

Coarsening of precipitates and dispersoids in aluminium alloy matrices: a consolidation of the available experimental data

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Experimental data on the coarsening of precipitates and dispersoids in aluminium-based matrices are reviewed. Available data are tabulated as $K = (r^3 - r_0^3)/t$ where r_0 is the initial particle radius and r is its value after time t at temperature T , and then plotted as $\log(KT)$ against $1/T$ for consolidation and assessment. The considerable body of data for δ' -Al₃Li in Li-containing alloys is well represented by $K = (K_0/T) \exp(-Q/RT)$ with $K_0 = (1.3_{-0.5}^{+3.0}) \times 10^{-13} \text{ m}^3 \text{ K s}^{-1}$ and $Q = 115 \pm 4 \text{ kJ mol}^{-1}$. The relatively limited data for θ' and θ'' in Cu-containing alloys are representable by the same relationship with $K_0 \simeq 4 \times 10^{-8}$ and $\simeq 4 \times 10^{-10} \text{ m}^3 \text{ K s}^{-1}$, respectively, and $Q \simeq 140 \text{ kJ mol}^{-1}$. Available data for coarsening of L1₂-Al₃(Zr, V) and related phases in Zr-containing alloys and of Al₁₂Fe₃Si and related phases in Al-Fe based alloys indicate (i) rates of coarsening at 375 to 475 °C (0.7 to 0.8 T_m) five to eight orders of magnitude less than would be expected for δ' , θ' and θ'' in this temperature range, and (ii) high activation energies of ~ 300 and 180 kJ mol^{-1} , respectively.

1. Introduction

The stability of mechanical properties at elevated temperature of both wrought and cast high-strength aluminium alloys depends ultimately on the resistance to dissolution and coarsening offered by the operative strengthening precipitates or dispersoids. Much attention has been given to the theory of coarsening of distributions of second-phase particles in matrices using the classical treatments of Lifshitz and Slyozov [1] and Wagner [2] as a starting point, and there have been numerous experimental studies for aluminium-based matrices. Many of these experimental data relate to coarsening of L1₂- δ' in Al-Li based matrices, first reported by Tamura *et al.* [3] in 1970 and by Noble and Thompson [4] in 1971, and reviewed by Ardell [5] in 1987 and by Sanders and Gokhale [6] in 1988. There is a smaller body of data for coarsening of θ' and related phases in Al-(Cu, Mg) based systems pioneered by Boyd and Nicholson [7] in 1971, which has not been critically assessed, and on the more coarsening-resistant L1₂ and related phases in Al-(Zr, V) and Al-Fe based matrices pioneered by Zedalis and Fine [8] and Skinner *et al.* [9], and reviewed by Angers *et al.* [10] in 1986. The present purpose, as the initial step in a new experimental programme, is to provide a consolidation of all these available data for Al-based systems, including, in particular, data on the important Al-(Cu, Mg) based systems and additional data on δ' in Li-containing alloys, not treated on a comparative basis recently.

2. Basis for analysis of data

Predictive treatments of isothermal coarsening kinetics of spherical particles in a matrix yield relation-

ship of the form

$$r^n - r_0^n = Kt \quad (1)$$

where r_0 is initial average particle radius, r is average radius at time t of treatment and K is a material constant proportional to the applicable solubility and diffusivity of solute and to the particle-matrix interfacial energy. The exponent n is 3 for coarsening governed by solute diffusion through the matrix [1, 2] increasing to 4 when controlled by solute diffusion along grain boundaries [11], and to 5 when diffusion along dislocation pipes is controlling [12].

The standard formulation of Equation 1 for coarsening via solute diffusion through the matrix assumes spherical particles of radius r . In other cases an equivalent radius should be used, such as the radius of a sphere of the same volume. For disc-shaped particles, such as θ' or θ'' in Al-Cu, thus r in Equation 1 must be replaced by $\rho(3/2a)^{1/3}$ where ρ is the radius of the flat face of the disc and a is the ratio of disc diameter to disc thickness (approximately 25 for θ'' in Al-Cu, giving $r = 0.40\rho$). For rod-shaped particles such as for θ -Al₂Cu in Al-Cu or θ -Al₁₃Fe₄ in Al-Fe, the same correction is applicable but with ρ as the rod radius and a as the ratio of rod diameter to its length (< 1 in this case giving $r > \rho$).

