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Grain growth in Cu–Zn–Al–Mn shape-memory alloy

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The kinetic grain growth has been determined in a Cu–Zn–Al–Mn alloy by the calculation of different grain-size parameters (perimeter, minimum and maximum diameter) and the ratio of the grain-boundary area per unit volume from measurements obtained at different temperatures and heat-treatment times. The growth order and activation energy have been evaluated.

1. Introduction

It has been observed that the addition of manganese to Cu–Zn–Al shape-memory alloys brings about an increase in the mechanical properties and a widening of the thermoelastic martensitic transformation temperature range associated with these alloys [1–3].

The grain growth is produced by the diffusion in such a way that by introducing thermal energy, surface energy is eliminated at the grain boundaries so bringing about an increase in the size and a decrease in the number of grains, hence a decrease in the total energy stored and greater thermodynamic stability. This kinetic grain growth at constant temperature follows the Arrhenius equation [4, 5].

$$D = Kt^n \qquad (1)$$

where K is a constant, t is the heat-treatment time, n the growth order and D the grain-growth parameter.

Moreover, if the atomic diffusion across a grain boundary is a simple activated process, it can then be demonstrated that the constant K in the above equation can be replaced by the expression [5, 6]

$$K = K_o \exp(-E_a/RT) \qquad (2)$$

where E_a is the activation energy for the process, T is the temperature (K) and R is the universal gas constant. Therefore, the law of grain growth can be written in the following way as a function of both temperature and time

$$D = K_o t^n \exp(-E_a/RT) \qquad (3)$$

2. Experimental procedure

The kinetic grain growth has been studied in an alloy with the chemical composition (at %) 19.28% Al, 6.09 % Zn and 3.44% Mn with β phase at room temperature ($M_S = 9\,^\circ C$). From the same bar 24 slices were cut, measuring 5 mm diameter and 4 mm thick. Three of these samples were used as reference samples, while the remaining 21 were subjected to different heat treatments at 700, 800 and 900 °C and 1, 3, 5, 10, 15, 30 and 60 min for each temperature.

Samples from the original alloy were introduced into the furnace at a fixed temperature and were then taken out one by one at the different times indicated above, and quenched into water at 25 °C. Afterwards, they were metallographically polished and etched with $FeCl_3$. Metallographic observation was carried out by optical microscopy at ×34 magnification and the grain boundaries were drawn on a projection screen.

The grain-size parameters (perimeter, minimum and maximum diameter) were obtained by the image analysis technique with a Matrox electronic Systems Ltd, MWP-AT installed in a PC-AT computer using software in a TITN SAMBA system. The image was enhanced in contrast and pseudocolour in order to facilitate its interpretation.

After this optimization process, parameters are identified and quantified. Finally, the image is coded by a computer and data are statistically analysed [7].

3. Results and discussion

The grain-size values obtained (perimeter, minimum and maximum diameter) are shown in relation to heat-treatment time and at each test temperature in Figs 1, 2 and 3 for each growth parameter. As expected, on raising the temperature the kinetics growth rate is faster and on extending the period of time at the same temperature, grain growth is greater.

The average grain perimeter has an initial value of 200 μm and after 60 min heat treatment the grains reach sizes of 736, 1240 and 1300 μm at 700, 800 and

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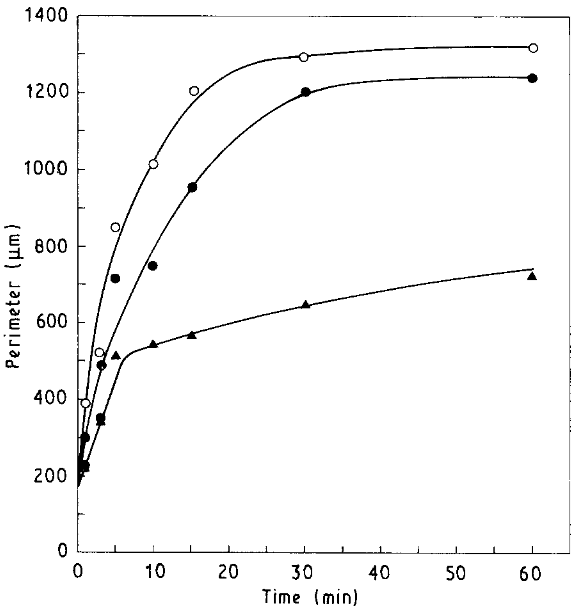

Figure 1 Perimeter growth in relation to heat-treatment time and at each test temperature: (▲) 700 °C, (●) 800 °C, (○) 900 °C.

