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A quantitative study on reversible structural relaxation of metallic glasses

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Abstract. Two phenomenological theories were investigated for describing the reversible structural relaxation in metallic glasses: the activation-energy spectrum model of two-level systems and the diffusion model based on the free volume theory, where the driving force is thought to be compositional ordering of different types of atoms. Two kinetic curves were measured and compared with those calculated from the models. For comparison the whole annealing procedure performed in the experiment was taken into account by using a new evaluation technique. In the temperature range investigated (160–270 °C) for $\text{Ni}_{60}\text{Fe}_{20}\text{P}_{20}$ the diffusion picture seems to describe the data better.

1. Introduction

A metallic glass produced by rapid quenching from the melt is in an unstable thermodynamic state, consequently structural rearrangements leading to the metastable state of the undercooled liquid take place in it. This phenomenon is called 'irreversible structural relaxation'. Compared with the time scale of this process, there occur even shorter relaxation processes in a metallic glass, having reversible character, that are superimposed on the irreversible background. In this case thermodynamic systems can be defined on a matrix that is considered to be static.

In this paper we deal with the quantitative analysis of reversible processes. The simultaneous treatment of reversible and irreversible processes would complicate the analysis, making it impossible to draw fine conclusions from it. The irreversible processes can be separated easily by proper preannealings so that the annealings exciting the reversible processes should not significantly influence the irreversible ones.

We examine two phenomenological relaxation theories. The first is the activation-energy spectrum (AES) model of two-level systems (TLS) [1, 2]. The second explains the reversible processes by compositional (or chemical) ordering of different types of atoms assuming, as in the former case, a spectrum for the activation energy of the processes [3, 4]. In this latter model the free volume theory [5] plays an essential role.

Both models successfully describe the qualitative features of the relaxation. A few semi-quantitative analyses have been published but in these studies either the irreversible and reversible processes were treated simultaneously [4, 6] or the whole annealing procedure was not taken into account [7]. An attempt was made for the latter

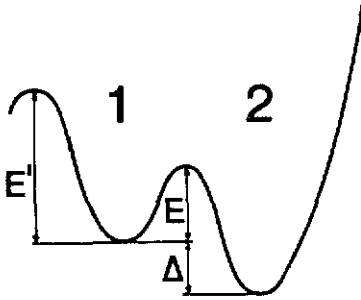


Figure 1. Schematic representation of a two-level system (TLS).

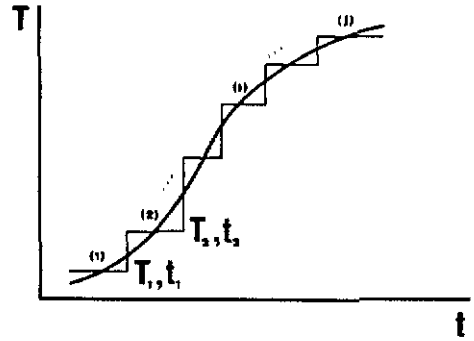


Figure 2. Schematic temperature time diagram of an arbitrary annealing process approximated by a series of small kinetics.

in the paper of Brüning *et al* [8] which approximates very roughly the real annealing procedure including two additional fitting parameters. Recently, there appeared papers [9, 10] calculating the AES spectrum exactly but only for irreversible processes.

Having eliminated the irreversible effects by a proper preannealing, we measured the time evolution of a selected physical quantity (the Young modulus (γM)) at two different temperatures, i.e. two types of kinetic curve, and we compared them with the theoretical kinetic curves derived from the two models considered in this study.

2. AES model of two-level systems

Suppose that in the amorphous material there are relaxation centres that can be described by separated two-level potential wells, see figure 1, i.e. an atom (or a group of atoms) can exist in two configurations of different energies, and transitions are possible between them via activation. In an amorphous material a quasi-continuous spectrum of the parameters (E , Δ) of the TLSs can be expected. Furthermore, the form and number of the TLSs are supposed to be unaltered. In this picture the relaxation reflects simply the population change of the TLSs in the investigated physical property.

First we investigate the population change of separated TLSs characterized by E and Δ , which are initially not in equilibrium. We denote the population of the 1st state by n_1 , the time derivative is denoted by a point.