The material constant K in Equation 1 is expected to exhibit a dependence on temperature T of the form

$$K = \frac{K_0}{T} \exp\left(-\frac{Q}{RT}\right) \quad (2)$$

where Q is the operative activation enthalpy for coar-

sening and R is the gas constant, neglecting the relatively small effects of temperature on volume per atom or on interfacial energy over the temperature range involved. Determination of K as the slope of plots of r^n against t thus allows the relative rates of coarsening of different dispersoids or precipitates in a matrix to be compared, for example by plotting [5, 6, 13] $\log(KT)$ against $1/T$, which has slope $-(Q/R) \log_{10}e$ and intercept $\log_{10}K_0$.

3. Comparison of coarsening rates in aluminium alloys

Available data on $K(T)$ for δ' -Al₃Li in Al–Li based alloys [3, 4, 13–37] are presented in Table I, that for θ -Al₂Cu and related phases [7, 20, 26, 28, 38–43] in Table II and for other phases [8, 9, 44–55] including Li₂–Al₃Zr and Al₁₂Fe₃Si and related phases in Table III. Corresponding plots of these data as $\log(KT)$ against $1/T$ are shown in Figs 1 to 3, respectively.

TABLE I Coarsening kinetic data for δ' -Al₃Li in Al–Li based alloys.

Alloy composition (wt %)	Temperature T of treatment ($^{\circ}\text{C}$) and resulting kinetic constant K ($\text{nm}^3 \text{s}^{-1}$)	Reference ^a
Al–2.5Li	200, 0.572	Tamura <i>et al.</i> [3]
Al–4Li	200, 0.125; 220, 0.683; 240, 1.72	Noble and Thompson [4]
Al–2.5Li–4.7Mg	120, 0.00307; 185, 0.0345	Cocco <i>et al.</i> [14]
Al–2.8Li	200, 0.30; 230, 0.9; 250, 3.8	Berezina <i>et al.</i> [15]
Al–2.8Li–0.3Mn	168, 0.00227; 220, 0.0215; 225, 0.0923	Kulwicki and Sanders [16]
Al, 2.2, 3.0, 3.7Li	200, 0.0208, 0.140, 0.264	Baumann and Williams [17]
Al–3.0Li	220, 0.182; 240, 0.456; 260, 1.81	Jensrud and Ryum [18]
Al–3.1Li–0.2Zr	160, 0.00169; 170, 0.00263; 180, 0.0116; 200, 0.0663; 240, 0.322	Makin and Ralph [19]
Al–2.5Li–1.2Cu–0.7Mg–0.1Zr (8090)	190, 0.205	Ahmad and Eriksson [20]
Al–2.8Li–0.14Zr	200, 0.0204 (Al ₃ Zr free), 0.0464 (contain Al ₃ Zr), 0.0239 (all)	Gu <i>et al.</i> [21]
Al–2.9Li–0.3Mn	168, 0.002 52; 200, 0.0220; 225, 0.0851	Gu <i>et al.</i> [22]
Al–2.5Li	150, 0.000 827	Livet and Bloch [23] ^b
Al–3.1Li	150, 0.001 03; 180, 0.0093	
Al–2.5Li	190, 0.0469; 210, 0.115; 230, 0.275; 250, 0.694	Broussard and Thomas [24]
Al–2.4Li	200, 0.0228; 225, 0.134	Gu <i>et al.</i> [25], Mahalingam <i>et al.</i> [27]
Al–3.0Li	200, 0.0381; 225, 0.150	
Al–3.1Li	200, 0.0475; 225, 0.163	
Al–4.0Li	200, 0.0547; 225, 0.308	
Al–4.5Li	200, 0.0786; 225, 0.567	
Al–2.3Li–2.9Cu–0.12Zr (2090)	160, 0.004 17; 190, 0.041	Huang and Ardell [26]
Al–2.9Li–1.0Cu–0.12Zr	160, 0.004 78; 190, 0.035	
Al–1.9Li–2.0Cu–1.3Mg–0.1Zr (2091)	150, 0.000 022 9; 190, 0.000 75	De Jesus and Ardell [28]
Al–2.3Li–2.9Cu–0.1Zr (2090)	150, 0.0005	
Al–2.45Li	160, 0.0023; 200, 0.0279; 220, 0.0600; 250, 0.34	Jung and Park [29]
Al–3.4Li	160, 0.037; 200, 0.0534; 228, 0.21	
Al–2.2Li–1.2Cu–0.6Mg–0.1Zr (8090)	120, 0.000 19; 130, 0.000 30; 140, 0.000 67; 150, 0.0014	Triolo <i>et al.</i> [30] ^b
Al–2.3Li–0.3Zr	160, 0.003 17; 190, 0.0226; 230, 0.269	Woo and Cho [31]
Al–1.9Li	130, 0.000 40; 140, 0.000 94; 160, 0.003 13	Shaiu <i>et al.</i> [32] ^b
Al–3.4Li	130, 0.000 306; 150, 0.002 56; 170, 0.001 54; 200, 0.174; 230, 0.532; 250, 1.61; 270, 6.6	
Al–1.9Li–2.7Cu	110, 0.000 084; 130, 0.000 362; 150, 0.002 02; 160, 0.004 72; 170, 0.010 82	Caponetti <i>et al.</i> [13] ^b
Al–2.6 and 3.2Li	150, 0.006 78, 0.006 33	Fujikawa and Furushawa [33] ^c
Al–2.6Li	100, 0.000 003 93; 128, 0.000 131; 165, 0.001 61; 178, 0.004 37; 209, 0.0415	Hoyt and Spooner [34] ^b
Al–2.2Li	120, 0.000 174; 130, 0.000 425; 140, 0.000 969; 150, 0.002 23	Lee <i>et al.</i> [35] ^b
Al–2.5Li	130, 0.000 625, 150, 0.003 47; 170, 0.0206	
Al–3.2Li	160, 0.003 12; 180, 0.0108; 200, 0.0469	Mahalingam <i>et al.</i> [36]
Al–2.3Li–1.2Cu	130, 0.0012; 150, 0.0055, 160, 0.009 99; 165, 0.009 89; 170, 0.0126; 175, 0.0201; 180, 0.0238	Floriano <i>et al.</i> [37] ^b

