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On the two-step ageing of a commercial Al–Zn–Mg alloy; a study by positron lifetime spectroscopy

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Abstract. Formation of Guinier–Preston zones and precipitation, induced by two-step ageing thermal treatments in an age-hardenable commercial Al–Zn–Mg-based alloy, have been studied by positron lifetime spectroscopy and Vickers microhardness measurements. In particular, an initial softening of the specimens, occurring in the early stages of the second ageing step (artificial ageing at 150 °C), appears to be correlated with a strong decrease in the positron lifetime, which indicates a partial dissolution of the GP zones. If the treatment at 150 °C is interrupted at this stage, and the ageing continues at a lower temperature (either room temperature or 70 °C), the positron lifetime and the microhardness recover to the values reached at the end of the first ageing step (natural ageing at room temperature for five days). The kinetics of this process is discussed in terms of reconstruction of GP zones; the activation energy value of this process is also obtained.

1. Introduction

The aluminium alloys having the greatest response to age hardening are based on the Al–Zn–Mg system. Their excellent combination of low density and high strength make them very attractive materials for the transportation industry. The desirable mechanical properties of this class of alloys are due to structural inhomogeneities at a nanometric scale. These are formed at an intermediate stage in the evolution of the supersaturated solid solution (αSSS) toward an equilibrium structure, where the excess solute is segregated as incoherent precipitates. The αSSS structure is obtained by a homogenization treatment (heating at a temperature sufficiently high to dissolve the minority components of the alloys in the base material, followed by quenching at a lower temperature). The decomposition process of the αSSS occurs by natural ageing of the material at room temperature (RT) or by artificial ageing at temperatures above RT. At ageing temperatures below approximately 180 °C, the first stage of decomposition is the formation of spherical solute-rich clusters (Guinier–Preston, or GP, zones). At later stages, semicoherent precipitates (η'-particles) with composition Mg(Zn, Al, Cu)$_2$ appear, which evolve, with no substantial composition change, into bigger particles of the incoherent equilibrium phase η [1]. The sequence of steps in the decomposition process depends on the composition of the alloy, on the quenching conditions, on the ageing temperatures, etc (for a review see [2]).

Positron annihilation spectroscopy (PAS) has proved to be a very useful and effective technique for studying the decomposition kinetics in age-hardenable alloys. More specifically, in the last few years, positron lifetime and Doppler-broadening measurements have been applied to study precipitation phenomena in prepared Al–Zn and Al–Zn–Mg alloys [3–6]. Only a few studies have been published [7, 8] regarding the use of PAS for investigations on the precipitation kinetics of commercial Al–Zn–Mg alloys.

In this investigation, the early stage of decomposition of the same Al–Zn–Mg alloy as studied in [7, 8] has been examined by a combination of positron lifetime spectroscopy and Vickers microhardness measurements, in a series of experiments designed for clarifying the microstructural changes that occur in these alloys during ageing treatments at RT or near to RT.

2. Experimental details

The composition of the alloy (commercial name Zergal 4) used in the present investigation is Al–6.0 wt% Zn–2.0 wt% Mg–1.0 wt% Cu (equivalent to Al–2.58 at.% Zn–2.31 at.% Mg–0.44 at.% Cu), in which the main impurities (in wt%) were 0.12 Zr, 0.10 Mn, 0.06 Ti, Fe < 0.25, Si < 0.15 and Cr < 0.04; detailed information on other properties of the alloy is given in [9]. Specimens in forms of discs of 1.5 mm thickness were cut from a rod of 10 mm diameter by a low-speed diamond saw. They were homogenized for 2 h at 470 °C in an air-circulating furnace and water quenched to room temperature. The first step of ageing (pre-ageing) was performed at RT for five days. The second step was performed at 150 °C for different times up to 2000 min. At the end of this step, for each ageing time, the samples were rapidly brought to RT in order to perform positron lifetime and microhardness measurements. For a few samples, the measurements were repeated at regular time intervals up to about 1.2×10^5 min, in order to monitor the structural changes occurring at RT after the interruption of the ageing at 150 °C; in a further series of experiments, this evolution was also studied at 70 °C. Ageing treatments were performed in a glycerine bath, and the delay time to reach the treatment temperature of the samples was shorter than 3 s in all cases. After the thermal treatments, the samples were given a metallographic final polish with diamond paste up to 1 μm, followed by a dilute Keller etching, prior to each positron lifetime and hardness measurement.

