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Thermal stability of the αZn–Mg_2Zn_{11} and αZn–βAl eutectics obtained by Bridgman growth

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The thermal stability of rod-like αZn–Mg_2Zn_{11} and lamellar αZn–βAl eutectics obtained by Bridgman growth of Zn–3.1 wt% Mg and Zn–5 wt% Al has been studied for soaking times up to 10 h at 300 and 350 °C, respectively. Two-dimensional coarsening resulted for αZn–Mg_2Zn_{11} grown at 0.5 and 1 mm s^{-1} while fault migration was operative for lamellar αZn–βAl grown at 0.1 and 1 mm s^{-1}. Hardness decreased with increased soaking time according to a Hall–Petch relationship with mean interphase spacing and the values H_0 and k_Y accord well with the values obtained from the Hall–Petch relationship for H_V of as-solidified αZn–Mg_2Zn_{11} and αZn–βAl with eutectic interphase spacing, respectively.

1. Introduction

Solidification microstructure selection and characterization in the Zn-rich Zn–Mg and Zn–Al systems have been investigated by Liu and Jones [1, 2]. The Zn-rich Zn–Mg system exhibits competitive growth between stable αZn–Mg_2Zn_{11} and metastable αZn–$MgZn_2$ eutectics while the Zn–Al system did not involve formation of new non-equilibrium phases for the conditions investigated. These studies were focused on the conditions for growth of these eutectics, on observed dependencies on growth velocity of eutectic interphase spacing λ and on dependencies on λ of microhardness H_V.

The objective of the present work was to study the thermal stability and microhardness of the rod-like αZn–Mg_2Zn_{11} eutectic grown at 0.5 and 1 mm s^{-1} and of lamellar eutectic αZn–βAl grown at 0.1 and 1 mm s^{-1} isothermally treated at 300 °C (0.90 T_m) and 350 °C (0.95 T_m) for up to 10 h, respectively.

2. Experimental procedure

Specimens for isothermal treatment were 2.5 mm diameter alloy rods (Zn–3.1 wt % Mg and Zn–5.0 wt % Al) prepared from 99.995% Zn and 99.99% Mg or 99.99% Al which had been Bridgman solidified in a temperature gradient of 15 K mm^{-1} as described earlier [1, 2]. Specimens were encapsulated under argon at 300 °C (for Zn–Mg) or 350 °C (for Zn–Al) for periods up to 10 h followed by water quenching. Longitudinal and transverse sections of samples were prepared for optical and scanning electron microscopy (SEM) and for microhardness (100 g load) testing. Counting of numbers of αZn elements per unit area in Zn–3.1 wt % Mg and determination of mean interlamellar spacing in Zn–5.0 wt % Al was performed on enlarged prints of scanning backscattered electron micrographs from transverse sections. At least 1000 elements were counted to evaluate the number of rods per unit area N. Hardness values were the average of at least 10 measurements on transverse sections using a 100 g load.

3. Results

The samples of Zn–3.12 wt % Mg Bridgman grown at 0.5 and 1 mm s^{-1} had fully αZn–Mg_2Zn_{11} rod eutectic microstructures prior to heat treatment at 300 °C. Figs 1 and 2 are SEM micrographs of transverse and longitudinal sections, respectively, showing the sequence of thermal coarsening of the rod-like eutectic Zn–Mg_2Zn_{11} of Zn–3.12 wt % Mg alloy grown at 0.5 mm s^{-1}. After 10 min at 300 °C, some rods had already coalesced, while others remained with their initial rod shape and size, as shown in Fig. 1b. After treatment for 1 h at 300 °C, the shape of the αZn rods became more irregular due to rapid advance of coalescence (Fig. 1c) and coarsening continued with increasing holding time (Fig. 1d). Results for the remaining number of αZn elements per unit area N, mean interphase spacing λ ($= N^{-1/2}$) and microhardness H_V from transverse sections as a function of holding time at 300 °C for Zn–3.12 wt % Mg grown at 0.5 and 1 mm s^{-1} are given in Table I. Both N and H_V decreased continuously with increasing holding time at 300 °C for both growth velocities.