Applying first-order kinetics and taking into account the possible partial transitions derived from figure 1 we obtain:

$$\dot{n}_1 = -\nu_E n_1 + \nu_{E+\Delta} n_2$$

where ν_E is the rate of the transition through the potential barrier with energy E . An Arrhenius expression is used for ν_E :

$$\nu_E = \nu_0 \exp(-E/kT).$$

Solving the above differential equation (indicating in detail the variables of the functions)

$$n_1(t) = [n_{10}(E, \Delta) - n_{1\infty}(\Delta, T)]\theta_{\nu_0}(E, T, t) + n_{1\infty}(\Delta, T) \quad (1)$$

where we introduce, for convenience, a function characterizing the annealing process and immediately drop its weak Δ dependence:

$$\theta_{\nu_0}(E, T, t) \equiv \exp[-\nu_0 t \exp(-E/kT)]$$

$$n_{1\infty}(\Delta, T) = 1/[1 + \exp(\Delta/kT)].$$

For an as-quenched material, $n_{10}(E, \Delta) = n_{1\infty}(\Delta, T_g)$ can be written ignoring the low energy TLSs already equilibrated at room temperature during storing. As $n_2(t) = 1 - n_1(t)$, we investigate only n_1 in the rest of this work, and we drop the index.

In order to see what restrictions should be imposed on a TLS in order that it can be considered as a closed system, let us allow the excitation of the particles out of the TLS (E' is finite in figure 1). It can be shown easily that if $E' - E \geq 5$ kT the ratio of the time constant of the intra-TLS transitions to that of the excitations out of the TLS is $\leq 10^{-2}$, consequently the TLS can be considered as a closed system. For example, at $T = 300^\circ\text{C}$, $E' - E \cong 0.2$ eV is required for a TLS to be a closed system. In an experiment TLSs with E values between 1 and 2 eV are generally excited. Fluctuations of the order of 0.2 eV with respect to E can be expected in a disordered system.

In order to be able to compare a model quantitatively with the experiment we have to trace an arbitrary annealing procedure in the model in question. We approximate an arbitrary annealing process $T(t)$ by a series of small kinetics (figure 2).

First let us write the contribution of one TLS, characterized by the parameters E, Δ , to the relaxation. The physical property change between the i th and j th annealing steps, called elementary relaxation, $R_{\text{elementary}}^{ij}$, is given by

$$R_{\text{elementary}}^{ij} = \Delta P = (n^{(i)} - n^{(j)})C$$

where $n^{(i)}$ is the population after the i th annealing step and C is a coupling factor connecting the population change to the physical property change.

After the first annealing step (at temperature T_1 for t_1) the population can be written according to (1):

$$n^{(1)} = (n_0^{(1)} - n_{\infty}^{(1)})\theta^{(1)} + n_{\infty}^{(1)}.$$

In the second annealing step, a similar equation is valid with $n_0^{(2)} = n^{(1)}$. In the k th step:

$$n^{(k)} = (n^{(k-1)} - n_{\infty}^{(k)})\theta^{(k)} + n_{\infty}^{(k)}.$$

In the case of a TLS spectrum the elementary TLS contributions must be summed. That a summation is possible follows from the assumption of no interaction between separated TLSs.

Thus,

$$R^{ij} = \int_0^\infty \int_0^\infty q(E, \Delta) \overline{C(E, \Delta)} [n^{(i)}(E, \Delta, T) - n^{(j)}(E, \Delta, T)] dE d\Delta$$

where $q(E, \Delta) dE d\Delta$ is the number of the TLSs having parameters between E and $E + dE$ and Δ and $\Delta + d\Delta$. The coupling term, $\overline{C(E, \Delta)}$, is an average value: TLSs characterized by the same parameters E and Δ can represent different atomic processes giving different contributions to the physical property change.

Now suppose that

$$q(E, \Delta) = q(E) \quad \text{if } \Delta < 5 \text{ kT}$$

where T is the maximum temperature used in the experiment, meaning that a TLS with any Δ value less than 5 kT can be found with equal probability in the material. This assumption is obvious because the TLSs with $\Delta > 5$ kT do not contribute to the reversible

effect [2], and because the (nearly) equal distribution of $q(E, \Delta)$ in Δ is suggested by the amorphous structure.