^a Measurements by TEM unless indicated: ^b SAXS, ^c SANS.

TABLE II Coarsening kinetic data for θ -Al₂Cu and related phases in Al-Cu based alloys (all measurements by TEM)

Alloy composition (wt %)	Phase	Temperature T of treatment ($^{\circ}$ C) and resulting kinetic constant K ($\text{nm}^3 \text{s}^{-1}$)	Reference
Al-5.1Cu	θ -Al ₂ Cu	450, 8650 ^a	Hawkes and Martin [38]
Al-4.0Cu	θ' discs	200, 17.4; 240, 690	Boyd and Nicholson [7]
	θ'' discs	110, 0.000175; 165, 0.0225; 175, 0.119	
Al-4.0Cu-0.1Cd	θ' discs	200, 3.5	
Al-2.0Cu-1.1Mg	S' laths	200, 0.0288; 230, 0.258	Cho [39]
Al-4.0Cu	θ' plates	475, 1.12; 200, 16.5; 225, 82.7; 250, 267; 275, 965	Merle <i>et al.</i> [40]
Al-6.0Cu	θ rods	450, 280	Janoff and Fine [41]
Al-1.2Cu-2.5Li-0.7Mg-0.1Zr (8090)	S'	190, 0.000 14	Ahmad and Eriksson [20]
Al-2.9Cu-2.3Li-0.1Zr (2090)	T ₁ plates	160, 1.54; 190, 32	Huang and Ardell [26]
Al-1.0Cu-2.9Li-0.1Zr	T ₁ plates	160, 85.4; 190, 6.74	
Al-4.8Cu-0.5Ag-0.2Mg-1.2Zn	Ω plates	140, 0.008 34; 155, 0.0348; 170, 0.123	Scott <i>et al.</i> [42]
Al-2.9Cu-2.3Li-0.1Zr (2090)	θ''	100, 0.000 060 7	De Jesus and Ardell [28]
Al-4.1Cu-2.0Mg-0.5Mn (2124)	S' plates	177, 8.0	Christman and Suresh [43]
Ditto + 15 wt % SiC _w	S' plates	177, 34	