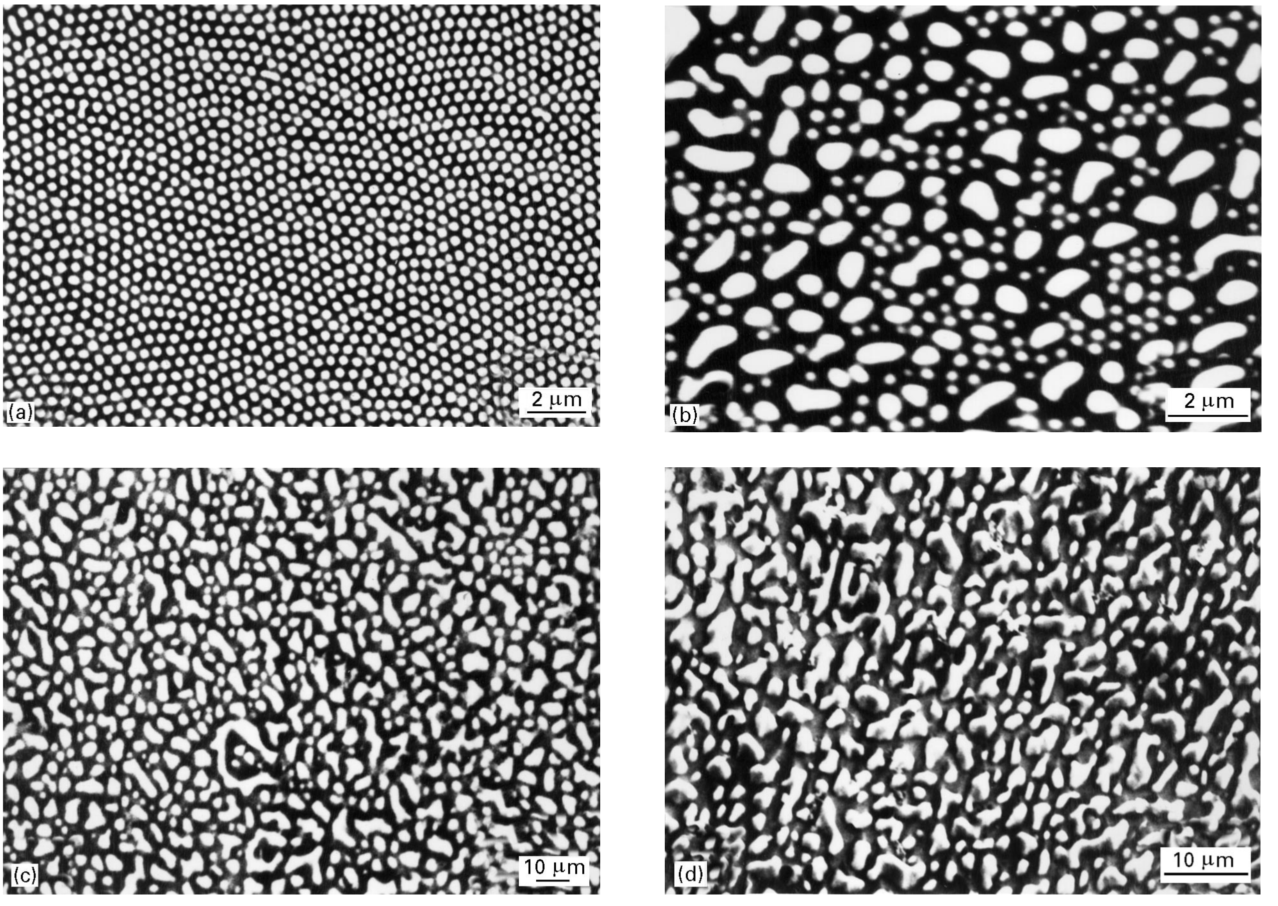

Figure 1 SEM micrographs showing the effect of time of isothermal treatment at 300 °C on progress of coarsening of Zn–Mg_2Zn_{11} in transverse section Zn–3.12 wt % Mg Bridgman grown at 0.5 mm s^{-1} samples. (a) As solidified; (b) 10 min; (c) 1 h; (d) 5 h.

