Calorimetric study of isothermal relaxation in a quenched β-Cu–Zn–Al alloy

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Abstract. The isothermal relaxation process in a β-Cu–Zn–Al single crystal which follows quenches from different T_q temperatures has been studied by means of an isothermal calorimetric technique at three T_a temperatures. The relaxation has been attributed mainly to a reordering process which takes place through a vacancy mechanism. The dissipated energy during the process has been measured for the different T_a and T_q temperatures. We have found that the relaxation process is not of a single exponential type and that, in all cases, the recorded curves giving the dissipated thermal power, $W(t)$, against time show long tails. The kinetics of the process have then been characterized by means of a relaxation time τ, defined as the time at which the product $tW(t)$ versus time shows a maximum. Assuming an Arrhenius law dependence of τ on T_a and T_q, we have obtained effective activation energies of 0.76 ± 0.03 eV and 0.43 ± 0.03 eV for vacancy migration and formation respectively.

1. Introduction

Within a certain range of composition the Cu–Zn–Al alloy system shows a BCC (β-phase) structure, stable at high temperatures (Ahlers 1986). The alloy exhibits a $B2$ superlattice below a temperature T_{B2} and orders to an L_{21} superlattice at a lower T_{L21} temperature (Rapacioli and Ahlers 1977). When such a system, in a disordered or partially ordered equilibrium state at a given temperature T_q, is rapidly quenched to a non-equilibrium state at a lower temperature T_a, it will eventually evolve to the equilibrium state corresponding to the new coupling conditions with the surroundings. During such a process, the excess of configurational energy of the system after the quench is dissipated in the form of heat. The purpose of the present work is to study this relaxational process by measuring this dissipated heat as a function of time by means of a calorimetric technique.

The relaxation taking place at T_a is essentially associated with an ordering process involving exchange of atoms among the different lattice sites. These exchanges are assumed to occur via the vacancy mechanism. As vacancies can be eliminated during the relaxation and their mobility affected as the ordering degree changes the process appears as a very complex one.

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Such kinds of kinetic process have been studied by different authors in several substitutional binary alloys, mainly by means of x-ray diffraction experiments (Oki *et al* 1974, Hasaka *et al* 1977, Murakami *et al* 1980) and resistivity measurements (Feder and Cahn 1960, Schulze and Lücke 1972, Balanzat and Hillairet 1981, Yamauchi *et al* 1985, Pfeiler 1988) and more recently using the Mössbauer technique (Fultz *et al* 1989). Its study is interesting not only from a fundamental point of view (it constitutes an interesting situation of the interdependence between ordering and vacancies), but also from more practical considerations because most of the physical properties of alloys are strongly dependent on the atom distribution on lattice sites. In particular, the Cu–Zn–Al alloy system considered in this work, undergoes a structural phase transition of the martensitic type at low temperatures (much lower than T_{L2_1}) and it is well known that its thermodynamic properties are strongly influenced by the state of atomic order at which it takes place (Rapacioli and Ahlers 1979, Planes *et al* 1983, Viñals *et al* 1984). It must then be considered that for a complete understanding of those physical properties that depend on atomic order we need to know, as a first step, the characteristic time of the relaxation process followed by the system to attain the equilibrium state at each given temperature.

In this work we use an isothermal calorimetric technique that has some points in common with that used by d'Heuerle and Gordon (1961) to study ordering kinetics in a Au_3Cu alloy. The relaxation processes that follow quenches from different T_q temperatures ranging between 400 K and 1100 K at different annealing temperatures T_a (= 283 K, 302 K and 312 K) are studied. From these calorimetric measurements we obtain the whole energy dissipated during the process (mainly attributed to the ordering process) as well as information on the kinetics of the process, essentially in the form of characteristic times. The dependence of such times on both T_q and T_a enables reasonable values for the vacancy formation and migration energies to be obtained. Furthermore, they prove to be suitable scale factors for all curves corresponding to a fixed quenching temperature.

Measurements of the same kind were presented in a previous work (Planes *et al* 1981). Those measurements were obtained with a less efficient experimental device. The present apparatus is characterized by a high sensitivity and a fast response. These characteristics enable us to work with much smaller samples than before, for which faster quenches from T_q are possible.

The paper is organized as follows. In section 2 the samples, experimental device and experimental procedure are briefly described. The experimental results are given in section 3. Finally in section 4 we discuss the results.