TABLE III Coarsening kinetic data for other phases in Al alloys

Alloy composition (wt %)	Phase	Temperature T of treatment ($^{\circ}$ C) and resulting kinetic constant K ($\text{nm}^3 \text{s}^{-1}$)	Reference
Al-3.5Ge	Ge	250, 0.0113; 300, 0.552	Tashiro <i>et al.</i> [46]
Al-13Si	Si spheres	400, 500; 490, 14 000; 530, 25 700	Adam and Jenkinson [44]
Al-14Ag	Ag ₂ Al plates	400, 1 210 000	Ferrante and Doherty [45]
Al-2.9Ni	Al ₃ Ni rods	600, 28.4; 625, 29.4	Pontikakos and Jones [47]
Al-2.6Fe	Al ₁₃ Fe ₄ rods	600, 3.31; 625, 3.60	
Al-11Mg	Al ₃ Mg ₂ (non-spherical)	250, 238, 316, 1270; 330, 1970	Kwan and Fine [48]
Al-8.7Fe-0.9V-1.5Si	Al ₁₂ Fe ₃ Si spheres	425, 0.0023	Skinner <i>et al.</i> [9] ^a
Al-6.9Fe-2.9V-1.5Si	Al ₁₂ Fe ₃ Si spheres	425, 0.0081	
Al-0.8Zr	Li ₂ -Al ₃ Zr	375, 0.000 339; 400, 0.002 09; 425, 0.006 92	Zedalis and Fine [8] ^a
Al-0.35V-0.1Zr	Li ₂ -Al ₃ (Zr, V)	425, 0.004 53/0.006 28	
	DO ₂₃ -Al ₃ (Zr, V)	425, 0.114 (Al ₃ Zr), 0.035 (Al ₃ (Zr ₁ V))	
Al-1.2Zr-1.8V	Li ₂ -Al ₃ (Zr, V)	425, 0.000 028 6	Chen <i>et al.</i> [49]
Al-4.5Cu-2Mn	Al ₆ Mn	500, 0.002 34 (0.0267); 570, 0.002 13; 620, 0.002 61	Skolianos <i>et al.</i> [50]
Al-8Fe-1.5V-1.5Si	Al ₁₂ Fe ₃ Si	425, 0.0081	Zedalis <i>et al.</i> [51] ^a
Al-10Fe-2.5V-2.0Si	Al ₁₂ Fe ₃ Si	425, 0.0080	
Al-12Fe-1.2V-2.3Si	Al ₁₂ Fe ₃ Si	425, 0.0022	
Al-8Fe	Al ₁₃ Fe ₄	425, 6.1	Gilman <i>et al.</i> [52] ^a
Al-10Fe-1.5Mo-1V	Al ₃ (Fe, Mo, V)	425, 4.7	
Al-8.9Ce-6.9Fe	Al ₈ Fe ₄ Ce	425, 11	
Al-8Fe-1.5V-1.5Si	Al ₁₂ Fe ₃ Si	425, 0.0081; 450, 0.013; 475, 0.020	Skinner [53] ^a
Al-8.9Fe-0.9V-1.5Si	Al ₁₂ Fe ₃ Si	425, 0.0023; 450, 0.0064; 475, 0.016	
Al-1.8V-1.1Zr	Li ₂ -Al ₃ (Zr, V)	425, 0.000 028 6; 450, 0.000 170; 500, 0.003 56	Chen <i>et al.</i> [54]
Al-22Si	Si	400/450, 176 000; 500/535, 1 020 000	Shih <i>et al.</i> [55]

^a Data reported had been corrected to zero volume fraction of coarsening phase: measured values would have been 2.5 to 3 times larger for Al-Fe-V-Si.

Although the data for δ' plotted in Fig. 1 cover a range of Li contents between 1.9 and 4.5 wt %, with or without other additions of up to 4.5 wt % Mg, 2.9 wt % Cu, 0.3 wt % Mn or 0.12 wt % Zr (including the commercial 2090, 2091, 8090 and 8091 compositions), they exhibit relatively little scatter, which is typically within an order of magnitude in KT at a given value of $1/T$. A particularly encouraging feature

is that there does not seem to be any significant difference between measurements made by TEM (open points) and those made by SAXS (closed points) which is being used very effectively to extend results to lower temperatures [13, 14, 23, 30, 32, 34-37]. The results are thus well represented by Equation 2 with $K_0 = (1.3^{+3.9}_{-0.9}) \times 10^{-13} \text{ m}^3 \text{ K s}^{-1}$ and $Q = 115 \pm 4 \text{ kJ mol}^{-1}$. This is consistent with previous estimates

