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Kinetic grain growth in Cu–Zn–Al shape memory alloys

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Kinetic grain growth has been evaluated in Cu–Zn–Al shape memory alloys by the calculation of different grain size parameters (perimeter, area, minimal and maximal diameter) in different alloys, and at different temperatures and heat treatment times. The growth order values have been worked out and the activation energy estimated.

1. Introduction

The driving force behind grain growth comes from the elimination of surface energy in the grain boundaries. This happens in such a way that by introducing thermal energy, diffusion is produced and with it an increase in size. The grain boundary area decreases, as does the total energy stored in it, with a resulting greater thermodynamic stability.

In Cu–Zn–Al alloys a great influence of grain size on singular transformation temperatures is observed [1, 2], and also on thermodynamic values, elastic and frictional energy [3, 4] and mechanical properties [5] among others. The main aim of this paper is to show how the grain size can be predicted at different temperatures and heat treatment times.

2. Experimental procedure

The kinetic grain growth was studied in two β-phase alloys at room temperature with the chemical compositions given in Table I. For each of these alloys, 30 slices were cut from the same bar, measuring 5 mm in diameter and 4 mm in height. Two of them were used as reference samples, while the rest were subjected to different heat treatments at 750, 800, 850 and 900 °C and for 3, 5, 10, 15, 20, 30 and 60 min at each temperature.

Samples from the same alloy were introduced into the furnace at a fixed temperature and were then taken out one by one according to the different times indicated above, and quenched in water at 25 °C. Afterwards, they were metallographically prepared.

Grain size parameters (perimeter, area, maximal and minimal diameter) were obtained by an image analysis technique. The image was acquired by means of a suitable camera and was then improved, enhancing its contrast and pseudocolour in order to facilitate its observation and thus its further interpretation. After this optimization process, parameters were identified and quantified. Finally, the image was codified by a computer and the data statistically analysed.

The data obtained for each temperature, alloy and heat treatment are shown by means of graphs as a function of treatment time t. The graphs obtained are similar to an exponential equation of the type

$$Y = A[1 - \exp(-bt)] \quad (1)$$

A and b being constant for each alloy and treatment temperature. The value of A is obtained by making an approximation to the limit of the growth function. Thus

$$\frac{A - Y}{A} = \exp(-bt) \quad (2)$$

$$\log\left(\frac{A - Y}{A}\right) = -0.434\, bt \quad (3)$$

$\log[(A - Y)/A]$ graphs in relation to time are made, Y being the perimeter, area, minimum and maximum diameter. Thus linear relationships of slope $-0.434b$ are obtained. The value of b for each temperature and alloy can be ascertained in this way.

With the values of A and b, kinetic grain growth equations can be made for each temperature, alloy and grain size parameter. These equations predict the grain size because they take account of the length of treatment time at a fixed temperature.

In order to calculate activation energy an Arrhenius type equation has been used, since the results obtained show that it assimilates the grain growth stage very well. Equations used are of the type

$$Y = K t^n \quad (4)$$

with k being a constant, t treatment time, n growth

TABLE I Alloy compositions

	Composition (wt %)		
Alloy	Cu	Zn	Al
Cu–Zn21–Al6.6	72.3	21.04	6.66
Cu–Zn21–Al6	73.0	20.85	6.15

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order and Y being chosen as the size parameter for the minimum diameter. Linear equations in which slopes reveal growth order are obtained by means of a graph plotting log Y against log t.

Moreover, if the atomic diffusion across a grain boundary is like a sample-activated process, it can then be demonstrated that the K constant in the former equation can be replaced by the expression

$$K = K_0 \exp(-E_a/RT) \quad (5)$$

where E_a is the heat of activation for the process, T is the absolute temperature and R the international gas constant. Therefore the law of grain growth can be written in the following way as a function of both temperature and time:

$$Y - Y_0 = K_0 t \exp(-E_a/RT) \quad (6)$$

By plotting $\log(Y - Y_0)$ against $1/2.3\,RT$ a straight line with a slope corresponding to the activation energy is given. In our case, this calculation has been carried out for the perimeter parameters, area and minimum diameter and for periods of 5 min, since approximately 50% total grain growth happens at this time. This criterion has been established by various authors in order to estimate the activation energy in a recrystallization process [6, 7].