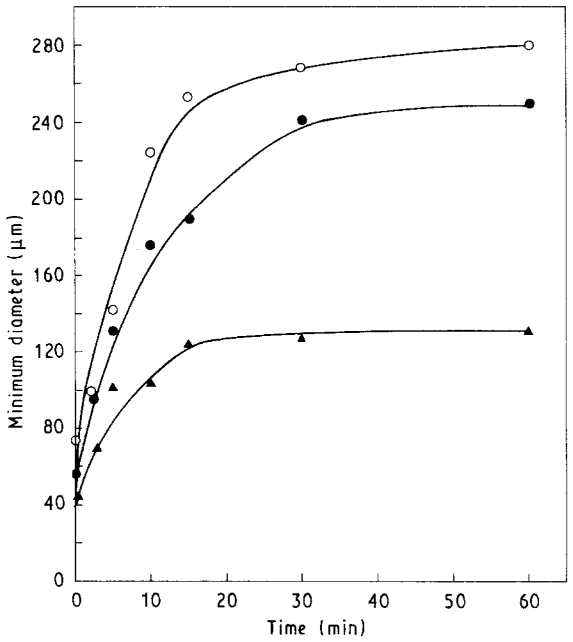

Figure 2 Minimum diameter growth in relation to heat-treatment time and at each test temperature: (▲) 700 °C, (●) 800 °C, (○) 900 °C.

900 °C, respectively, which are 3.7, 6.2 and 6.5 times greater than the original average perimeter of the alloy grains.

The graphs show very rapid grain growth up to 10 min heat-treatment time; after this the growth rate decreases. This drop in the rate is due to the fact that as the grain size increases, the grain-boundary area per unit of volume decreases, as does the interfacial energy per unit volume. The driving force for growth is lower, so producing a slower kinetic process.

Kinetic grain growth follows Hillert's distribution, because the maximum radius is 1.8 times higher than the average radius value. This means that uniform growth occurs in the whole sample and size distribution obeys an asymptotic law particular to the state of equilibrium itself [8]. This kinetic process behaves in accordance with Equation 1 in which there is a linear relationship between log D and log t. The slope of which gives the growth order, n. The n values are given, together with the linear function, in Table I for each temperature and grain-size parameter; the results show little standard deviation: perimeter from 0.28–0.34, for minimum diameter from 0.26–0.37 and for maximum diameter from 0.27–0.36. The average growth order is 0.32. This value is low when compared with other metallic alloys which have body centred cubic structures (open structures) where the diffusion process is favoured. For instance, the growth order of α-iron is 0.5 at 800 °C [9], whereas the β-brasses range from 0.35 at 500 °C to 0.60 at 850 °C [10, 11].

The activation energy has also been obtained from Equation 3. This calculation has been carried out for the parameters, minimum and maximum diameters and perimeter and after 10 min heat-treatment time, because approximately 50% of the total grain growth occurs at this time. This type of criterion has been used by various authors to estimate the activation energy in a recrystallization process [12, 13].

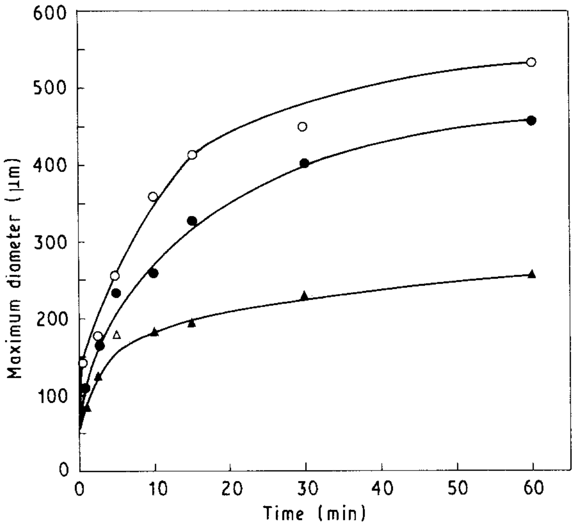

Figure 3 Maximum diameter growth in relation to heat-treatment time and at each test temperature: (▲) 700 °C, (●) 800 °C, (○) 900 °C.