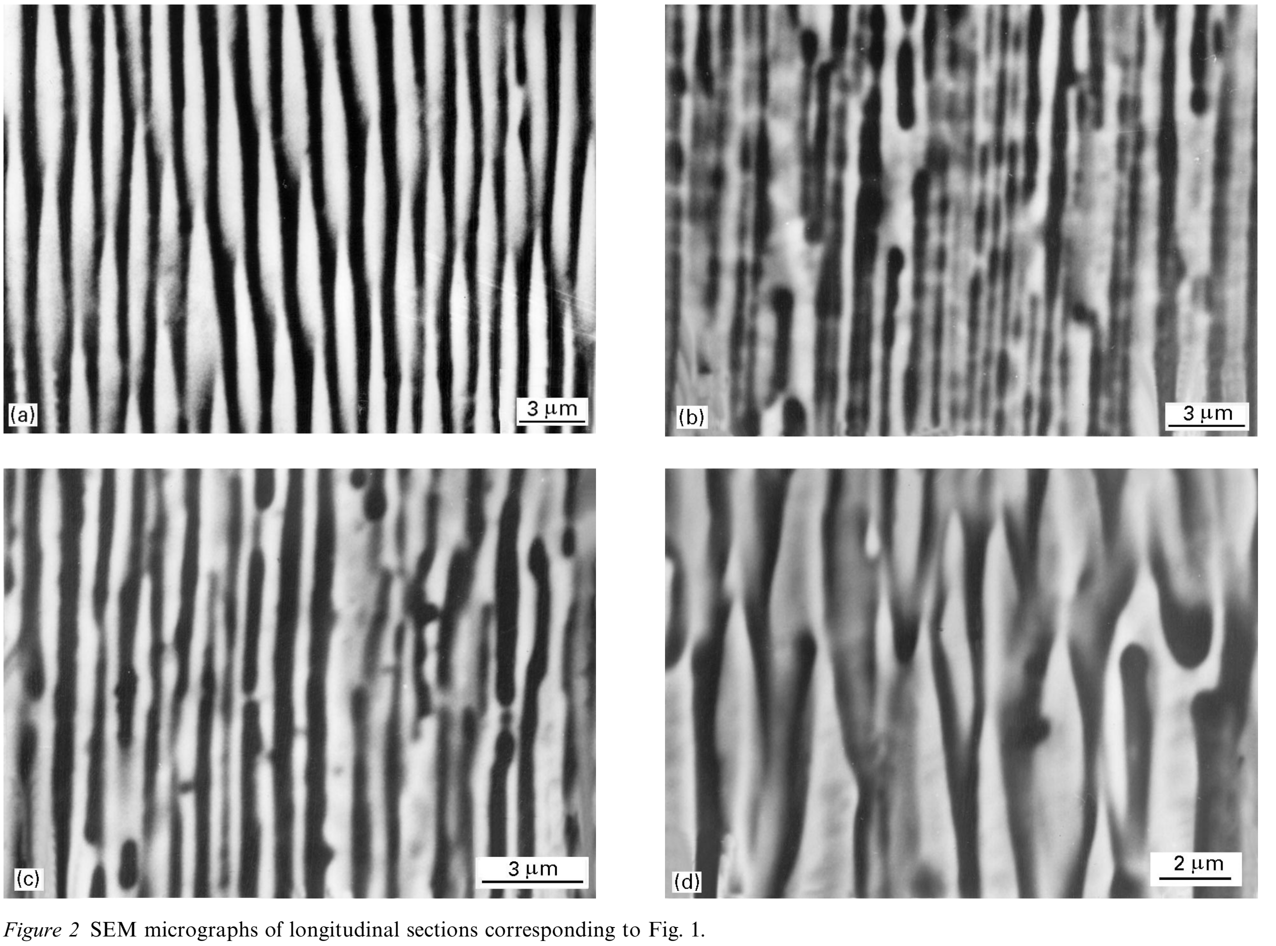

Figure 2 SEM micrographs of longitudinal sections corresponding to Fig. 1.