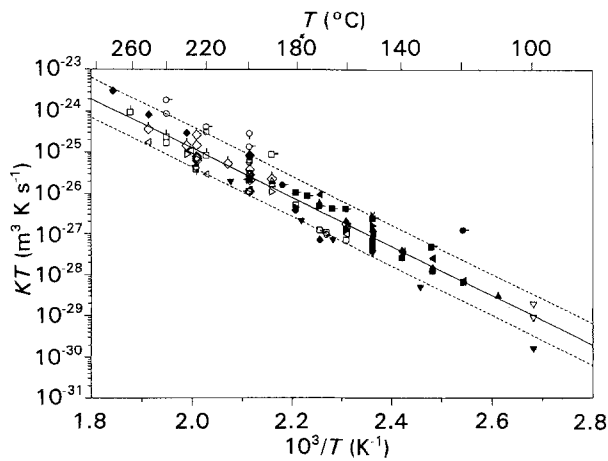


Figure 1 Coarsening parameter KT plotted logarithmically against $1/T$ for δ' - Al_3Li in Al-Li based alloys (data from Table I). Symbols and references: (\circ) [3], (\odot) [4], (\ominus) [14], (\bullet) [15], (\ominus) [16], (\odot) [17], (\square) [18], (\square) [19], (\square) [20], (\square) [21], (\square) [22], (\bullet) [23], (\diamond) [24], (\diamond) [25, 27], (\triangle) [26], (∇) [28], (\triangleleft) [29], (\blacksquare) [30], (\triangleright) [31], (\blacklozenge) [32], (\blacktriangle) [13], (\times) [33], (\blacktriangledown) [34], (\blacktriangleleft) [35], (\blacktriangleright) [36], (\blacksquare) [37]. (—) Least-squares line, (---) factor of 3 scatter band.

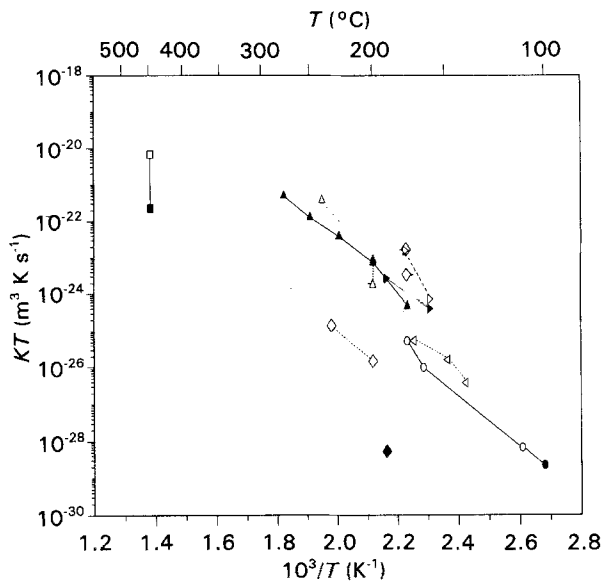


Figure 2 As Fig. 1 but for Cu-containing phases in aluminium alloys (data from Table II). Phases, symbols, alloys and references as follows: Θ (\square) AO [38], Θ' (\triangle) A [7], Θ' (∇) B [7], Θ'' (\circ) A [7], S' (\diamond) C [39], Θ' (\blacktriangle) A [40], Θ (\blacksquare) D [41], S' (\blacklozenge) E [20], T_1 (\triangleright) F [26], T_1 (\blacktriangleright) G [26], Ω (\triangleleft) H [42], Θ'' (\bullet) F [28], S' (\diamond) I [43], S' (\diamond) J [43]. Alloy compositions (wt %): AO = Al-5.1Cu; A = Al-4.0Cu; B = Al-4.0Cu-0.1Cd; C = Al-2.0Cu-1.1Mg; D = Al-6.0Cu; E = Al-1.2Cu-2.5Li-0.7Mg-0.1Zr; F = Al-2.9Cu-2.3Li-0.1Zr; G = Al-1.0Cu-2.9Li-0.1Zr; H = Al-4.8Cu-0.5Ag-0.2Mg-1.2Zn; I = Al-4.1Cu-2.0Mg-0.5Mn; J = I + 15 wt % SiC_w.

ranging from 90 to 140 kJ mol⁻¹ [4, 13, 15, 19, 27, 28, 30, 32, 35-37, 61] from individual, more limited, sets of data, and with an activation energy for diffusion of Li in Al of 119 [56] or 126 [57] kJ mol⁻¹. There is some evidence for an effect of Li alloying content on K . This effect is large, according to Baumann and Williams [17], K at 200 °C increasing from 2.1×10^{-29} to 6.2×10^{-28} m³ s⁻¹ (i.e. 30-fold) with an increase in Li content from 2.2 to 3.7 wt % Li. Gu *et al.* [25, 27] found a smaller effect with K at 200 °C increasing