3. Results

3.1. Estimating the kinetic equation

Parameters are obtained for each alloy, temperature and time of treatment in the furnace. Perimeter and maximal and minimal diameter are expressed in micrometres and their area in square micrometres. The mean diameter is taken as the average value of maximal and minimal diameters.

Figs 1 and 2 show those parameters as a function of temperature and experimental time for alloys Cu–Zn21–Al6.6 and Cu–Zn21–Al6, respectively. These curves are well fitted by an exponential-type equation (Equation 1).

According to the results, it is observed that as time is increased the grain size parameters become constant. As can be observed, there is a linear relationship

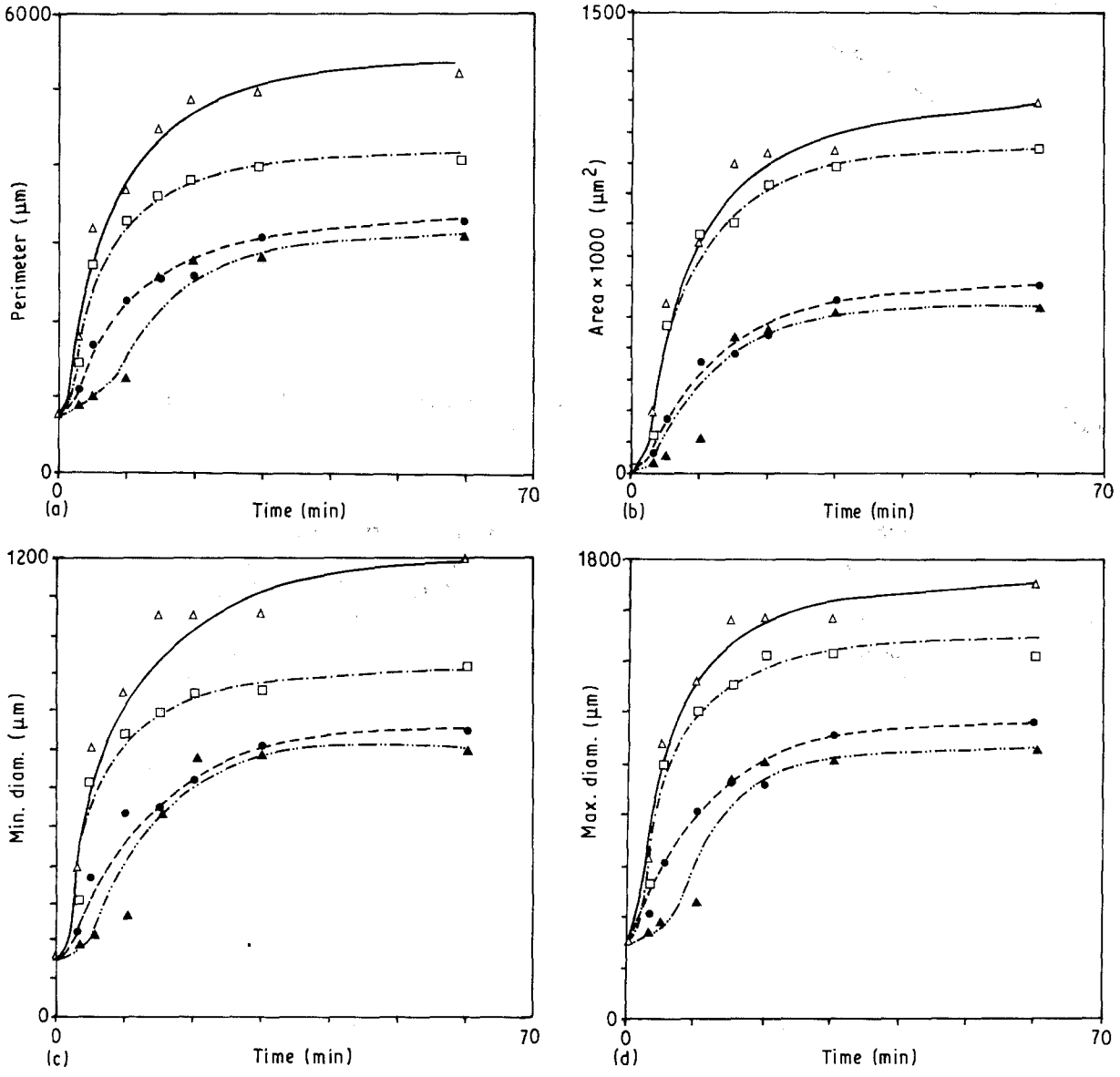

Figure 1 Grain size parameters at different temperatures and heat treatment times for alloy Cu–Zn21–Al6.6: (a) perimeter, (b) area, (c) minimal diameter, (d) maximal diameter. (▲) 750 °C, (●) 800 °C, (□) 850 °C, (△) 900 °C.