TABLE I Remaining number of αZn per unit area N, mean interphase spacing λ ($= N^{-1/2}$) and microhardness H_V as a function of holding time t at 300 °C for Zn–3.1 wt % Mg Bridgman grown at 0.5 and 1 mm s^{-1}

Holding time (h)	$V = 0.5$ mm s^{-1}			$V = 1$ mm s^{-1}		
	H_V (kg mm^{-2})	N (μm^{-2})	λ (μm)	H_V (kg mm^{-2})	N (μm^{-2})	λ (μm)
0	222 ± 3	4.3 ± 0.6	0.49	253 ± 3	10.8 ± 1.8	0.30
0.17	207 ± 5	1.8 ± 0.5	0.75	208 ± 4	2.3 ± 0.2	0.66
0.5	199 ± 3	0.58 ± 0.02	1.31	200 ± 4	0.40 ± 0.06	1.58
1	195 ± 6	0.40 ± 0.03	1.58	198 ± 3	0.31 ± 0.02	1.80
2	183 ± 5	0.23 ± 0.04	2.09	189 ± 5	0.20 ± 0.05	2.24
5	175 ± 5	0.12 ± 0.01	2.89	173 ± 3	0.13 ± 0.01	2.77
10	160 ± 3	0.07 ± 0.01	3.78	165 ± 4	0.07 ± 0.01	3.78