The lifetime spectrometer was a fast–fast timing coincidence system with a time resolution (FWHM) of 255 ps. A 20 μCi source of ^{22}NaCl deposited on a thin Kapton foil (1.1 mg cm^{-2}) was sandwiched between two identical alloy specimens. The source contribution and the response function were evaluated by using the code RESOLUTION [10]. The source contributes to the spectra with only one component ($\tau_S = 382$ ps, $I_S = 10.5\%$). The lifetime spectra were analysed using the POSITRONFIT program [10]. After subtracting the source component, the spectra were satisfactorily analysed as a single-lifetime component; in some cases the separation of two components is also possible, but this requires the use of constraints derived from the application of the trapping model with specific hypotheses on annihilation characteristics. We report below only the data coming from free one-component fits, with the caveat that the apparent single lifetime τ has the meaning of an average over an unresolved complex lifetime spectrum. The total number of counts in each spectrum was about 10^6, accumulated in a time interval of 14 400 s. Vickers microhardness measurements (H_V) were performed after each positron lifetime measurement; the diagonal of the square explored by the indentor was about 40 μm.

Positron lifetime τ and microhardness H_V versus ageing time at 150 °C are shown in figure 1. The increase of the hardness with natural ageing after quenching is a well-known phenomenon; the decrease of the average positron lifetime has also been observed for other Al alloys [11]. The present data show that after five days at room temperature both

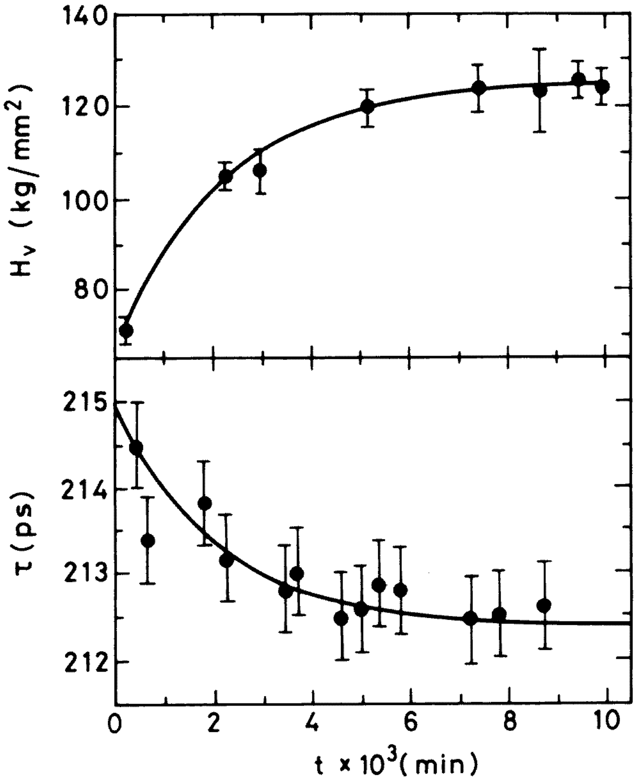

Figure 1. Decrease of the average positron lifetime τ and increase of the Vickers microhardness H_V during ageing at RT.

parameters have reached saturation. The apparent equilibrium is metastable; as shown in figure 2, the evolution starts again if the temperature increases to 150 °C. The time-scale in figure 2 is $t^{1/3}$; this is a convenient choice for representing a structural evolution occurring in a coalescence regime, as implied by the Lifshitz–Slyozov–Wagner coarsening theory (see [7] for a discussion of the validity of this theory as a description of the coarsening of GP zones in the present material). In accordance with earlier results [2, 12], figure 2 shows a softening of the material for the early stages of the artificial ageing treatment. In contrast, the decrease of the positron lifetime is new information, which the measurements described in [7, 8], performed several weeks after the interruption of the artificial annealing [13], could not reveal. The reason is that the decrease of the positron lifetime, as well as the softening of the material, is only temporary: indeed, figure 2 also shows that the values of τ and H_V, measured a few days after the interruption of the artificial ageing (open triangles in figure 2), are approximately the same as one obtains at the end of the RT pre-ageing, before any treatment at 150 °C. The time laws governing the evolution of τ and H_V at room temperature and at 70 °C , after partial ageing at 150 °C, are shown in figure 3.