2. Experimental details

2.1. Experimental device and sample

Measurements were carried out in a highly sensitive (at room temperature its sensitivity is of around 400 mV W^{-1}) differential conduction microcalorimeter described elsewhere (Guénin *et al* 1987). The microcalorimeter was immersed into a copper block which acted as heat reservoir. Surrounding this there was a multilayer system of large thermal inertia. The constant temperature was provided by a heating device placed around the multilayer system and whose temperature was regulated externally. The drift of the base line of the whole apparatus is less than 1 μW/day.

Data acquisition was governed by a computer. A reading of the power delivered by the microcalorimeter was made every second and then averaged over N readings ($N =$

30 in the early stages of the relaxation, and $N = 300$ for the later stages). All averages so obtained were then recorded for future off-line treatments.

All measurements have been made on a Cu–Zn–Al single crystal (grown by the Bridgman method with elements of purity 99.99%). Its composition (checked after growth) is Cu; 14 at.% Zn; 17 at.% Al. Disc-shaped specimens (of 13.5 mm diameter and 1.5 mm thickness) were cut from the original crystal with a low-speed diamond saw and the surfaces were mechanically polished. The selected composition results in a mean number of valence electrons per atom of 1.48. The nominal M_s temperature is 245 K and the order–disorder transition temperatures as measured by DSC are $T_{B2} = 800$ K and $T_{L21} = 640$ K. Neutron diffraction experiments on samples of very close composition give temperatures consistent with these values (Planes *et al* 1991).

2.2. *Experimental procedure*

In order to eliminate the possible influence of previous heat treatments, the sample was, in all experiments, first maintained at 1073 K for 360 s and then immersed into a bath at temperature T_q ($T_a < T_q \leqslant 1073$ K) during a time long enough for the corresponding equilibrium degree of atomic order and vacancy concentration presumably to be reached. The minimum time required to reach the equilibrium state at T_q, was estimated from the variation of the M_s temperature measured just after quench from T_q, as a function of the annealing time at T_a. The sample was then quenched into an ice-water mixture ($T = 273$ K) and immersed for 30 s into an oil bath at the annealing temperature T_a (together with the reference sample). Then, both sample and reference, are placed, as quickly as possible, in the microcalorimeter. The total elapsed time between the quench and the first averaged acquisition was typically 120 s.

3. Results

Typical experimental examples giving the thermal power $W(t, T_a, T_q)$ versus time, are presented in figure 1 for a fixed temperature $T_a = 302$ K and different quenching temperatures T_q and over a short time interval of 1800 s. The thermal power at short times was deduced by an extrapolation procedure described in the caption of figure 1. The time origin has been taken as the moment when the sample was immersed into the oil bath at T_a.

It is worth noting that all the recorded curves show long tails (see the inset in figure 1) which slightly complicates their analysis and constitutes a constant source of uncertainty in experimental results. The time necessary for the signal to be masked by the noise is, in all cases, greater than 6 h and can be as long as several days for $T_a = 283$ K and T_q around 500 K.

3.1. *Excess energy*

The excess energy ΔE of the system at T_a just after quenches from different T_q temperatures, has been determined, in each case, as the energy dissipated during the relaxation process. Actually, calorimetric measurements at constant pressure give the enthalpy change, ΔH, in the process. The work $p\Delta V$, associated with the volume change has been evaluated, from dilatometric measurements, to be lower than 3×10^{-6} J mol^{-1}. Hence, ΔE is calculated as follows

$$\Delta E \approx -\Delta H = -(H(t \to \infty) - H(t = 0)) = -\int_0^\infty W(t, T_a, T_q) \, dt \qquad (1)$$