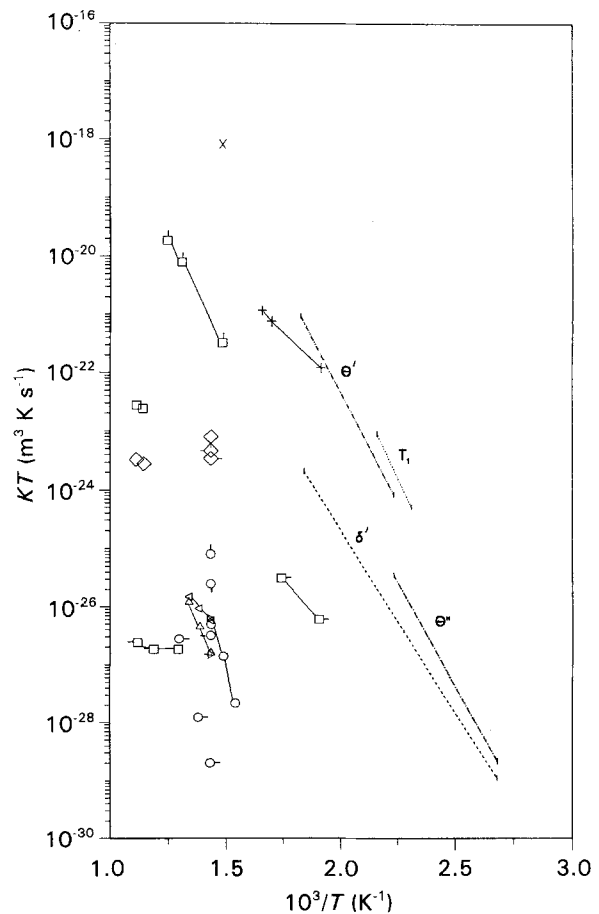


Figure 3 As Figs. 1 and 2 but for other phases in aluminium alloys (data from Table III). Phases, symbols, alloys and references as follows: Ag_2Al (\times) KO [45], Ge (\square) K [46], Si (\square) L [44], Al_3Ni (\square) M [47], Al_3Fe_4 (\diamond) N [47], Al_3Mg_2 (+) O [48], $\text{Al}_2\text{Fe}_3\text{Si}$ (\triangle) P [9, 53] (∇), P1 [9], $\text{Li}_2\text{-Al}_3\text{Zr}$ (\circ) Q [8], $\text{Li}_2\text{-Al}_3(\text{Zr, V})$ (\ominus) Q1 [8], $\text{DO}_{23}\text{-Al}_3\text{Zr}$ (\odot) Q1 [8], $\text{DO}_{23}\text{-Al}_3(\text{Zr, V})$ (\odot) Q1 [8], $\text{Li}_2\text{-Al}_3(\text{Zr, V})$ (\ominus) Q2 [49, 54], Al_6Mn (\square) R [50], $\text{Al}_{12}\text{Fe}_3\text{Si}$ (\triangleleft) S [51, 53], (\triangleright) S1 [51], (\blacktriangleright) S2 [51], Al_3Fe_4 (\diamond) N1 [51], $\text{Al}_{13}(\text{Fe, Mo, V})_4$ (\diamond) T [51], $\text{Al}_8\text{Fe}_4\text{Ce}$ (\diamond) U [51]. Alloy compositions (wt %): KO = Al-14Ag; K = Al-3.5Ge; L = Al-13Si; M = Al-22Si; N = Al-2.9Ni; O = Al-2.6Fe; P = Al-8.9Fe-0.9V-1.5Si; Q = Al-0.8Zr; Q1 = Al-0.35V-0.1Zr; Q2 = Al-1.2Zr-1.8V; R = Al-4.5Cu-2Mn; S = Al-8Fe-1.5V-1.5Si; S1 = Al-10Fe-2.5V-2Si; S2 = Al-12Fe-1.2V-2.3Si; T = 10Fe-1.5Mo-1V; U = Al-8.9Ce-6.9Fe. Least-squares lines: (---) δ' from Fig. 1; from Fig. 2 (---) Θ'' , (-.-.) Θ' , (---) T_1 .

from 2.3×10^{-29} m³ s⁻¹ at 2.4 wt % Li to 7.9×10^{-29} m³ s⁻¹ at 4.5 wt % Li (i.e. 3-fold) and at 225 °C from 1.3×10^{-28} at 2.4 wt % Li to 5.7×10^{-28} m³ s⁻¹ at 4.5 wt % Li (i.e. 4-fold). Jung and Park [29] found 16- and 2-fold increases in K at 160 and 200 °C with increase in Li content from 2.45 to 3.41 wt %. Shaiu *et al.* [32] obtained a 25% decrease in K at 130 °C by increasing the Li content from 1.9 to 3.4 wt %, while Livet and Bloch [23] observed a 25% increase in K at 150 °C when the Li content was increased from 2.5 to 3.1 wt %. The results of Gu *et al.* [21] at 200 °C indicate that Zr-containing δ' in Al-2.8 wt % Li-0.14 wt % Zr coarsens at double the rate of Zr-free δ' in the same alloy, the overall rate exceeding that for δ' in a Zr-free alloy [25, 27] of similar Li content. The indications are that addition of 0.3 wt % Mn to Al-3 wt % Li [16, 22] reduces the rate

at 200 and 225 °C compared with the Mn-free alloy [25, 27]*. The effects of Cu and Mg additions are less clear from the available data, but appear to be within a factor of two for the levels of addition involved.