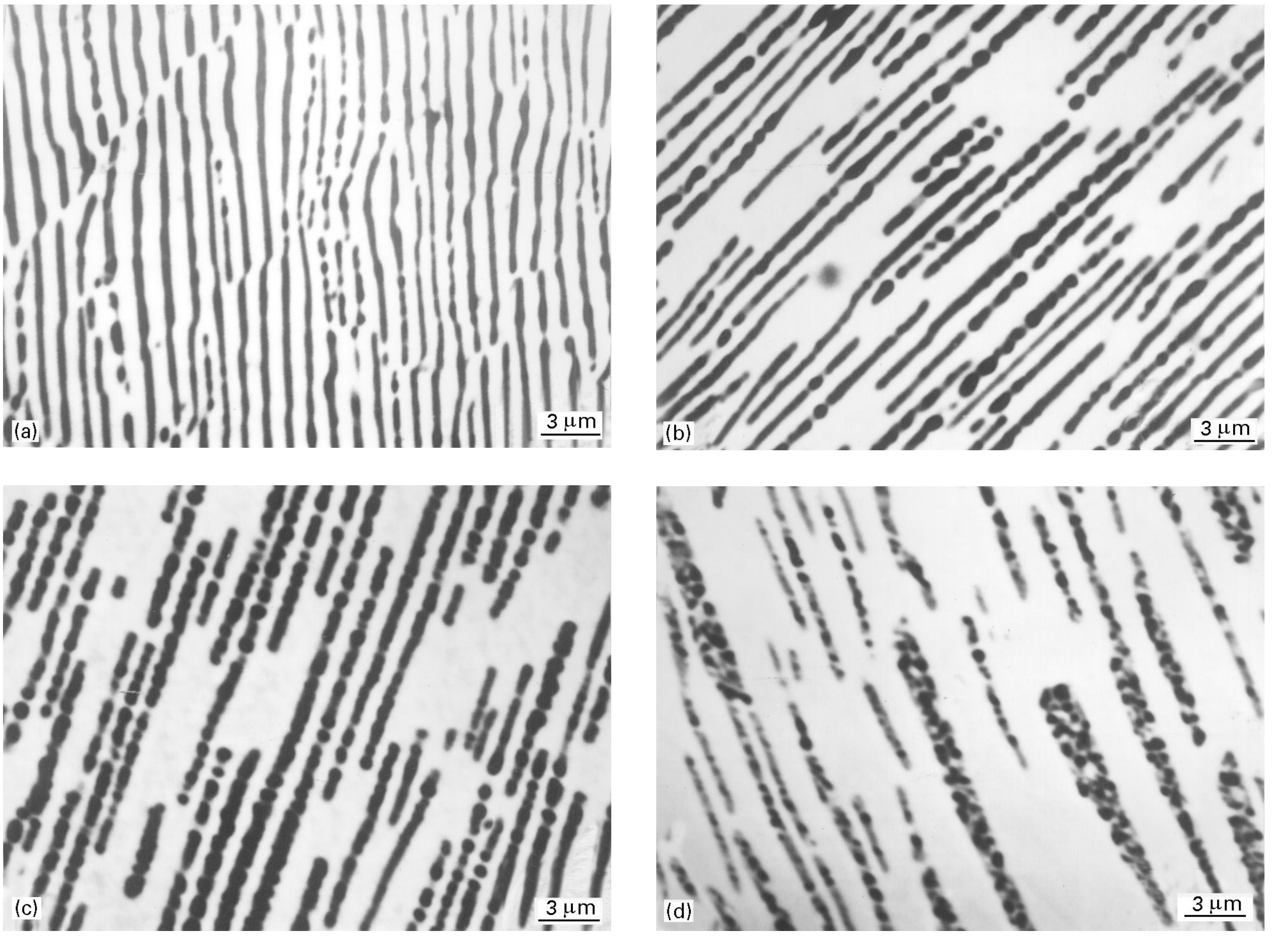

Figure 3 SEM micrographs of transverse sections showing progress of coarsening during isothermal treatment at 350 °C for αZn–βAl eutectic Bridgman grown at 0.1 mm s^{-1}. (a) As-solidified; (b) 2 h; (c) 5 h; (d) 10 h; at 350 °C.

The corresponding samples of Zn–5.1 wt % Al Bridgman grown at 0.1 and 1 mm s^{-1} had fully lamellar αZn–βAl eutectic microstructures prior to heat treatment at 350 °C. Fig. 3 shows SEM micrographs of transverse sections showing the sequence of thermal coarsening of the lamellar αZn–βAl eutectic grown at 0.1 mm s^{-1}. The initial structure was characterized by periodic terminations of the βAl phase associated with faulting of the lamellar eutectic structure (Fig. 3a). This βAl subsequently spheroidized and dissolved in some areas resulting in a βAl interphase spacing several times the thickness of the original lamellae in some areas and leaving other lamellar regions unchanged (Fig. 3b and c), giving an overall coarsening (Fig. 3d). The mean interphase spacing λ and microhardness H_V are given as a function of isothermal time in Table II. The mean interphase spacing λ increased while microhardness H_V decreased with increasing isothermal time.

4. Discussion

4.1. Thermal stability of eutectics

Cline [3] distinguished between (i) pinching-off and spheroidization, (ii) two dimensional coarsening and (iii) fault migration, as mechanisms involved in

TABLE II Mean interphase spacing λ and microhardness H_V as a function of holding time t at 350 °C for αZn–βAl eutectic in Zn–5 wt % Al Bridgman grown at 0.1 and 1 mm s^{-1}

Holding time (h)	$V = 0.1$ mm s^{-1}		$V = 1$ mm s^{-1}	
	λ (μm)	H_V (kg mm^{-2})	λ (μm)	H_V (kg mm^{-2})
0	0.76	81.5 ± 4.1	0.24	86.5 ± 3.9
0.5	0.9 ± 0.2	80.0 ± 3.6	0.4 ± 0.1	83.2 ± 4.0
1	1.0 ± 0.2	77.1 ± 3.7	0.8 ± 0.2	80.7 ± 6.3
2	1.2 ± 0.3	75.9 ± 2.1	1.0 ± 0.2	79.2 ± 4.9
5	1.7 ± 0.2	71.5 ± 2.9	1.5 ± 0.2	66.6 ± 2.9
10	2.8 ± 0.3	68.6 ± 2.0	2.4 ± 0.4	65.2 ± 1.8