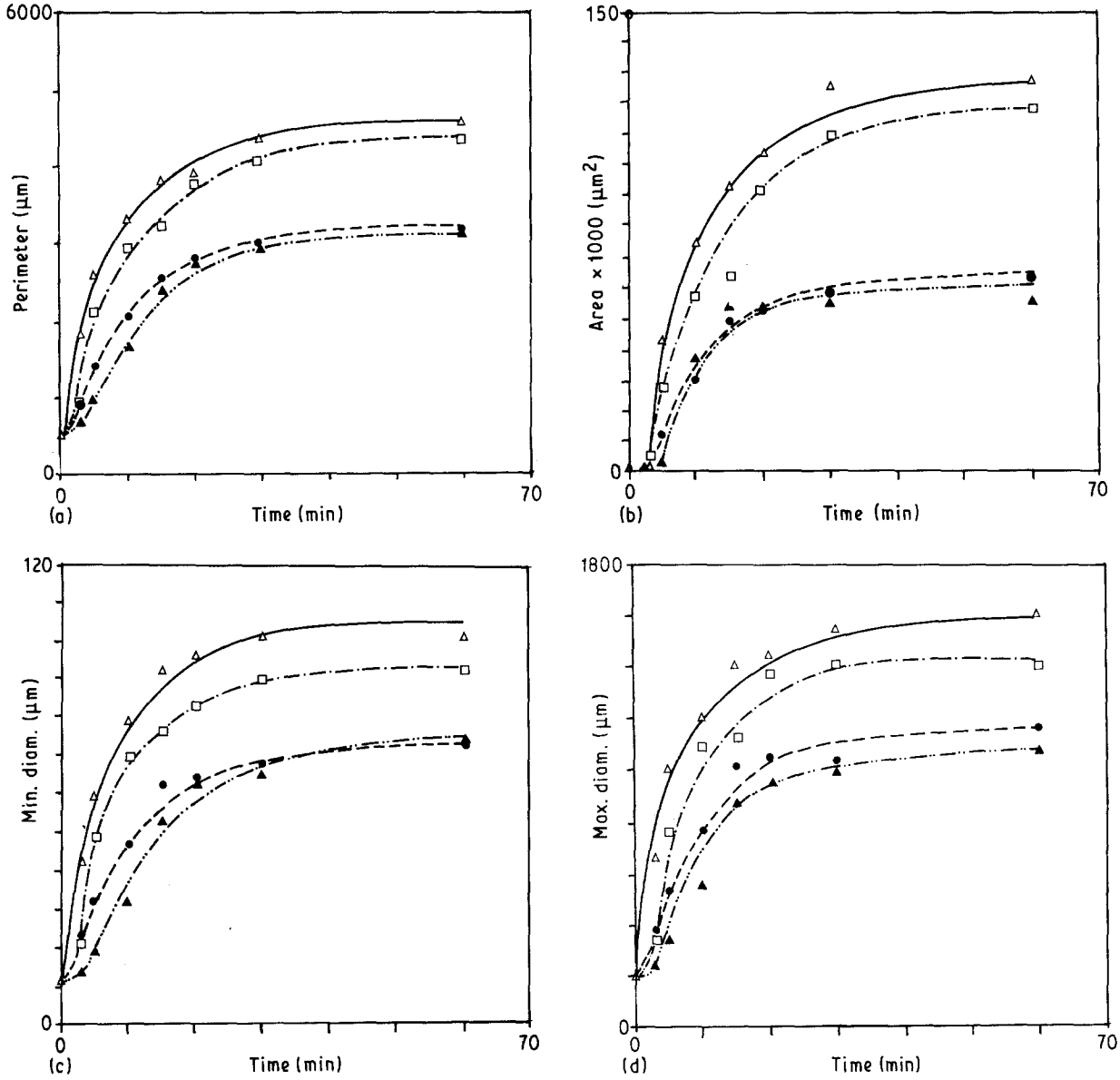

Figure 2 Grain size parameters at different temperatures and heat treatment times for alloy Cu–Zn21–Al6: (a) perimeter, (b) area, (c) minimal diameter, (d) maximal diameter. (▲) 750 °C, (●) 800 °C, (□) 850 °C, (△) 900 °C.

with a slope of $-0.434b$, where b is obtained for each alloy and temperature. In Table II and from A and b values, kinetic equations of grain growth for temperature and grain size parameters (perimeter, area, minimal and maximal diameters) are shown for each alloy. In these equations the final grain size obtained after a certain time of heat treatment at a fixed temperature can be found.

As is to be expected, when the temperature rises the kinetic effect is quicker and at the same set temperature an increase in time brings about a greater grain growth. Bearing in mind that we were working from alloys with an average grain size of 180 μm mean diameter, final grain sizes of (1350 μm) are reached after 60 min. This means that the grain sizes are 7.5 times greater than those at the beginning. At 850 °C, grain sizes which are approximately 6.5 times greater are reached. At 800 °C, and still at the same treatment time, the grain size is five times greater. Finally, at 750 °C mean diameter is 4.5 times greater.

As can be seen from the graphs of grain growth, the alloy grows very quickly up to 10–15 min, and after this treatment time the growth is much slower. For a temperature of 900 °C and with a 10 min treatment time, the average diameter grows approximately six times; at 850 °C growth is five times greater, at 800 °C it grows about four times more and at 750 °C nearly three. Nevertheless, when the final grain size after 60 min of heat treatment is compared with that obtained after 10 min, the grain growth is approximately 1.5 times higher for all temperatures.

3.2. Calculation of the growth order and activation energy

The results of the former paragraph show that the grain growth kinetics of these alloys can be divided into two sections: one from 0 to 10–15 min, where the growth can be similar to Arrhenius-type kinetics, and another at times greater than 10–15 min where the grain size parameters grow slowly and tend towards a constant value, indicating that the system has some