We complete the presentation of our experimental data with a plot H_V versus τ in figure 4. The merit of this unusual plot is to demonstrate that H_V and τ respond differently to the microstructural changes of the material, although in some situations they change in a very similar way (see, for instance, figures 2 and 3). In fact, these parameters behave

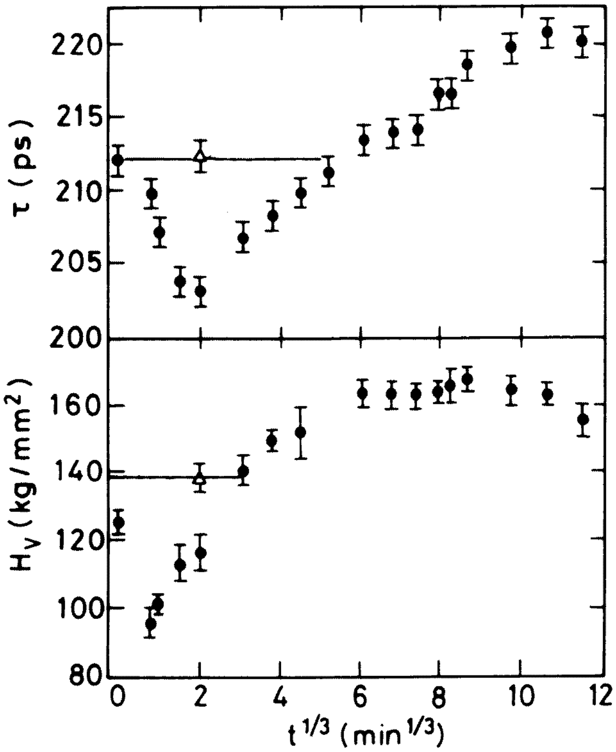

Figure 2. Changes of the microhardness H_V and of the average positron lifetime τ during ageing at 150 °C, after five days' pre-ageing at room temperature (full circles). The open triangles refer to the condition reached after the interruption of the treatment at 150 °C after 8 min, followed by ageing at RT or at 70 °C (see figure 3).

as two independent variables which can be used for representing the state of the alloy and the transformations that occur during ageing or other thermal treatments. We use below figure 4 as a guideline for the discussion of the experimental results.

3. Discussion

The positron lifetime in the bulk of the matrix, which essentially is a diluted solid solution of Zn and Mg in Al, is expected to be near to the value for pure Al (~160 ps). However, we always observe average lifetimes well above this value; we also observe that the lifetime changes during natural and artificial ageing. These results are a manifestation of the well-documented phenomenon of positron trapping, consisting in the localization of positrons at open-volume defects, where they form bound states with a lifetime longer than the bulk value. In the present case, the dominant species of trapping centres are vacancies, vacancy clusters, and misfit regions at the interfaces between the matrix and incoherent or semicoherent precipitates [3–6], with concentrations and spatial distributions depending on the thermal history of the samples. The hardness of the alloy also changes during natural and artificial ageing, but this has nothing to do with open-volume defects; as is well known, the origin of the hardness variations is the formation, the transformation or the dissolution of