thermal coarsening of fibrous eutectics. Many eutectics, such as Al–Si [4], Cu–Cu_2S and Cu–Cu_2O [5], FeS–Fe [6], NiAl–Cr [7] and Al–Al_6 Fe [8], showed coarsening by pinching off and spheroidization rather than by the two-dimensional coarsening process. The coarsening in Al–Al_3Ni eutectic occurred in three stages, two-dimensional coarsening, stabilization then followed by fault migration established by repeated studies [9–11]. The present results (Figs 1 and 2) for αZn–Mg_2Zn_{11} eutectic grown at 0.5 and 1 mm s^{-1} heat treated at 300 °C for 10 min to 10 h suggest that two-dimensional coarsening assumes more importance. The system Zn–Mg_2Zn_{11} has about 0.5 volume fraction of αZn rods in a matrix of Mg_2Zn_{11}. This is consistent with Cline's expectation [3] that if the rod volume fraction exceeds 0.2, a two-dimensional coarsening mode occurs more rapidly than spheroidization of the rods. However, Cline's prediction is not supported by the observation of coarsening by pinching off and spheroidization in NiAl–Cr [7] having a rod volume fraction 0.34.

For two-dimensional coarsening [5, 12], analysis shows that

$$(N_0/N)^{3/2} = 1 + Kt \tag{1}$$

where N_0 is the initial number of rods per unit area, N is the same quantity after time t, and K is constant. Fig. 4 shows $(N_0/N)^{3/2}$ plotted against t for Zn–3.12 wt % Mg grown at 0.5 and 1 mm s^{-1}. Results conform to Equation 1 with slope K as 43 ± 5 h^{-1} for αZn–Mg_2Zn_{11} grown at 0.5 mm s^{-1} and K as 183 ± 10 h^{-1} for αZn–Mg_2Zn_{11} grown at 1 mm s^{-1}.

Studies of the coarsening mechanism for lamellar eutectics, such as Al–Al_2Cu [13] (containing 0.45 volume fraction Al_2Cu) and Sn–Cd [14] (containing volume fraction 0.3 of Sn-rich phase) established that faults dominated the coarsening mechanism rather than perturbation or two-dimensional coarsening. Graham and Kraft [13] predicted that for lamellar eutectic coarsening

$$S_V^{-1} - S_0^{-1} = Kt \tag{2}$$

where S_V (= 2/λ, where λ is mean interphase spacing) is interphase area per unit volume at isothermal time t and S_0 is initial interphase area per unit volume. Fig. 5 plots $(S_V^{-1} - S_0^{-1})$ as a function of isothermal time t at 350 °C for αZn–βAl eutectic (containing 0.26 volume fraction βAl) grown at 0.1 and 1 mm s^{-1}. The results are consistent with Equation 2, with slope K increasing slightly from 0.10 (mm h)$^{-1}$ for growth at 0.1 mm s^{-1} to 0.13 (mm h)$^{-1}$ for growth at 1 mm s^{-1}. This relationship embodied in Equation 2 was also observed for lamellar αAl–Al_2Cu eutectic [13] at various temperatures of isothermal treatment.

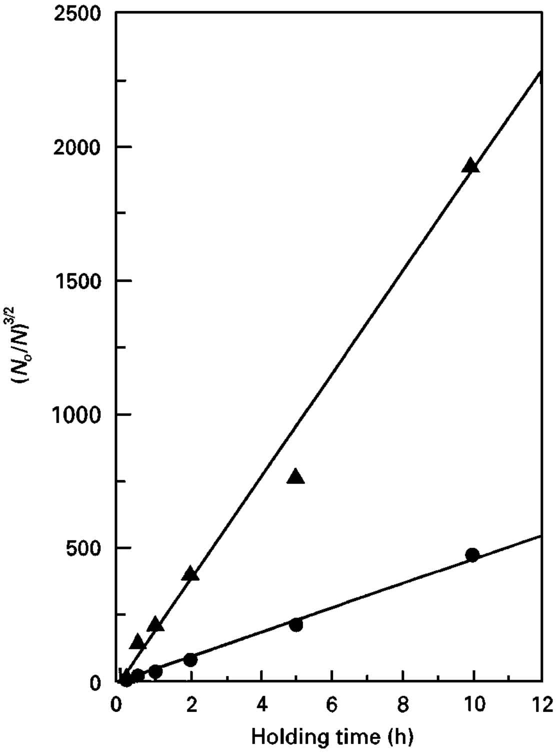

Figure 4 $N_0/N^{3/2}$ as a function of isothermal treatment time t at 300 °C for rod-like αZn–Mg_2Zn_{11} eutectic grown at (●) 0.5 mm s^{-1} and (▲) at 1 mm s^{-1}.