where $W = dH/dt$ is the experimentally measured thermal power as a function of
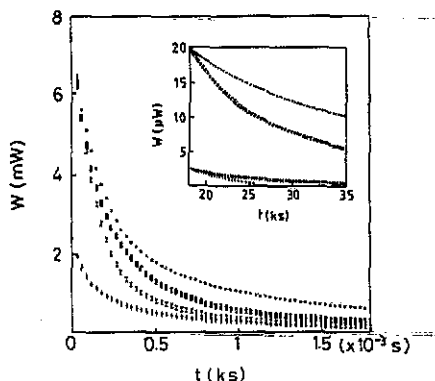
Figure 1. Typical examples giving the recorded thermal power W as a function of time for $T_q =$ 423 K ($+$), 567 K ($\bullet$), 781 K ($\times$), 1073 K ($\square$) and $T_a = 302$ K. The inset shows the same four curves over very long time. In all cases the first points (around five) are obtained by extrapolation. The extrapolation has been carried out assuming an 'exponential' decay with varying 'time constant'. A linear fit for the 'time constant' versus time to the first significant points has been used.
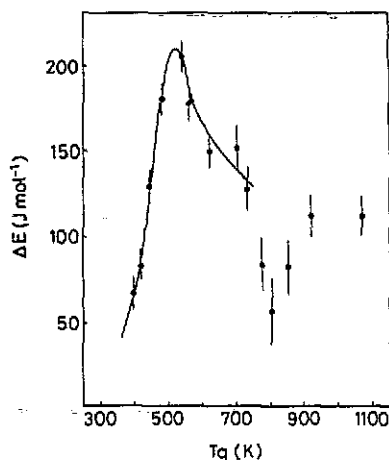
Figure 2. Energy dissipated during the relaxation process as a function of the quenching temperature T_q. Points represent mean values obtained from measurements at the three T_a temperatures. The line is a guide for the eyes.

time. Two major difficulties appear in calculating ΔE from (1). They come from the equilibration of the calorimeter baseline during the very early stages of the measurement and from the validity of the extrapolation procedure to evaluate the thermal power during this period of time.

The noise and baseline drift impose a cut-off time on the integral (1). In spite of the fact that the relaxation shows long tails, we have, however, estimated by extrapolation the very small residual energy associated with this cut-off.

In figure 2 we present the obtained excess energy ΔE as a function of T_q. Measurements have been carried out at different temperatures T_a. Within the experimental uncertainties no differences have been obtained for measurements at these different T_a temperatures. ΔE first increases with T_q, shows a maximum for T_q around 550 K (in what follows, we will call this temperature T_{max}) and decreases for higher temperatures. Unexpected low values of ΔE are obtained for T_q around 800 K. We note, however, that the experimental scatter affecting energy measurements corresponding to quenches from temperatures close to 800 K is larger than the scatter corresponding to measurements from T_q far enough away from 800 K.

We have simultaneously measured (using a sample identical to that used for the measurement of the excess energy as a function of T_q) the martensitic transition temperature just after the quench and after the relaxation process at T_a. In figure 3 we show the obtained results. The behaviour of M_s as a function of T_q is the same as reported in previous works (Rapacioli and Ahlers 1979 and Planes *et al* 1990) for samples with a composition close to the composition of the sample used here. Concerning the M_s measured after the ageing process at T_a, we note that it still shows a dependence on T_q. As M_s depends on the thermodynamic state of the system, this seems to indicate that the 'final state' reached by the system after the relaxation process is not the same for
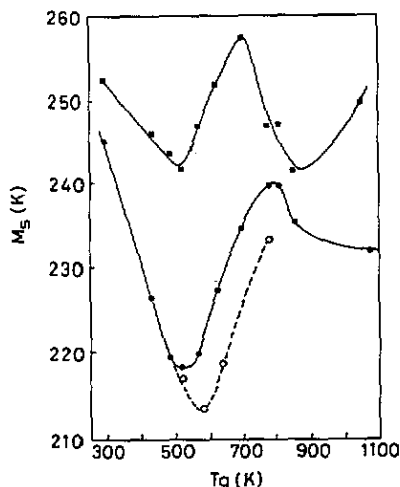
Figure 3. Evolution, as a function of T_q, of the martensitic transition temperature M_s obtained immediately after the quench (●) and after the quench followed by the relaxation process (■). (○) are values obtained just after the quench using a thinner sample for which the quench rate is faster. Full and broken curves are guides for the eyes.
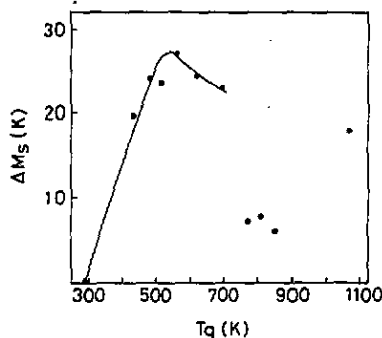
Figure 4. $\Delta M_s = [M_s(t \rightarrow \infty) - M_s(t = 0)]$ as a function of the quenching temperature T_q. The line is a guide for the eyes.

different T_q temperatures and hence that the dissipated energy is measured in each case in relation to different reference states ('final states'), which depend on T_q. When comparing ΔE (see figure 2) and the difference ΔM_s between M_s after ageing ($M_s(t \rightarrow \infty)$) and M_s just after quench ($M_s(t = 0)$) for each T_q (see figure 4), we observe the same qualitative behaviour of both quantities. The maximum is located at the same position and also low values are obtained in both cases for T_q around 800 K.