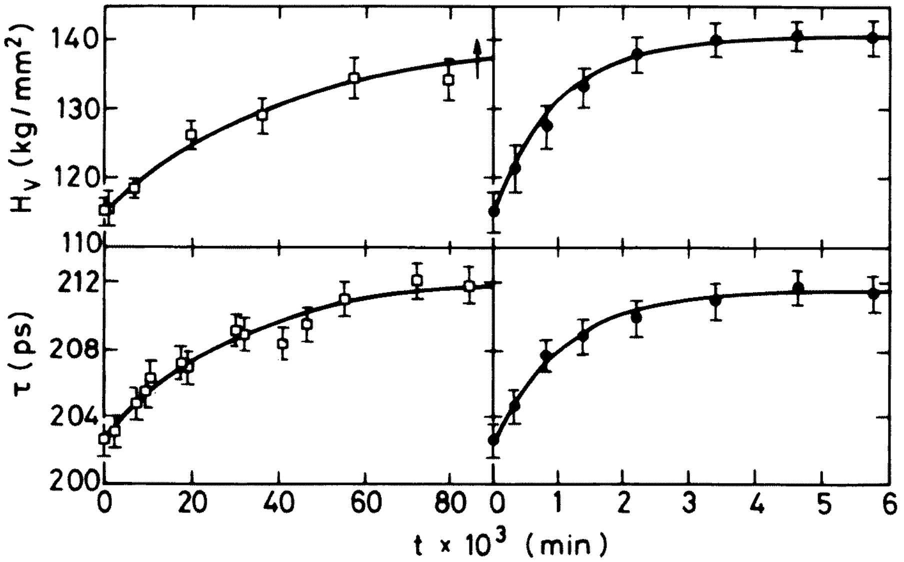

Figure 3. Evolution of microhardness H_V and average positron lifetime τ occurring during ageing at RT (open symbols) and at 70 °C (full symbols). The initial condition of the material corresponds to the minimum of τ in figure 1 (ageing at 150 °C for 8 min). The asymptotic values of the curves correspond to the open triangles in figure 1. The arrow indicates that the fitting with the exponential function (see the text) is made under the assumption that the asymptotic value of H_V at RT is the same as is observed for 70 °C.

chemical or structural inhomogeneities (GP zones and precipitates), which act as obstacles for the dislocation motion. When these inhomogeneities are associated with open-volume defects, there is an indirect link between hardness and average positron lifetime; otherwise H_V and τ move independently. These few basic concepts enable us to interpret the complex evolution represented in figure 4 as follows.

3.1. RT pre-ageing

Let us follow the evolution of the alloy starting from point 1 in figure 4. Here the sample has been prepared in the αSSS phase by solubilization and quenching in cold water. The microhardness is at its lowest level, as is normal in the absence of structural inhomogeneities at a nanometric scale. On the other hand, the αSSS phase obtained by quenching may contain a non-equilibrium concentration of vacancies in the form of vacancy–rich clusters and of vacancy–solute pairs, which justifies the high value of the lifetime (~215 ps). During RT pre-ageing (figure 1 and transformation 1 → 2 in figure 4), τ decreases and H_V increases; the opposite trends of these two parameters tell us that we are observing two independent processes. The most effective positron trapping centres (probably the vacancy–rich clusters) are disappearing, while new obstacles to the motion of the dislocations (the GP zones) begin to appear. In the present experiment we have continued pre-ageing until H_V and τ reach an apparent saturation level (point 2 in figure 4). This point corresponds to a condition of metastable equilibrium at RT: (a) the initial supersaturation of the matrix has been removed and the excess solute has been spent to form a population of small GP zones (radius of a few nanometres); (b) the vacancy-rich clusters are completely dissolved while vacancy–