By representing log D in relation to $1/2.3RT$ a straight line with a slope corresponding to the activation energy, which has changed sign, is given for each grain-size parameter. Table II shows the results which range between 33 and 35 kJ mol^{-1}. These energies are lower in relation to other shape-memory alloys such as Cu–Zn–Al with activation energies of approximately 90 kJ mol^{-1} [14]. This means that the grain-growth process in Cu–Zn–Al–Mn shape-memory alloys is more thermodynamically favoured than kinetically favoured. Thus the kinetic factor acts as a grain-growth impediment because the decrease in grain-growth order is very sharp in the Cu–Zn–Al–Mn alloy.

The ratio of the grain-boundary area per unit volume, G_v, has been determined for each temperature

TABLE I Variation of growth order of different grain-size parameters with heat-treatment temperatures and times (min).

Parameter	T(°C)	Equation	r^a	Growth order, n
Perimeter,	700	$\log P = 2.41 + 0.28 \log t$	0.97	0.28
P(μm)	800	$\log P = 2.52 + 0.34 \log t$	0.98	0.34
	900	$\log P = 2.64 + 0.32 \log t$	0.95	0.32
Diameter,				
Minimum	700	$\log d = 1.74 + 0.26 \log t$	0.92	0.26
d(μm)	800	$\log d = 1.82 + 0.37 \log t$	0.99	0.37
	900	$\log d = 1.89 + 0.36 \log t$	0.96	0.36
Maximum,	700	$\log D = 1.97 + 0.27 \log t$	0.97	0.27
D(μm)	800	$\log D = 2.07 + 0.35 \log t$	0.99	0.35
	900	$\log D = 2.12 + 0.36 \log t$	0.98	0.36

$^a r$ is the correlation coefficient.

TABLE II Activation energy in Cu–Al–Zn–Mn alloy

	Activation energy		
	($\log K'$)	Slope $-E_{act}$ (kJ/mol^{-1})	Correlation Coefficient
Perimeter	4.54	34	0.99
Minimum diameter	3.92	35	0.99
Maximum diameter	4.03	33	0.99

and heat-treatment time. Assuming that the grains have the ideal shape of a tetrakaidecahedron, the value of G_v can be determined from the mean grain-boundary area on a random section, A, from the relationship [15]

$$G_v = 3.059/A^{1/2} \tag{4}$$

Fig. 4 shows a very rapid decrease of G_v with times of up to 10 min. At longer times there appears to be an asymptotic approach to a limiting grain size.

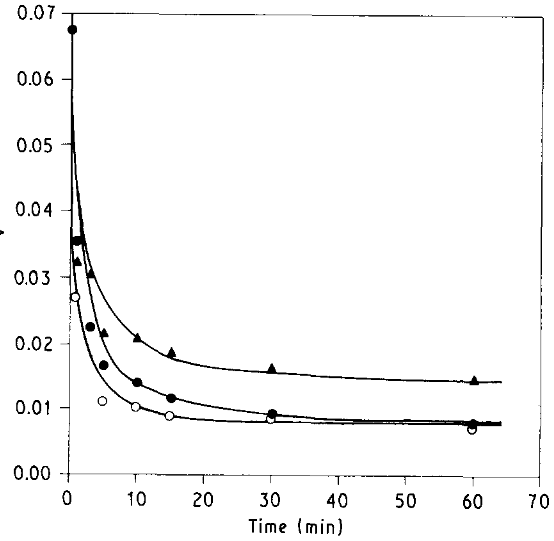

Figure 4 Ratio of the grain-boundary area per unit volume, G_v, versus heat-treatment time at each test temperature: (▲) 700 °C, (●) 800 °C, (○) 900 °C.

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