For the Δ dependence of the coupling factor, we examine the possibility of two assumptions:

$$(i) \overline{C(E, \Delta)} = \overline{C(E)} \quad \text{if } \Delta < 5 kT.$$

Thus

$$R^i = \int_0^\infty q(E) \overline{C(E)} \left(\int_0^\infty n^{(i)}(E, \Delta, T) d\Delta - \int_0^\infty n^{(i)}(E, \Delta, T) d\Delta \right) dE$$

where

$$\int_0^\infty n^{(i)}(E, \Delta, T) d\Delta = \int_0^\infty \{ [n^{(i-1)}(E, \Delta, T) - n_{\frac{x}{2}}^{(i)}(\Delta, T)] \theta^{(i)}(E, T, t) + n_{\frac{x}{2}}^{(i)}(\Delta, T) \} d\Delta.$$

The integral with respect to Δ gives:

$$\int_0^\infty n_{\frac{x}{2}}^{(i)}(\Delta, T) d\Delta = \int_0^\infty \frac{d\Delta}{1 + \exp(\Delta/kT_i)} = kT_i \ln 2 \propto T_i$$

and

$$\int_0^\infty \frac{d\Delta}{1 + \exp(\Delta/kT_i)} \cong \int_0^{\Delta \gg 5kT} \frac{d\Delta}{1 + \exp(\Delta/kT_i)}$$

Finally we get a very simple construction:

$$n^{(i)}(E) \cong \int_0^\infty n^{(i)}(E, \Delta, T) d\Delta = \text{const} \{ [\dots [(\Delta T_1 \theta^{(1)} + \Delta T_2) \theta^{(2)} + \Delta T_3] \theta^{(3)} \dots] \theta^{(i)} + T_i \}$$

where $\Delta T_k = T_{k-1} - T_k$; $\theta^{(k)} = \exp[-\nu_0 t_k \exp(-E/kT_k)]$.

(ii) Assuming $\overline{C(E, \Delta)} = \overline{C(E)} \Delta$ we get

$$\int_0^\infty n_{\frac{x}{2}}^{(i)}(\Delta, T) \Delta d\Delta \propto T_i^2.$$

The calculation to obtain $n^{(i)}(E)$ is now straightforward. Note that in differential scanning-calorimeter (DSC) measurements $\overline{C(E, \Delta)} \propto \Delta$ [11], since the contribution of a TLS with a parameter Δ to the heat evolution is proportional to Δ . (In the case of other physical quantities it is difficult to give the $\overline{C(E, \Delta)}$ function.)

The relaxation between the i th and j th step can be written in the form

$$R^{ij} = \int_0^\infty p(E) \theta^{ij}(E) dE \quad (2)$$

where $p(E) = \overline{C(E)} q(E)$ is characteristic for the material; $\theta^{ij} \equiv n^{(i)}(E) - n^{(j)}(E)$ is characteristic for the annealing (depending on the model). $\theta^{ij}(E)$ can be calculated from the annealing process $T(t)$ used in the experiment. $p(E)$ is unknown. However, if a relatively small energy interval is swept out by choosing a proper $\theta^{ij}(E)$, which is automatically the case when measuring kinetics, $p(E)$ can be considered to be constant in the chosen interval. This assumption is at least a good starting point and we apply it

in the evaluation process of our data. It is possible to map $p(E)$ over a large energy interval by kinetic measurements at different temperatures.

It is worth mentioning that (2) is of general validity in the framework of the given model, i.e. not only for $p(E) \equiv \text{const}$, but also for $p(E) \equiv \delta(E_0)$ (discrete spectrum). The exact form of $\theta^{\text{fl}}(E)$ must be taken into account in every case.

2.1. The experiment

2.1.1. Physical quantity. As a physical quantity, the Young modulus (YM) was measured, it being very sensitive to the relaxation. The YM was calculated by measuring the period (T) of a flexurally vibrating metallic glass ribbon (vibrating reed method): $M \propto 1/T^2$; the relative YM change is $M_r \equiv (M - M_0)/M_0 = (T_0^2 - T^2)/T^2$ where M_0 , T_0 are the values of these quantities in a reference state, e.g. at the beginning of the experiment at room temperature.