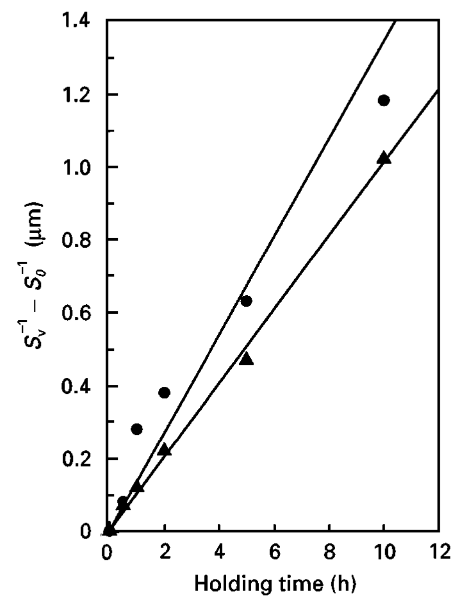

Figure 5 Plot of $1/S_V - 1/S_0$ versus time t at 350 °C for lamellar αZn–βAl eutectic grown at (●) 1 mm s^{-1} and (▲) at 0.1 mm s^{-1}.

4.2. Hardness measurements

For rod-like αZn–Mg_2Zn_{11}, the decreases of hardness from 220 to 160 kg mm^{-2} for samples grown at 0.5 mm s^{-1} and from 250 to 165 kg mm^{-2} for samples grown at 1 mm s^{-1} correspond to decreases in number of αZn elements per unit area from 4.2 or 10.8 to 0.07 μm^{-2} with increasing holding time at 300 °C. For lamellar αZn–βAl eutectic, the decreases of hardness from 82 to 69 kg mm^{-2} for samples grown at 0.1 mm s^{-1} and from 87 to 65 kg mm^{-2} for samples grown at 1 mm s^{-1} correspond to increases in mean interphase spacing from 0.76 to 2.8 μm and from 0.24 to 2.4 μm, respectively, with increasing holding time at 350 °C. Similar results have been reported for Al–Si [6] and Al–Al_6Fe [11] eutectics and have been characterized by Hall–Petch or Orowan relationships. Figs 6 and 7 show hardness H_V plotted against $\lambda^{-1/2}$ conforming to a Hall–Petch relationship: $H_V = H_0 + k_Y\lambda^{-1/2}$ with $H_0 = 141 \pm 5$ kg mm^{-2} and $k_Y = 1.9 \pm 0.2$ kg mm$^{-3/2}$ for αZn–Mg_2Zn_{11} and $H_0 = 61 \pm 3$ kg mm^{-2} and $k_Y = 0.46 \pm 0.09$ kg mm$^{-3/2}$ for αZn–βAl, respectively. These values of H_0 and k_Y accord well with the values of $H_0 = 135 \pm 7$ kg mm^{-2} and $k_Y = 2.2 \pm 0.2$ kg mm$^{-3/2}$ and 59 ± 1 kg mm^{-2} and 0.34 ± 0.02 kg mm$^{-3/2}$ for H_V of as-solidified αZn–Mg_2Zn_{11} and αZn–βAl, respectively, reflecting the fact that the hardening continues to be characterized mainly by a Hall–Petch relationship with mean interphase spacing during thermal coarsening process.