In order to study the potential influence of the quenching rate on experimental results, measurements of M_s just after quench from different T_q have been carried out with thinner samples (thickness 0.1 mm) of the same composition and section as those used for measurements presented before (thickness 1.5 mm). Results appear also in figure 3. They clearly show that the quenching rate becomes relevant for T_q temperatures greater than 500 K.

3.2. Characteristic relaxation times

The analysis of the dissipated thermal power versus time curves has clearly shown that the relaxation process is not of a single exponential type. Instead, a continuous slowing down exists extending the process to periods of time which are in some cases of the order of a few days. However, it is always possible to define an effective relaxation time to characterize the process. If we denote by x the relevant quantity which relaxes from an initial value x_0 to a final one x_∞, the standard way to define a characteristic time is (Sancho 1988, Jiménez-Aquino and Sancho 1991)

$$\tau = \int_0^\infty (x(t) - x_\infty)/(x_0 - x_\infty) \, \mathrm{d}t. \tag{2}$$

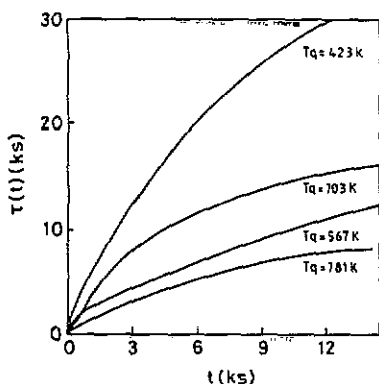If we take x as the dissipated power W, τ is obtained as

Figure 5. Typical evolution of $\tau(t)$, as defined in (4), as a function of time for four different T_q temperatures and $T_a = 302$ K.
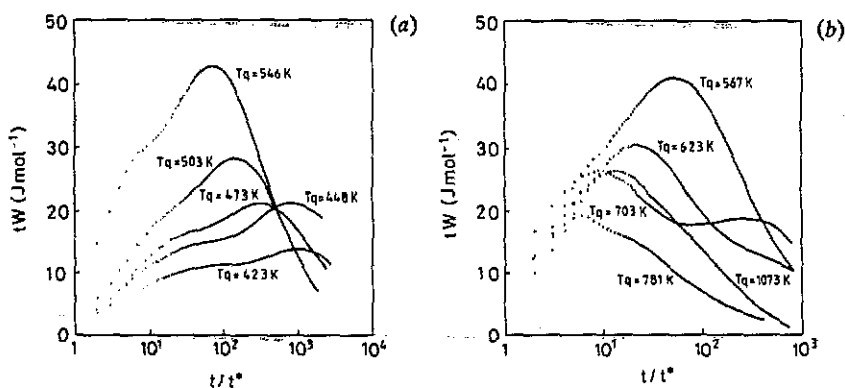

Figure 6. Curves giving $tW(t)$ against t (in logarithmic scale) for different studied T_q temperatures and $T_a = 302$ K. (a) T_q up to 546 K; (b) T_q from 546 K up to 1073 K. $t^* = 30$ s is the sampling time.

$$\tau = 1/W(t=0) \int_0^\infty W(t)\,\mathrm{d}t = -\Delta E/W(t=0). \tag{3}$$

In our case, such a method is not very desirable from the experimental viewpoint mainly because of our bad knowledge of the value of $W(t=0)$. This relaxation time (3) can, however, be evaluated by extrapolation at $t \to 0$ of the quantity $\tau(t)$ defined by

$$\tau(t) = 1/W(t) \int_t^\infty W(t)\,\mathrm{d}t = -\Delta E(t)/W(t) \tag{4}$$

where $\Delta E(t)$ is the excess energy that remains in the system at time t. In figure 5 we show the typical behaviour of $\tau(t)$ versus t for some T_q temperatures. We observe that $\tau(t)$ always increases with time, making clear the continuous slowing down of the relaxation mentioned above. It is worth noting that in case of a single exponential decay the characteristic time τ obtained using this method is, as expected, the time constant of the exponential.