The results in Fig. 2 for Cu-containing precipitates are much more limited in scope. The results of Boyd and Nicholson [7] and Merle *et al.* [40] for θ' in Al–4.0 wt % Cu are in good agreement and give results similar to those of Huang and Ardell [26] for T_1 in two Al–Cu–Li–Zr alloys. Notably, these measured values of KT for θ' and T_1 are one to two orders of magnitude larger than for δ' in Li-containing Al alloys. Boyd and Nicholson reported a significant effect of adding 0.1 wt % Cd in decreasing KT for θ'' by a factor of 5 in Al–4 wt % Cu at 200 °C, and a virtual cessation of θ coarsening after 200 h at this temperature†. This latter effect was confirmed by Merle *et al.* [40], who also showed that the time to cessation decreased strongly with increasing temperature up to 275 °C. This phenomenon still awaits a convincing explanation. The results of Boyd and Nicholson [7] and of De Jesus and Ardell [28] for KT of θ'' in Al–4.0 wt % Cu and in Al–Cu–Li–Zr alloy, respectively, are also in good accord and are similar to the results of Scott *et al.* [42] for so-called Ω -phase in an Al–Cu–Ag–Mg–Zn alloy. Reported data for KT of S' -phase, in contrast, are not mutually consistent. The results of Christman and Suresh [43] for S' in Al–4Cu–2Mg–0.5 Mn at 177 °C give KT values similar to T_1 in Al–Cu–Li–Zr, while those of Cho [39] for Al–2Cu–1Mg at 200 and 230 °C give values of KT two orders of magnitude less, similar to the lowest values measured for δ' at these temperatures. The measurement of Ahmad and Eriksson [20] for Al–2.5Li–1.2Cu–0.7 Mg–0.1Zr gives an even lower value of KT , some five orders of magnitude less than reported by Christman and Suresh for Al–4Cu–2Mg–0.5Mn. This low value of KT for S' is, anachronistically, in good correspondence‡ with the single measurement of KT for θ phase reported by Janoff and Fine [41] for Al–6Cu at 450 °C. Such low values of KT are of considerable interest from the viewpoint of designing compositions that are resistant to coarsening, though it is not clear to what extent they are typical of S' in aluminium alloys. The individual sets of results in Fig. 2 are well characterized by an activation energy $Q \approx 140 \text{ kJ mol}^{-1}$, with the results for θ' and T_1 having an associated $K_0 \approx 4 \times 10^{-8} \text{ m}^3 \text{ K s}^{-1}$ and those for θ'' an associated $K_0 \approx 4 \times 10^{-10} \text{ m}^3 \text{ K s}^{-1}$. This value of Q compares with 138 kJ mol^{-1} determined [59] for volume diffusion of Cu in Al.

Fig. 3 corresponds to Figs 1 and 2 for the remaining data listed in Table III plus representations of the data for δ' from Fig. 1 and for θ' , T_1 , θ'' , Ω and S' from Fig. 2. The results for Al_3Mg_2 in Al–11Mg [48] indicate values of KT similar to those of θ' and T_1 , i.e. coarsening one to two orders of magnitude faster than δ' . Results for Si in Al–13Si [44] give values of KT at 400