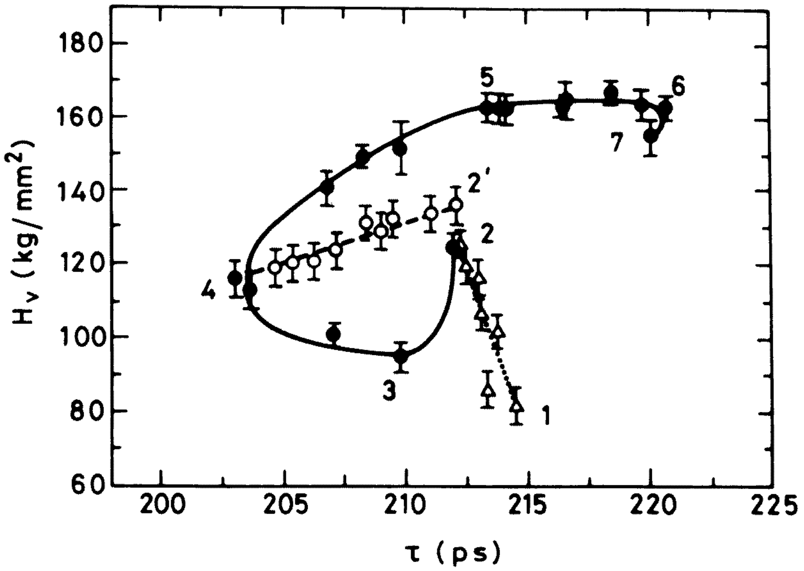

Figure 4. Evolution of the alloy represented in the H_V–τ plane. Point 1 is the condition after solubilization and quenching in cold water. The dotted line from 1 to 2 represents pre-ageing at RT (we have omitted some of the data reported in figure 1 to avoid too many overlapping points in the H_V–τ plane). The full line from 2 to 7 represents ageing at 150 °C. Point 4 is the condition reached after 8 min at 150 °C. The dashed line from 4 to 2′ is the evolution that occurs if the treatment at 150 °C is interrupted at point 4 and the sample, rapidly brought to RT, is left to age at this temperature. Horizontal error bars are not shown in this plot, but the equivalent information is given with vertical error bars for τ in figures 1–3.

solute pairs survive in the limits of the thermal equilibrium. In spite of the dissolution of the vacancy-rich clusters, the average positron lifetime remains above the bulk value; the residual trapping centres are stable vacancies associated with Mg atoms, which are contained in the GP zones as structural components [3–6]. The positron capture cross-section of these vacancies is amplified by the difference in the positron affinities between Al and Zn, which favours the localization of the positrons in the Zn-rich regions.

3.2. Ageing at 150 °C

When the temperature is raised to 150 °C, the GP zones become unstable and are transformed into semicoherent particles η'. In accordance with the experimental results of [7], the transformation GP $\rightarrow$ η' is expected to increase the hardness (η'-particles are more effective obstacles to the motion of the dislocations than the GP zones) as well as the average positron lifetime (positrons captured in the misfit region at the incoherent interfaces have a longer lifetime than those captured inside the GP zones [3–6]). Indeed, the position in the τ–H_V plane reached by the alloy in the last stages of ageing (points from 5 to 7 in figure 4) is well above and to the right of point 2, thus confirming these expectations. However, the curly line in figure 4 tells us that the kinetics leading to this final condition is rather complicated. The transformation GP $\rightarrow$ η' is the last stage of a coarsening process that begins with the dissolution of the smallest GP zones and the release of the solute into the matrix. Only in a later stage is the excess solute captured by the biggest GP zones, which grow until the coherency with the matrix becomes energetically unfavourable; at this point, GP zones become η'-particles. The concomitant decrease of τ and H_{V}, corresponding to the portion of the curve in figure 4 from point 2 to point 3, shows that the dissolution of the smallest GP zones is not immediately compensated by the coarsening and the transformation of the surviving zones. This means that the dissolution is fast in comparison with the migration of the solute, and probably approaches completion before the effects on τ and H_{V} of the GP $\rightarrow$ η' transformation become manifest. The point of inversion of the balance between dissolution and coarsening is not exactly the same for τ and H_{V}, a result that we ascribe to a different sensitivity of these parameters to the dissolution of GP zones and to the initial presence of η'-particles. Beyond point 3 for H_{V} and point 4 for τ, the effect of coarsening becomes dominant and the two parameters rise up to point 5. Here begins an apparent saturation of the hardness (points from 5 to 6), but the continuing evolution of the material is revealed by increase of the positron lifetime. The process of decomposition of the alloy continues with the coarsening of the η'-particles, that eventually leads to the formation of the stable phase η. The large precipitates of the system in an advanced state of decomposition are less effective positron traps than the smaller particles in the initial stage of precipitation, because a larger size implies a smaller extension of the misfit surface per unit volume. Thus, if ageing is pushed to this final stage, we should expect not only a softening of the material (overageing) but also the decrease of the average positron lifetime. It is hard to say whether the inversion of the curve from point 6 to point 7, where our experiment stops, is an accidental fluctuation or a true symptom of incipient overageing.