A different method of defining an effective relaxation time for the whole process consists in taking the time τ at which $(\partial \Delta E(t)/\partial \ln t) = tW(t)$ presents its most pro-
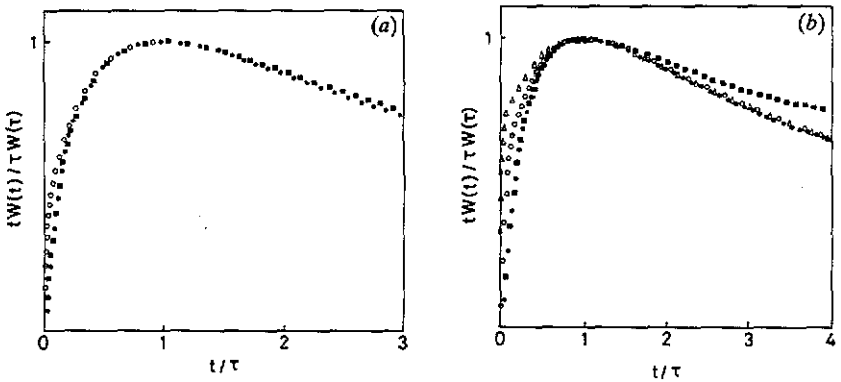
Figure 7. Scaled representation of $tW(t)/\tau W(\tau)$ against t/τ. (*a*) For a fixed $T_q = 546$ K and $T_a = 312$ K (O), 302 K (●) and 282.5 K (■); (*b*) for a fixed $T_a = 302$ K and $T_q = 473$ K (∇), 567 K (O), 623 K (●) and 703 K (■).

nounced maximum (Nowick and Berry 1972). In figures 6(*a*) and (*b*) we show, for $T_a = 302$ K and different T_q, tW as a function of time. We note that in all cases, these curves present a well-defined maximum which justifies the use of the method.

In the case of single exponential decay, it might be easily shown that both methods give rise to the same characteristic time and hence that they are somewhat equivalent. In our case, the comparison of the characteristic times obtained by the two methods, shows that both coincide approximately for sufficiently high T_q temperatures ($T_q \geqslant 500$ K). Nevertheless, for low quenching temperatures discrepancies between both methods of even one order of magnitude are found. It is easily understood that the essential difference between the two methods lies in their capacity for revealing the simultaneous contribution of various relaxation times. Thus, whereas the first method provides only one single (average) characteristic time, the second method may prove the existence of various times, as discussed by Tewari (1974). Actually, in the curves presented in figure 6, a secondary and generally less marked maximum seems to exist for certain T_q temperatures. The corresponding 'secondary' characteristic time is shorter than τ for $T_q < T_{max}$ (figure 6(*a*)) and greater than τ for $T_q > T_{max}$ (figure 6(*b*)). Specially noteworthy is the secondary maximum exhibited by the curve corresponding to $T_q = 703$ K. It is also interesting to note that, from an experimental point of view, the second of these two methods is less influenced than the first by a poor knowledge of the dissipated power during the very early stages of the process, and by the long tails shown by calorimetric curves. It is for all these reasons (principally for the last one just mentioned) that we have used the method of the maxima to evaluate characteristic times. This method of defining τ has been previously used by Balanzat and Hillairet (1981) to study short range ordering kinetics in alloys. These effective relaxation times have also been used as scale factors in order to collapse all the curves in a single one. The results appear in figure 7, where we have represented $tW(t)/\tau W(\tau)$ versus t/τ. As can be observed, a quite good superposition is obtained when relaxation processes from the same T_q, at different annealing temperatures T_a, are considered (figure 7(*a*)). Nevertheless, for fixed T_a and different quenching temperatures T_q (figure 7(*b*)) the superposition is not as good as in the former case. Note that the scaling of the $tW(t)$ versus t curves is equivalent to the scaling of the thermograms ($W(t)$ versus t). We have used the scaled representation of tW versus t because it is more sensitive to possible deviations from a single collapsed curve.

