for the $Fe_{34}Ni_{36}Cr_{10}P_{14}B_6$ amorphous alloy. The different ν_0 values are indicated in sec^{-1}.

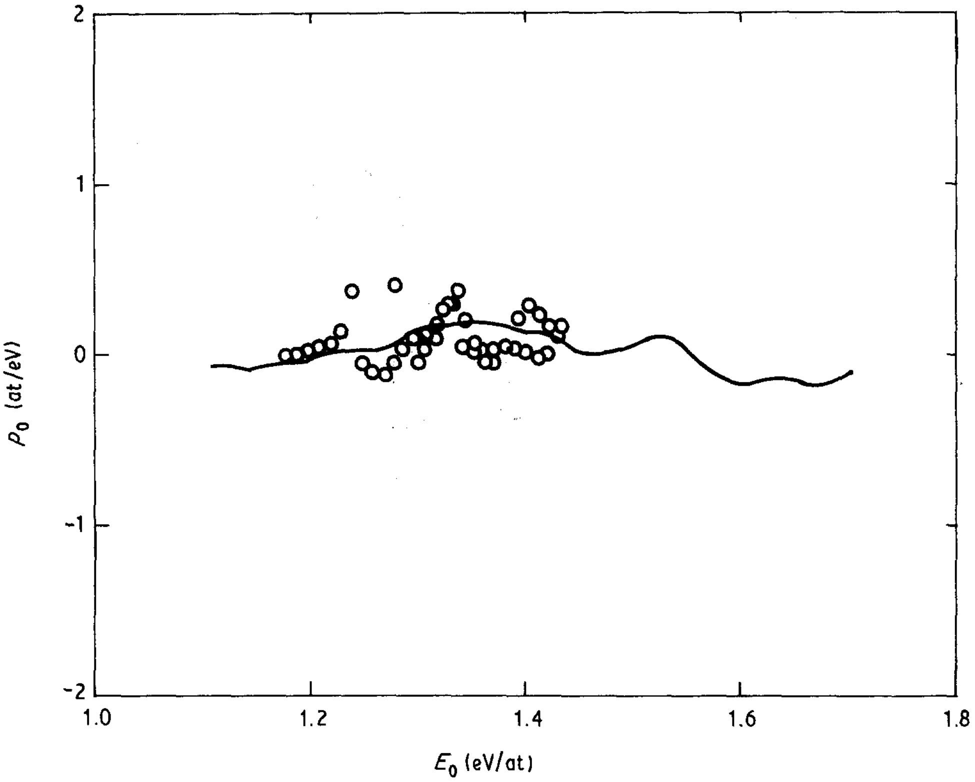

Figure 8 Initial activation energy spectra obtained in isothermal (○) and tempering (full line) conditions for a pre-annealed sample of $Fe_{34}Ni_{36}Cr_{10}P_{14}B_6$ amorphous alloy.

the value obtained, in a different way (from Young's modulus variations) for an amorphous alloy with similar composition [20]. This value, considerably lower than the Debye frequency for single atomic jumps, supports the hypothesis of cooperative atomic motions during structural relaxation, as suggested by H. S. Chen [1].

Starting from Equation 5, it is possible to note that the actual form of the $p_0(E)$ curve is related both to the $q_0(E)$ function (i.e. the number of phenomena occurring in the energy range between E and $E + dE$) and to the coupling factor $\langle c(E) \rangle$ (expressing the role played on the property change by the processes taking place in this energy range). Since $q_0(E)$ is always positive by definition, the appearance of negative as well as positive values of $p_0(E)$ for different energies, implies a competing influence of different relaxation phenomena on the change of electrical resistivity of these amorphous alloys. As a consequence, the use of a constant $\langle c(E) \rangle$ value would be an oversimplification in the present case. By comparing the $p_0(E)$ curves obtained for the alloys with different Cr content, it can be deduced that the overall behaviour is rather similar, with a small shift towards higher energy values for the 10% Cr amorphous alloy. Since the comparison of isothermal and tempering spectra leads, for both alloys, to the same best value of 10^9 sec^{-1} for the attack frequency, and since comparable values of $\langle c(E) \rangle$ may be hypothesized for alloys with similar composition, an increase in the Cr content seems to enhance the thermal stability against the structural relaxation of the considered alloy, as just pointed out by the authors in a previous paper [18].

5.2. Reversible processes

The effect of reversible and irreversible processes on the electrical resistivity variations, has been investigated by carrying out an isothermal and tempering analysis of the $Fe_{34}Ni_{36}Cr_{10}P_{14}B_6$ amorphous alloy in different structural conditions. An as-quenched sample of this alloy was submitted to a temperature run at 0.66 K sec^{-1} up to 660 K, i.e. a few degrees before the crystallization temperature. Using this treatment, most of the irreversible relaxation phenomena were annealed out, and the resistivity against temperature curve did not change during successive heating and cooling cycles up to 660 K, as shown elsewhere [21]. No detectable crystallinity was observed after repeated temperature cycles.