The vibrating length of the sample was 7.4 mm, the vibration frequency ≈ 150 Hz and the nominal composition $\text{Ni}_{60}\text{Fe}_{20}\text{P}_{20}$.

2.1.2. Annealing treatment. In principle any annealing treatment could test the models. Trivially, it is possible to make θ^{fl} non-zero in a short energy interval by measuring at constant temperature.

The YM was measured at two different temperatures. Annealing at the lower temperature for a long time resulted in an increase of the YM, in the subsequent annealing at the higher temperature the YM decreased first, then increased (crossover effect) (see details later). The comparison of these two kinetic curves with the theoretical ones should provide a sharp test of the models because both kinetic curves have to be described by the same model parameters. There is only one trivial fitting parameter setting the amplitude of the curves for both annealing treatments.

Having discussed the general implications of the experiments we summarize the exact annealing process:

(i) Preannealing at $T_p = 279$ °C for $t_p = 3$ h for the elimination of the irreversible effects.

(ii) Cooling from $T_p = 279$ °C to $T_2 = 159$ °C with a cooling rate of approximately 3 °C min^{-1} .

(iii) Annealing at $T_1 = 159$ °C for $t_1 = 20$ h.

(iv) Heating from $T_1 = 159$ °C to $T_2 = 201$ °C with a heating rate of approx. 5 °C min^{-1} .

(v) Annealing at $T_2 = 201$ °C for $t_2 = 3$ h.

2.2. Tracing the annealing process in the model

We examined the variants $\overline{C(E, \Delta)} = \text{const}$ and $\overline{C(E, \Delta)} \propto \Delta$. Let us take $\nu_0 = 10^{13}$ Hz, which is of the order of the Debye frequency, because this value, corresponding to the atomic migration frequency, is the only conceivable one in the TLS picture. Note that according to our definition of the TLS model, the transition between the two states of the TLS occurs in one step. $p(E) \equiv \text{const}$ was generally assumed during the fitting procedure.

Tracing the influence of the annealing procedure on the TLS the $n(E)$ functions in the initial (i) and final (f) states of the annealing at temperatures T_1 (figure 3) and at T_2

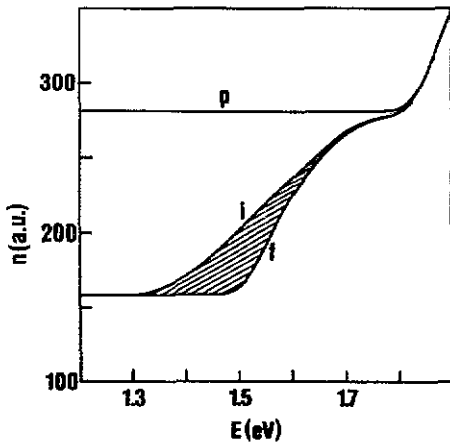


Figure 3. $n(E)$ function (for definition see text) after preannealing (p) at 279 °C and in the initial (i) and final (f) states of the kinetic measurement at 159 °C.

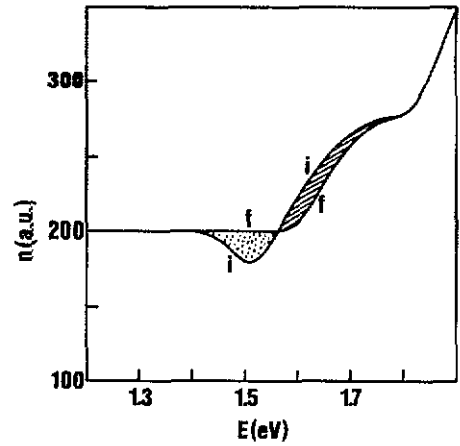


Figure 4. $n(E)$ function in the initial (i) and final (f) states of the kinetic measurement at 201 °C.