4. Discussion

In this paper we have studied the isothermal relaxation process in a β-Cu–Zn–Al single crystal that follows quenches from different T_q temperatures. As mentioned above, this alloy exhibits a $B2$ ordered structure below a temperature T_{B2} and orders to an $L2_1$ structure at a lower T_{L2_1} temperature. At T_q, just before the quench, the system is assumed to be in the equilibrium state corresponding to such temperature. When quenched at a temperature T_a, it will be frozen in a non-equilibrium state in which some parameters have not yet relaxed to its equilibrium values. In particular, a degree of configurational order different to that of equilibrium at T_a and an excess of vacancies will exist, the deviations from equilibrium values depending in both cases on T_q and also on the quenching rate. In this work, we fix our attention on these two quantities, which are assumed to be the most relevant in the relaxation process. Actually, additional possible effects of the quench must always be kept in mind, in particular the appearance of internal strains (Macqueron *et al* 1990). Nevertheless, we assume that their possible influence on the relaxation of the order and vacancy concentration parameters, can be disregarded.

Previous works (Suzuki *et al* 1990) have shown that owing to finite quenching rates, the $B2$ ordering already reaches, in practically all cases, its equilibrium value during the quench itself. For example, in Cu–16 at.% Al–16 at.% Zn only for relatively low quench temperatures ($T_q \leqslant 430$ K) a relaxation of the Bragg peak corresponding to the $B2$ superlattice (200 peak) has been observed. One thinks that the reason why the $B2$ structure forms so rapidly is that it involves only exchanges of nearest-neighbour atoms, whereas the $L2_1$ ordering also requires exchanges of next-nearest-neighbour pairs. Therefore, the ordering process taking place after the quench can be mainly attributed to the reconstruction of the $L2_1$ ordering state corresponding to the T_a temperature. Clearly, this ordering process takes place through the exchange of atoms among different lattice sites and we assume here, as is usual in BCC alloys, that these exchanges proceed via a vacancy mechanism. However, as mentioned before, the simultaneous elimination of vacancies must also be considered. This mechanism gives rise to a coupling between the relaxation of both ordering and excess of vacancies. We suggest that these coupling effects are precisely responsible for the initial rapid decay and for the continuous slowing down of the relaxation rate that yields the long tails shown by the calorimetric curves. It should be considered that long range diffusion of vacancies is obviously necessary before the vacancies can be eliminated at free surfaces or even in defects like dislocations or antiphase boundaries and hence it seems clear that an initial large vacancy concentration strongly favours the ordering process. In addition, when the ordering degree is close to its equilibrium value at T_a, the remaining free vacancies are less effective in assisting the ordering process (in other words, its migration cannot take place randomly; see Arita *et al* 1989) and their mobility is then strongly decreased (its migration energy increases with ordering; see Girifalco 1964 and Kulkarni 1973). This fact will certainly contribute to the slowing down of the final stages of the relaxation.

If we assume, as usual, that the contribution to the excess energy after the quench coming from the excess of thermal vacancies is negligibly small when compared to the excess energy associated to purely configurational disordering, it can be considered that the whole dissipated energy gives the difference between the configurational energy at T_q and the configurational energy of the state reached after the relaxation. In our experiments, we have pointed out that these final states are still dependent on the quenching T_q temperature. Presumably, this is so because the relaxation rates become
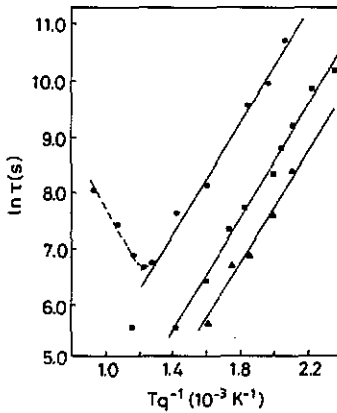
Figure 8. ln τ versus T_q^{-1} for $T_a = 312$ K ($\triangle$), 302 K ($\blacksquare$) and 281.5 K ($\bullet$). Continuous lines are linear fits to the experimental points. τ is given to better than 5%.

extremely slow at these measurement scales ($\sim$ days) and at such scales the system behaves as it would in equilibrium, although with a 'frozen' disorder degree.