3.3. Reconstruction of GP zones at RT and at 70 °C

After ageing for 8 min at 150 °C, the positron lifetime has reached its minimum; this shows that the dissolution of the smallest GP zones is well advanced or even complete. The coarsening of GP zones and the formation of η'-particles have not taken place yet or still are at a very initial stage. If the thermal treatment at 150 °C is interrupted at this point by rapid cooling at RT, coarsening and transformation do not occur and the excess solute initially present in the matrix is redistributed in a dissemination of small GP zones. The effects of the artificial ageing are, in practice, cancelled. This is shown in figure 4 by the straight line going from point 4 to point 2′, i.e. to a condition almost coincident with the state of the material before the treatment at 150 °C (point 2). The apparent linear correlation of τ and H_{V} in this part of the plot reflects the variation of a single factor (the concentration of GP zones) rather than of a combination of different physical processes. The data of figure 3 give us quantitative information on the time law governing the reconstruction of the GP zones, and show that this process occurs at 70 °C as well as at RT, but with different rates. The rate is determined by the migration of the slowest solute species that contributes to the formation of the GP zones. We have fitted these data with curves corresponding to exponential time laws of the form

$$F = F_f - (F_f - F_i)\mathrm{e}^{-t/t_c} \tag{1}$$

where F represents either H_{V} or τ, subscripts f and i represent the final and initial values of F and t_c is a characteristic time. The possibility of fitting microhardness data and positron lifetimes with almost identical values of t_c confirms that the two different parameters respond, in this case, to the same microstructural change.

We may use the expression of Panseri and Federighi [14]:

$$t_c = t_0 \exp(E/kT) \tag{2}$$

where t_0 is a constant and k the Boltzmann constant, to obtain from the data taken at two temperatures the activation energy E for the migration of the solute. The average of the E-values determined from the independent analysis of microhardness and positron lifetime data is $E = 0.62 \pm 0.03$ eV. This value is close to the result of 0.59 eV obtained by Jürgens *et al* [15, 16] for Al–2.5 at.% Zn–X at.% Mg ($X = 0.3$ to 2.5) and Al–3 at.% Zn–X at.% Mg alloys by means of measurements of Young's modulus, of 0.59 eV obtained by Panseri and Federighi [14] for Al–4.4 at.% Zn–0.1 at.% Mg by means of isothermal resistance measurements, and of 0.67 eV obtained by Ceresara and Fiorini [17] for Al–4.4 at.% Zn–X at.% Mg ($X = 1.1$ to 3.5) also from resistance measurements. All the above values are near to the migration energy of Mg atoms in Al (0.6 eV; see [2] and references therein), enabling us to identify Mg as the limiting factor in the formation of the GP zones. This confirms the hypothesis of Dlubek *et al* [3–6] concerning the essential role of vacancy–Mg atom complexes in the effects of GP zones on the positron lifetime. In contrast, Mg seems unimportant in the last stages of coarsening, which lead to the transformation of GP zones into semi-coherent η'-particles. This conclusion comes from the comparison of the activation energy for the formation of GP zones, determined in the present work, with the activation energy (0.32 ± 0.02 eV) that relates to the transformation GP $\rightarrow \eta'$, obtained in reference [8] for the same alloy. A different activation energy means a different diffusing species: with a value of about 0.3 eV, the reasonable candidate is a Zn atom associated with a vacancy. According to the literature, the activation energy for the migration of this complex is 0.42 eV in Al–Zn [13] and 0.21 in Al–Zn–Mg [15] with an atomic concentration ratio $c_{\mathrm{Mg}}/c_{\mathrm{Zn}}$ between 0.38 and 1.7 (in the alloy studied in the present work, the ratio $c_{\mathrm{Mg}}/c_{\mathrm{Zn}}$ is 0.9). Note that the presence of vacancies stabilized by Mg atoms, which is essential for determining the increase of the positron lifetime when capture occurs at GP zones, becomes irrelevant when the lifetime increase is dominated by positron trapping at the misfit surfaces of the η'-particles.

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