TABLE II Kinetic grain growth equations

T(°C)	Perimeter, $(P - P_0)$ (μm)	Area, $(A - A_0)$ (μm^2)	Min. diam., $(D_m - D_{mo})$ (μm)	Max. diam., $(D_M - D_{Mo})$ (μm)	Average diam., $(D_M - D_{Mo})$ (μm)
Alloy Cu–Zn21–Al6.6					
900	5083[1 − exp(− 0.097t)]	1 200 000[1 − exp(− 0.073t)]	1196[1 − exp(− 0.057t)]	1700[1 − exp(− 0.076t)]	1448[1 − exp(− 0.070t)]
850	4001[1 − exp(− 0.179t)]	1 060 000[1 − exp(− 0.091t)]	916[1 − exp(− 0.080t)]	1437[1 − exp(− 0.188t)]	1176[1 − exp(− 0.115t)]
800	3056[1 − exp(− 0.084t)]	624 000[1 − exp(− 0.080t)]	704[1 − exp(− 0.110t)]	1116[1 − exp(− 0.140t)]	910[1 − exp(− 0.168t)]
750	2810[1 − exp(− 0.090t)]	555 000[1 − exp(− 0.139t)]	690[1 − exp(− 0.165t)]	999[1 − exp(− 0.291t)]	844[1 − exp(− 0.199t)]
Alloy Cu–Zn21–Al6					
900	4510[1 − exp(− 0.093t)]	1 270 000[1 − exp(− 0.159t)]	1016[1 − exp(− 0.164t)]	1595[1 − exp(− 0.100t)]	1306[1 − exp(− 0.085t)]
850	3974[1 − exp(− 0.230t)]	1 100 000[1 − exp(− 0.091t)]	424[1 − exp(− 0.110t)]	1410[1 − exp(− 0.140t)]	1167[1 − exp(− 0.140t)]
800	3160[1 − exp(− 0.106t)]	587 000[1 − exp(− 0.225t)]	713[1 − exp(− 0.102t)]	1160[1 − exp(− 0.074t)]	936[1 − exp(− 0.083t)]
750	3231[1 − exp(− 0.090t)]	575 000[1 − exp(− 0.240t)]	750[1 − exp(− 0.074t)]	1040[1 − exp(− 0.054t)]	895[1 − exp(− 0.117t)]

TABLE III Growth order values

T(°C)	Equation	Growth order
Alloy Cu–Zn21–Al6.6		
900	$\log D = 2.34 + 0.62 \log t$	0.62
850	$\log D = 2.21 + 0.70 \log t$	0.70
800	$\log D = 2.02 + 0.71 \log t$	0.71
750	$\log D = 1.91 + 0.69 \log t$	0.69
Alloy Cu–Zn21–Al6		
900	$\log D = 2.31 + 0.63 \log t$	0.63
850	$\log D = 2.04 + 0.77 \log t$	0.77
800	$\log D = 2.03 + 0.65 \log t$	0.65
750	$\log D = 1.78 + 0.73 \log t$	0.73

TABLE IV Activation energy

Alloy	Origin	Slope (10^5 J mol^{-1})	E_a (kJ mol^{-1})
Perimeter			
Cu–Zn21–Al6.6	10.91	− 1.6	160
Cu–Zn21–Al6	8.21	− 1.1	110
Area			
Cu–Zn21–Al6.6	14.40	− 1.9	190
Cu–Zn21–Al6	13.70	− 1.8	180
Minimal diameter			
Cu–Zn21–Al6.6	9.79	− 1.6	160
Cu–Zn21–Al6	8.06	− 1.2	120

physical impediment which does not allow the kinetics to thrive.

In order to estimate the activation energy, experimental grain size values were used until the point of inflexion on the kinetic curve was located. These curves were similar in type to Equation 4.

By showing log$Y$ in relation to log$t$ by means of a graph, linear equations can be obtained where the slope will give us the growth order. The n values are given together with the linear function in Table III. For each alloy and temperature these results vary very little, reaching values which in the case of the alloy Cu–Zn21–Al6.6 range from 0.62 to 0.71 with a mean value of 0.68 the values for alloy Cu–Zn21–Al6 range from 0.63 to 0.77 with a mean value of 0.70. The growth order is given by the mean value, corresponding to 0.69.