to 530 °C corresponding to what would be expected for δ' or θ'' if they could be stabilized in this temperature range. Results for Ge in Al–3.5Ge at 250 and 300 °C give KT one to two orders of magnitude less than expected for δ' or θ'' extrapolated into this temperature range. Of most interest in Fig. 3 are the results for $\text{Li}_2\text{–Al}_3\text{Zr}$, $\text{Al}_{12}\text{Fe}_3\text{Si}$ and related phases at temperatures in the range 375 to 475 °C. Even the highest values of KT , for $\text{Al}_{12}\text{Fe}_3\text{Si}$ in Al–8Fe–1.5V–1.5Si and $\text{Li}_2\text{–Al}_3\text{Zr}$ in Al–0.8Zr, are five to six orders of magnitude less than for Si in this temperature range, while the lowest values, for $\text{Li}_2\text{–Al}_3\text{(Zr, V)}$ in Al–1.2Zr–1.8V, are six to eight orders of magnitude smaller. The magnitudes of KT for these phases in these alloys, at 10^{-29} to $10^{-26} \text{ m}^3 \text{ K s}^{-1}$ in this temperature range (0.7 to $0.8T_m$), are in fact identical with those for θ'' in Al–Cu alloys at much less elevated temperatures (0.4 to $0.5T_m$). These results are characterized by particularly high activation energies of $\sim 300 \text{ kJ mol}^{-1}$ for $\text{Al}_3\text{(Zr, V)}$ in Al–1.2Zr–1.8V and $\sim 180 \text{ kJ mol}^{-1}$ for $\text{Al}_{12}\text{Fe}_3\text{Si}$ in Al–8.9Fe–0.7V–1.5Si. These compare with activation energies of 240 and 180 kJ mol^{-1} for volume diffusion of Zr [60] and Fe [59] in aluminium, respectively. The values of KT of $\sim 3 \times 10^{-24} \text{ m}^3 \text{ K s}^{-1}$ obtained by Pontikakos and Jones [47] for $\text{Al}_{13}\text{Fe}_4$ at 600 and 625 °C are entirely consistent with the results in Fig. 3 for related $\text{Al}_{12}\text{Fe}_3\text{Si}$ at 425 to 475 °C, Al_3Ni giving KT an order of magnitude higher, attributable to a higher diffusivity of Ni in Al. The cluster of KT values of $\sim 5 \times 10^{-24} \text{ m}^3 \text{ K s}^{-1}$ for $\text{Al}_{13}\text{Fe}_4$, $\text{Al}_{13}\text{(Fe, Mo, V)}_4$ and $\text{Al}_8\text{Fe}_4\text{Ce}$ at 425 °C seems unrelated to the other measurements and could reflect control of coarsening by short-circuit diffusion, such as along grain boundaries, at least for the $\text{Al}_{13}\text{Fe}_4$ [47]. The exceptionally low values of $KT \approx 2 \times 10^{-27} \text{ m}^3 \text{ K s}^{-1}$ obtained by Skolianos *et al.* [50] for Al_6Mn in Al–4.5Cu–2Mn at 500 to 620 °C are also out of line with the other results. Possibly the coarsening behaviour was complicated by concurrent transformation of Al_6Mn to $\text{Al}_{20}\text{Cu}_2\text{Mn}_3$, noted by the authors to have occurred within the 1000 h time-scale of their experiment.

4. Conclusions

1. The considerable body of data for coarsening of δ' - Al_3Li in Li-containing aluminium alloys are well represented by the single relationship

$$r^3 - r_0^3 = \frac{K_0}{T} \exp\left(-\frac{Q}{RT}\right)t$$

with $K_0 = (1.3^{+3.9}_{-0.3}) \times 10^{-13} \text{ m}^3 \text{ K s}^{-1}$ and $Q = 115 \pm 4 \text{ kJ mol}^{-1}$.

2. The relatively limited data for coarsening of θ' and θ'' in Cu-containing aluminium alloys are correspondingly, representable by the same relationship with $K_0 \approx 4 \times 10^{-8}$ and $\sim 4 \times 10^{-10} \text{ m}^3 \text{ K s}^{-1}$, respectively, and $Q \approx 140 \text{ kJ mol}^{-1}$.

* Lieblisch and Torralba [58] for Al–(1.8 to 2.1) Li–(0.1 to 0.3)B obtained $K \approx 3 \times 10^{-30} \text{ m}^3 \text{ s}^{-1}$ at 200 °C, significantly below any of the values in Table I for this temperature, indicating a retarding effect of boron by an order of magnitude.

† Lieblisch and Torralba [58] found a similar effect for Al–1.8Li–0.3B after 100 h at 200 °C.

‡ Assuming $Q = 140 \text{ kJ mol}^{-1}$.

3. Available data for coarsening of $\text{Li}_2\text{-Al}_3(\text{Zr, V})$ and related phases in Al–Zr based alloys and of $\text{Al}_{12}\text{Fe}_3\text{Si}$ and related phases in Al–Fe based alloys indicate (i) rates of coarsening five to eight orders of magnitude slower at 375 to 475 °C than would be expected for δ' , θ' and θ'' in this temperature range, and (ii) high activation energies of ~ 300 and 180 kJ mol^{-1} , respectively.

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