(figure 4) are shown for $C = \text{const}$. The qualitative features of these functions are unaltered for $\bar{C}(E, \Delta) \propto \Delta$. Preannealing the material produces the curve labelled (p) on figure 3. An equilibrium value of $n(E) \propto T_p (= 279 \text{ °C})$ is set for $E \leq 1.8$ eV. Above 1.8 eV the high $n(E)$ value reflecting T_g (i.e. the as-quenched state) remains unchanged. It is obvious from curve (i) of figure 3 that every TLS with energy ranging from 0 to 1.3 eV has been equilibrated (provided $p(E) \neq 0$ in this energy interval) before the sample is cooled down to T_1 . Thus these processes disappear for the kinetic experiment as they merge into the base line. If we increased the cooling rate significantly, e.g. to 160 °C min^{-1} , the highest energy of the equilibrated TLSS would not be less than 1 eV, meaning that the low-energy TLSS cannot be practically frozen in. The isothermal annealing at T_1 sweeps out only a relatively small portion of the spectrum, which makes more plausible the $p(E) \equiv \text{const}$ assumption. The area $n_{T_1}^{(i)} - n_{T_1}^{(f)}$ ($= \theta^{\text{eff}}$) is proportional to the relaxation provided $p(E) \equiv \text{const}$ (see (2)).

During isothermal annealing at T_2 the area $n_{T_1}^{(f)} - n_{T_2}^{(i)}$ is lost, as it merges into the baseline, and only the dotted area (figure 4) contributes to the decrease of the YM. The value of the dotted area depends strongly on the means of reaching the annealing temperature. Approaching this temperature slowly, a significant area (i.e. YM change) is lost for the measurement. Figure 4 shows that for longer times the TLSS with higher energies are also equilibrated, giving rise to an increase of the YM (shaded area, $n_{T_2}^{(i)} - n_{T_2}^{(f)}$). The resulting curve will show a minimum with respect to time. Note that the curves in figures 3 and 4 are non-trivial, calculated ones having no free parameters. They are determined by the annealing process as is actually performed in the experiment. It is obvious from the figures that the box spectrum approximation used up until now in the literature in order to account for the annealing procedure [8] is very rough.

2.3. Kinetic curves

The kinetic curves derived from the model by tracing the time evolution of the area between the (i) and (f) states are compared with the measured ones in figure 5. At T_1

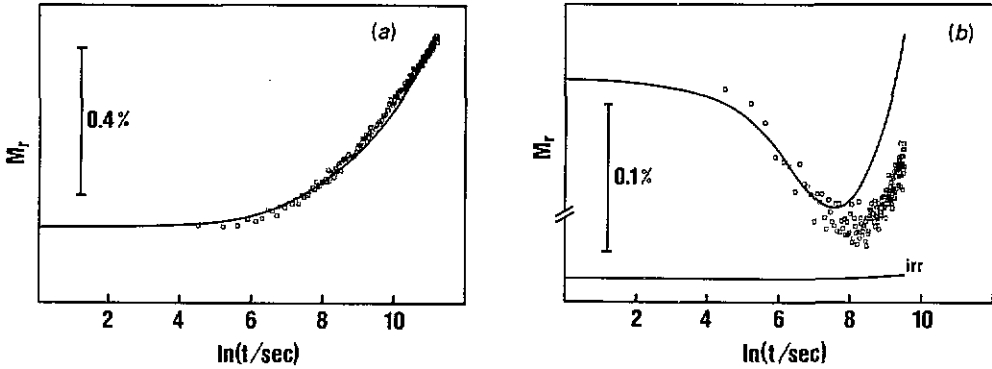


Figure 5. Relative Young-modulus change plotted against the logarithm of time. Measurements (\square) and theory (full curve) according to the TLS model for $\nu_0 = 10^{13}$ Hz, (a) at 159°C and (b) at 201°C . The irreversible contribution (irr) at 201°C is shown separately.

the agreement is rather good, but at T_2 this is not the case. Assuming $\overline{C(E, \Delta)} \propto \Delta$, the fitting will be even worse (not shown).

Here we note that annealing at T_2 , actually gives a very small contribution to the irreversible relaxation, which modifies slightly the kinetic curves. However, an arbitrary high preannealing temperature, which could eliminate this contribution completely, cannot be used because crystallization would intervene. The irreversible effect can be easily estimated [12], this being taken into account in the kinetic curves. The irreversible contribution is shown separately in the figure.