The activation energy has also been calculated from Equation 6 at a heat treatment time of 5 min, taking as a grain size parameter the perimeter, area and minimum diameter. By means of a graph showing $\log(Y - Y_0)$ in relation to $1/2.3\,RT$, linear equations for alloys Cu–Zn21–Al6.6 and Cu–Zn21–Al6 are obtained, the slopes of which represent the activation energies which have changed sign in each alloy.

In Table IV the results, which as expected fluctuate for each alloy, are shown. This is due to the fact that the activation energy depends on the chemical composition. The energy margins for each alloy are contained between the calculated parameters.

4. Discussion

In Cu–Zn–Al alloys, a very fast grain growth is observed up to a period of 10 to 15 min. Subsequently,

growth is very slow with a practically constant grain size after 60 min of continuous heat treatment. This fact can be explained as a consequence of a kinetic impediment, either by accumulation of impurities and defects or by lack of continuity in the solid; thus grain growth is prevented although thermal energy is applied.

In spite of this fact, the 158 μm initial grain size (as average diameter) for alloy Cu–Zn21–Al6 becomes an 1167 μm average final diameter after 60 min of heat treatment (850 °C and water-quenched). After the first 15 min of heat treatment, a 938 μm grain size was attained. In other words, after 15 min the original grain size grows six times, and after 60 min grows to only 7.5 times its original size.

This shows the variation of grain growth rate as a function of time under heat treatment. All the above must be kept in mind when performing the necessary heat treatments after moulding and other possible forming processes.

Form the graphical representations of grain size as a function of time (Figs 1 and 2) it can be seen that for treatment temperatures of 750 and 800 °C at 3 and 5 min time, the real time for which the sample undergoes these temperatures is lower than the pre-fixed experimental time. This difference in time is spent in heating the sample from room temperature up to the experimental temperature, as can be observed by a slight upward curvature in the slope. As the temperature increases, the tendency to curve decreases but the slope continues to rise.

From the different parameter values for grain size as a function of time, it can be stated that the increment in final grain growth is bigger between 850 and 900 °C than the increment between 750 and 850 °C, this fact being in accordance with the kinetic equations obtained in the grain growth processes.

The growth order, using an Arrhenius-type equation, is calculated with average growth values corresponding to a treatment time of 3 to 15 min between which the kinetics adjust to this type of equation. An average growth order value of 0.69 is obtained for each alloy. This value is high compared with those for other metallic alloys, which are generally no greater than 0.5 in value. Thus Fullman [8] establishes that the growth order in commercial brass is from 0.2 to 0.3, and in what he terms "high purity brass" the order varies between 0.4 and 0.6. This shows that the grain size for our alloys grows very quickly as time elapses. Taking into account the aforementioned kinetic impediments, it must also be pointed out that after 15 min, the average growth order decreases.

Activation energy values have also been obtained, and as expected this energy varies considerably according to chemical composition; because there is an atomic diffusion process through a grain boundary, the kinetics will depend on the amount of atoms present in one element or another.

These results show a great variation in activation energy with the chemical composition. The results are consistent with the fact that as the copper solute content increases the copper diffusion coefficient at the same temperature decreases, thus increasing the grain growth activation energy.

Experimental growth data supposedly adjust to a simple law of activation, and consequently the dependence on grain growth temperature does not give a constant value for activation energy on many occasions. It must be taken into account that the results obtained represent values which, although not exact, are the most accurate available according to experimental results.

5. Conclusions

In both Cu–Zn–Al alloys very fast grain growth is observed at a given temperature for up to 10 to 15 min heat treatment but becoming slower after this time, giving a constant grain size at times above 60 min at the test temperature.

The growth order is 0.69, the value of which is higher when compared with other alloys which do not go beyond the value of 0.5.

The average activation energy for the alloy Cu–Zn21–Al6.6 is 170 kJ mol^{-1} and for Cu–Zn21–Al6 it is 136 kJ mol^{-1}.

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