Some isothermal anneal treatments have been performed in this fully relaxed sample, and a master curve has been obtained as before. By heating the sample at 0.66 K sec^{-1} the appropriate value of the resulting linear coefficient was 0.00233 K^{-1}, slightly higher than the one of the as-quenched samples with the same composition, in agreement with the results obtained for different amorphous alloys [22]. The $p_0(E)$ curves, obtained in the same way as for the as-quenched samples, are shown in Fig. 8.

As it can be seen by comparing the spectra obtained for the as-quenched and the pre-heated samples, the irreversible processes have an important effect on the resistivity changes associated to structural relaxation phenomena. First, the negative part of the $p_0(E)$ curve is nearly completely absent in the fully relaxed ribbon, suggesting that the reduction of the resistivity observed during structural relaxation of the as-quenched sample is due mainly to irreversible processes. This is in agreement with analogous considerations by Mulder *et al.*

on an amorphous alloy with similar composition [23]. These authors relate the irreversible relaxation effects with a reduction of the frozen-in free volume, associated with a resistivity decrease. The observed change of the $p_0(E)$ curve after pre-heating of the sample indicates an influence of the irreversible processes on the reversible ones, and suggests that the chemical short range ordering is quite reduced by free volume annihilation.

Some reversible effects may also be inferred from the $p_0(E)$ curves obtained in tempering conditions on the as-quenched samples. As it can be observed in Fig. 5, in the first part of the $p_0(E)$ curve (up to about 1.15 eV/at), the change of the resistivity variations is just opposite to the one observed at higher energy values. The storage of the sample at room temperature for a rather long time (about two years at 293 K in the present case), is equivalent to an anneal treatment affecting only the lowest values of $p_0(E)$. In the considered materials, for instance, all the relaxation processes with an activation energy less than 1.15 eV/at have been annealed out. Any subsequent heat treatments, as in tempering measurements, lead to a rearrangement of the atomic positions (i.e. of the TLS equilibrium). According to the AES model [3], a negative resistivity change should occur in this case, as shown in Fig. 5. Such an effect cannot be observed in the $p_0(E)$ curves obtained through isothermal measurements, owing to the finite time needed to reach the chosen temperature.

5.3. Extrapolation at low temperatures

The knowledge of a complete $p_0(E)$ curve enables one to predict the behaviour of a property for long-time annealing treatments at very low temperatures, i.e. under conditions which can hardly be experimentally fulfilled. In the case of the resistivity, for instance, this possibility may be of interest for commercial applications of magnetic amorphous alloys as transformer cores. The long-time behaviour of the resistivity of the $Fe_{34}Ni_{36}Cr_{10}P_{14}B_6$ amorphous alloy at two different temperatures (300 K and 360 K) is shown in Fig. 9. It can be deduced that, at 360 K, the resistivity keeps increasing with time for about 8 years. Although the reported resistivity variations are quite small in the present case, these predictions may be in principle very useful in determining the range of times in which a given property of an amorphous alloy remains within acceptable limits in operating conditions. Finally, it should be noted that, in the present kinetic analysis, we did not consider the effect of crystallization that modifies completely the resistivity of the considered amorphous alloys [19].

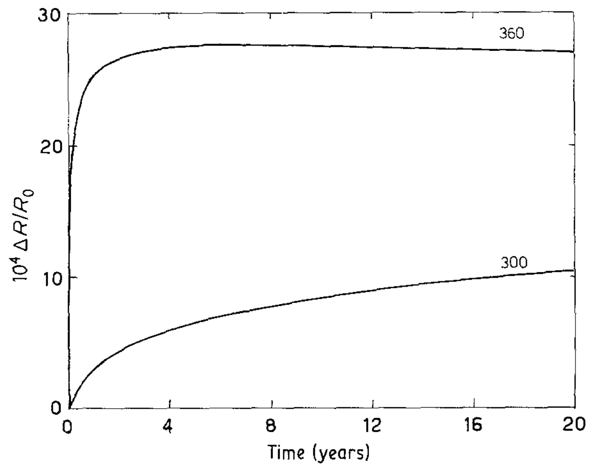

Figure 9 Relative electrical resistivity variations computed at low temperatures for a very long time. $\Delta R = R - R_0$, R_0 being the electrical resistance value at the start of the isothermal anneal.

6. Conclusion

Primak's treatment of activated processes distributed in activation energy has been used to analyze electrical resistivity measurements performed on two FeNiCrPB amorphous alloys with different Cr content. The $p_0(E)$ spectra obtained from both isothermal and tempering measurements have been computed. From their comparison, a best value of $10^9\,\text{sec}^{-1}$ for the attack frequency has been obtained for both alloys. The change in sign, observed in both $p_0(E)$ spectra at about 1.4 eV/at, may indicate the presence of two kinds of ordering processes, playing opposite roles on the electrical resistivity and characterized by distinct average activation energies. In the alloy with higher Cr content, a shift of the spectrum towards higher energy values is observed, showing a higher thermal stability against structural relaxation. The effects of both reversible and irreversible ordering processes on the resistivity have been elucidated. In the case of the $Fe_{34}Ni_{36}Cr_{10}P_{14}B_6$ amorphous alloy, a "fully relaxed" sample has a very small and mostly positive spectrum for the electrical resistivity variations.

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