3. Compositional (or chemical) ordering model

The reversible relaxation processes observed in metallic glasses with more than two components are often attributed to compositional (or chemical) short-range ordering (CSRO). A typical example is the (FeNi)ME system (where ME is metalloid).

For pair ordering in the high temperature limit the equilibrium short-range order is described [13] by:

$$\alpha_e = \text{const}/T.$$

The kinetic equation for the CSRO is given by

$$\dot{\alpha} = -(\alpha - \alpha_e)\nu$$

where $\nu = \nu_0 \exp(-\gamma v^*/v_f) \exp(-E/kT)$ [5]; γ , $\frac{1}{2} < \gamma < 1$, is a geometrical factor; v^* is the critical (specific) volume and v_f is the average free volume of an atom.

Solving this equation we get

$$\alpha = (\alpha_0 - \alpha_e)\theta_\alpha + \alpha_e$$

which has the form of (1). Assuming a spectrum for the activation energy, E , and that

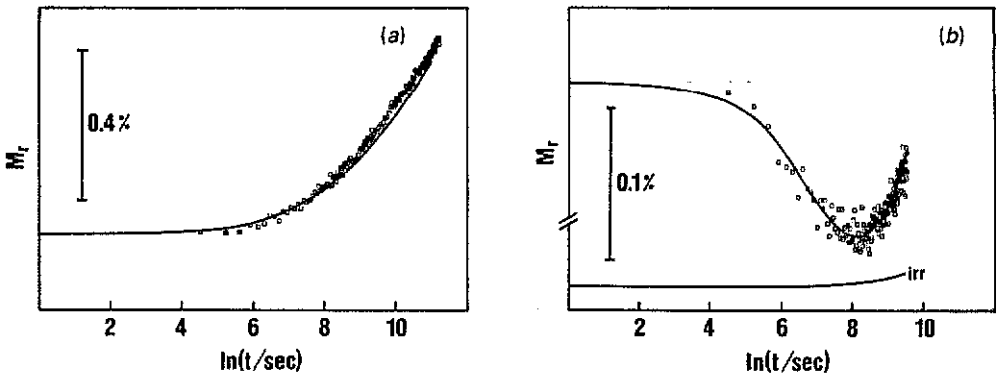


Figure 6. The relative Young modulus change plotted against the logarithm of time. Measurements (\square) and theory (full curve) according to the compositional ordering model for $\nu_0' = 10^{10}$ Hz, (a) at 159 °C and (b) at 201 °C. The irreversible contribution (irr) at 201 °C is shown separately.

$\alpha_c(T)$ is independent of the atomic process, a calculation similar to that for the case of the TLSs leads, for an arbitrary annealing procedure, to

$$R_{\alpha}^{ij} = \int_0^{\infty} p_{\alpha}(E) \theta_{\alpha}^{ij}(E) dE$$

where

$$\theta_{\alpha}^{ij} = -(\alpha^{(i)}(E) - \alpha^{(j)}(E))$$

$$\alpha^{(i)}(E) = \text{const}[\{ \dots [\Delta(1/T_1)\theta_{\alpha}^{(1)} + \Delta(1/T_2)]\theta_{\alpha}^{(2)} + \dots \}\theta_{\alpha}^{(i)} + 1/T_i]$$

$$\Delta 1/T_k = 1/T_{k-1} - 1/T_k \quad \theta_{\alpha}^{(k)} = \exp(-\nu_0' t_k \exp(-E_k/kT))$$

$$\nu_0' = \nu_0 e^{-\gamma\nu^*/\nu_0}$$

The frequency factor is decreased in this model by $e^{-\gamma\nu^*/\nu_0}$.

The negative sign in the equation for θ_{α}^{ij} means that in contrast to the TLS picture, in which a large n value corresponds to a low state of ordering (high temperature), in this model a large α value indicates a high state of ordering (low temperature).

The kinetic curves calculated with $\nu_0' = 10^{10}$ Hz on the base of this model are compared with the experimental ones in figure 6. Here the irreversible effect at T_2 was also taken into account (see section 2). The agreement with the kinetic curve at T_1 is acceptable, and for the curve at T_2 is excellent.