Our results also show (figure 3) that the quenching rate seems not to affect the measured excess energy for T_q up to temperatures close to T_{max} at which point the measured excess energy is a maximum. The location of such a temperature depends, however, on the quenching rate. Thus, for a given quenching procedure, this result indicates that for $T_q < T_{max}$ the configurational state at T_q is frozen by the quench, but this is no longer the case for higher quenching temperatures. The observed decrease in the whole dissipated energy is then interpreted as proof of the existence of a significant ordering process taking place during the quench (the time scale for ordering becomes comparable to the typical time scale involved in the quench). Similar results have already been found in other Cu-based alloys—in measurements of electrical resistivity just after quenches from T_q—and the same interpretation has been provided (see, for example Andries *et al* 1972). Such a partial ordering may be easily understood in terms of the large enough vacancy concentration existing for temperatures $T_q \geq T_{max}$ and indeed this picture has been confirmed by a Monte Carlo simulation study of the ordering process during the quench itself when vacancies are taken into account (Castán 1991).

As discussed in section 3.2, the relaxation rate has been characterized by means of an effective relaxation time τ (the maximum of the curve giving $tW(t)$ versus t) and we have considered the dependence of this characteristic time on both T_q and T_a in terms of an Arrhenius law

$$\tau = A \exp(E_f/kT_q) \exp(E_m/kT_a). \tag{5}$$

The results (figure 8) show that τ effectively obeys such a law with respect to both temperatures, except for $T_q \geq 800$ K. Within the framework of ordering through a vacancy mechanism, we assume that τ^{-1} is proportional to the initial equilibrium vacancy concentration at T_q and to its mobility at T_a (Balanzat and Hillairet 1981) and hence the parameters E_f and E_m of (5) may be interpreted as effective vacancy formation and migration energies. A linear fit gives these parameters the values $E_m = 0.76 \pm 0.03$ eV and $E_f = 0.43 \pm 0.03$ eV. On one hand, this migration energy is slightly higher than the one (0.68 ± 0.03 eV) obtained previously from positron annihilation measurements on a very similar alloy system (Van Humbeeck 1985). On the other hand, the formation energy is very close to the one reported for the β-Cu–Zn alloy (Wayman *et al* 1963).

However our value is small when compared with the value (0.63) obtained from an expression proposed by Fukushima and Doyama (1979) for Cu-based alloys derived from positron annihilation studies.

From figure 8 we also note that for $T_q \geqslant 800$ K, τ seems to increase, a fact that in the above context could be interpreted as a proof of the existence of a partial elimination of vacancies during the quench itself. Since this behaviour is observed for T_q higher than 800 K, a temperature close to T_{B2}, it has been suggested (Planes *et al* 1990) that such elimination of vacancies may be due to its trapping at the antiphase boundaries of the *B*2 ordered domains which form during the quench. Moreover, it should be pointed out that if this vacancy elimination becomes sufficiently relevant, it may involve a much less important ordering during the quench and therefore it may give rise to an increase in the excess energy ΔE of the system for $T_q \geqslant 800$ K. Actually, this seems to be the observed behaviour (see figure 2). Nevertheless, it must be noticed that the existence of a minimum in ΔE at T_q around 800 K may be only apparent. So it can be argued that owing to the large vacancy concentration quenched in the sample for T_q around this temperature (figure 8) the corresponding relaxation time is so small that a considerable fraction of the excess energy is dissipated in the very first moments of the relaxation and it cannot be measured (figure 2). We think that this is only partially true and that it constitutes the reason by which a much more important dispersion exists in data from this region. It is also worth noting from figure 8 that the minimum of τ is not located at the temperature T_{max} where the whole dissipated energy ΔE exhibits its maximum. This presumably proves the existence of a domain of T_q temperatures (between 500 K and 800 K in our sample) within which the order parameter relaxes during the quench whereas the vacancy concentration does not. This would confirm the fact that ΔE indeed exhibits a maximum instead of a flat or slightly increasing region.

The characteristic times τ have also been used as scale factors in order to fit all the calorimetric curves on a single one. Figure 7(*a*) shows that a quite good superposition exists when relaxation from identical initial states (same T_q) are considered, but at different annealing temperatures T_a. This means that, as expected, all such relaxation processes will only differ in the rate at which they take place, the 'path' followed by the system being practically the same in all cases. For a fixed T_a and different quenching temperatures T_q, however, figure 7(*b*) shows that the superposition is not so good. In fact, there is no reason by which one should find a good scaling in this case, because the relaxation takes place from different initial states. Moreover, from figure 6, there seems to exist a 'secondary' characteristic time associated with the maxima whose relevance and location depend upon the quench temperature T_q. The existence of such maxima suggest the possibility of a change in the kinetics of the relaxation, but it requires a much more refined study to elucidate their meaning and for the moment we are not able to explain them.

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