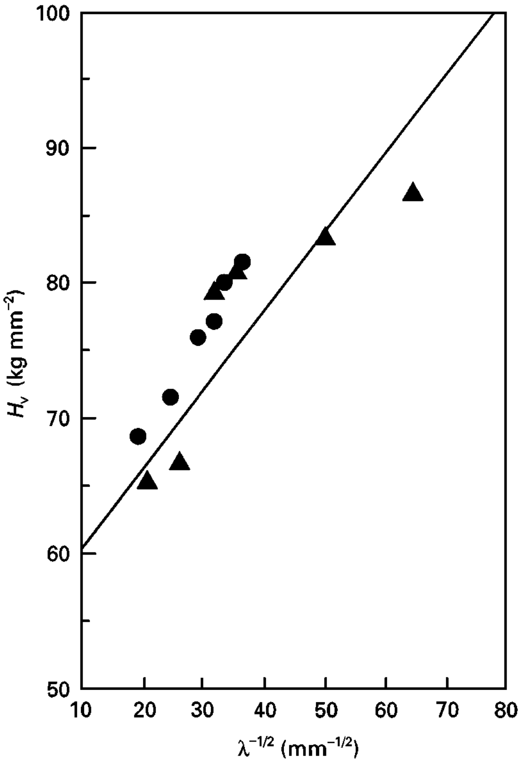

Figure 7 Microhardness H_V as a function of mean interphase λ to the power minus one-half for lamellar αZn–βAl eutectic grown at (●) 0.1 mm s^{-1} and (▲) at 1 mm s^{-1} isothermally treated at 350 °C for up to 10 h.

5. Conclusions

1. Two-dimensional coarsening dominated the response of rod-like αZn–Mg_2Zn_{11} eutectic (Zn–3.1 wt % Mg Bridgman grown at 0.5 and 1 mm s^{-1}) to isothermal treatment for up to 10 h at 300 °C.

2. Correspondingly, fault migration governed the response of lamellar αZn–βAl eutectic (Zn–5.0 wt % Al Bridgman grown at 0.1 and 1 mm s^{-1}) to isothermal treatment at 350 °C for up to 10 h.

3. Hardness of rod-like αZn–Mg_2Zn_{11} and of lamellar αZn–βAl so treated at 300 °C and 350 °C exhibited a Hall–Petch relationship with the mean interphase spacing. The applicable values of H_0 and k_Y accord well with the values obtained from the Hall–Petch relationship for H_V of as-solidified αZn–Mg_2Zn_{11} and αZn–βAl eutectics where the relationship is with eutectic interphase spacing.

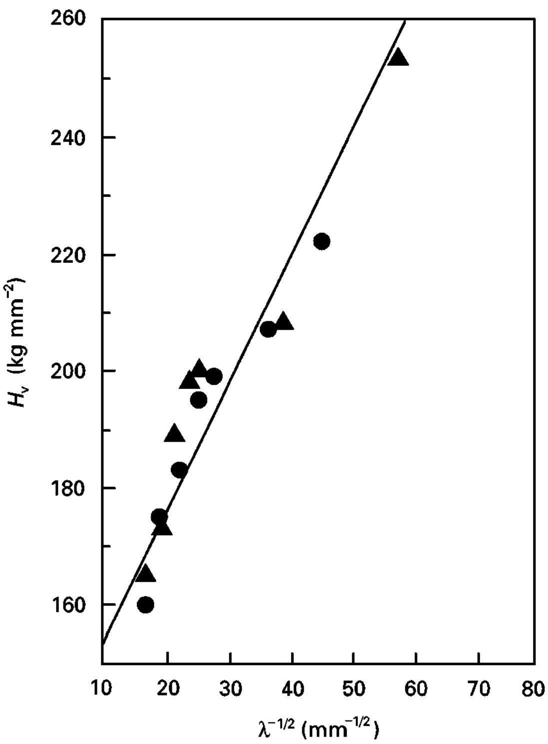

Figure 6 Microhardness H_V as a function of mean interphase λ to the power minus one-half for rod-like αZn–Mg_2Zn_{11} eutectic grown at (●) 1 mm s^{-1} and (▲) at 0.1 mm s^{-1} isothermally treated at 300 °C for up to 10 h.

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