Here we note that a similar excellent fitting can be obtained in the TLS picture using $\nu_0 = 10^7$ Hz, but such a small frequency factor in this picture has no physical reality.

The low-frequency factor of $\nu_0' = 10^{10}$ Hz suggests a diffusion-like process. A diffusion mechanism for the reversible relaxation is also suggested in [14]. However, the question remains as to what is the driving force of the process. We supposed CSRO as a first approximation, which is physically plausible and supported by several papers [4, 15–17]. Brüning and Stöm-Olsen [18] suggested that diffusion in $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ might be controlled solely by TSRO. This is based on the monotonous concentration dependence of the reversible relaxation [14] in metal–metal–metalloid systems, which is not convincing

because of the small concentration range available. The role of the CSRO in metal-metal-metalloid glasses surely cannot be neglected, which is suggested by the fact that the relaxation in metal-metal-metalloid glasses is at least five times larger than in metal-metalloid glasses.

4. Conclusion

Two structural relaxation models were examined quantitatively by comparing the experimental and theoretical curves of two subsequent kinetics. For the amorphous material and temperature range investigated the diffusion picture seems to describe the reversible relaxation more successfully.

The investigations showed that a quantitative comparison of the experiments with the models is possible only if the whole real annealing procedure performed in the experiment is taken into account.

Though in the present investigation the diffusion picture seems to be valid, the conditions for a TLS picture, i.e. separation ($E' - E \geq 5 \text{ kT}$) and rigidity of the TLSs, could be satisfied at low temperatures. Consequently, the two reversible relaxation mechanisms could switch, which could be checked experimentally.

Acknowledgments

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References

- [1] Gibbs MR J, Evetts J E and Leake J A 1983 *J. Mat. Sci.* **18** 278-88
- [2] Hygate G and Gibbs MR J 1987 *J. Phys. F: Met. Phys.* **17** 815-26
- [3] van den Beukel A and Radelaar S 1983 *Acta Metall.* **31** 419-27
- [4] Majewska-Glabus I, Thijsse B J and Radelaar S 1984 *J. Non-Cryst. Solids* **61**, **62** 553-8
- [5] Spaepen F 1977 *Acta Metall.* **25** 407-15
- [6] van den Beukel A, van der Zwaag S and Mulder A L 1984 *Acta Metall.* **32** 1895-902
- [7] Gibbs MR J 1985 *Rapidly Quenched Metals* ed S Steeb and H Warlimont (Amsterdam: Elsevier) p 643
- [8] Brüning R, Altounian Z and Ström-Olsen J O 1987 *J. Appl. Phys.* **62** 3633-8
- [9] de Ceuninck W, Ruyan Zhao, Knuyt G, de Schepper L and Stals L M 1988 *Mat. Sci. Eng.* **97** 545-7
- [10] Friedrichs H and Neuhäuser H 1989 *J. Phys.: Condens. Matter* **1** 8305-18
- [11] Leake J A, Woldt E and Evetts J E 1988 *Mat. Sci. Eng.* **97** 469-72
- [12] Fogarassy B, Böhönyey A, Cziráki A, Szabó I, Gránásy L, Lovas A and Bakonyi I 1985 *J. Physique Coll.* **46 C8** 473-7
- [13] Cargill G S and Spaepen F 1981 *J. Non-Cryst. Solids* **43** 91
- [14] Ström-Olsen J O, Brüning R, Altounian Z and Ryan D H 1988 *J. Less-Common Metals* **145** 327-38
- [15] Drijver J W, Mulder A L and Radelaar S 1982 *Proc. 4th Int. Conf. on Rapidly Quenched Metals (Sendai, 1981)* ed T Masumoto and K Suzuki (The Japan Institute of Metals) pp 535-8
- [16] Shen Z Y, Hong J X, Yin X J, Zhang Y and He S A 1990 *J. Appl. Phys.* **67** 3655-60
- [17] Komatsu T, Fujita K, Matusita K, Nakajima K and Okamoto S 1990 *J. Appl. Phys.* **68** 2091-9
- [18] Brüning R and Ström-Olsen J O 1990 *Phys. Rev. B* **41** 2678-83