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Effect of phosphorus additions on the spacing between primary silicon particles in a Bridgman solidified hypereutectic Al-Si alloy

W. J. KYFFIN, W. M. RAINFORTH, H. JONES
Department of Engineering Materials, University of Sheffield, Sheffield, S1 3JD, UK

The effect of 100 ppm addition of phosphorus on primary silicon particle number density per unit area N_A and corresponding interparticle spacing λ is reported for a Bridgman solidified Al-20 wt%Si base alloy. The phosphorus (added as Al-Fe-P base or Al-Cu-P alloys) results in a factor of 3 increase in N_A and a factor of 2 reduction in λ for the range of conditions studied. In its absence the results conform to $\lambda\dot{T}^{1/3} = 256 \pm 24\ \mu\text{m}\ (\text{K/s})^{1/3}$ where $\dot{T}$ is cooling rate during solidification in good agreement with earlier data. When published data on the effect of 0.02 to 0.2 wt%P are included the combined results are well represented by $\lambda\dot{T}^{1/3} = 250 - 215\ (\text{wt\%P})^{0.17}$ (λ in μm, $\dot{T}$ in K/s). © *2001 Kluwer Academic Publishers*

1. Introduction

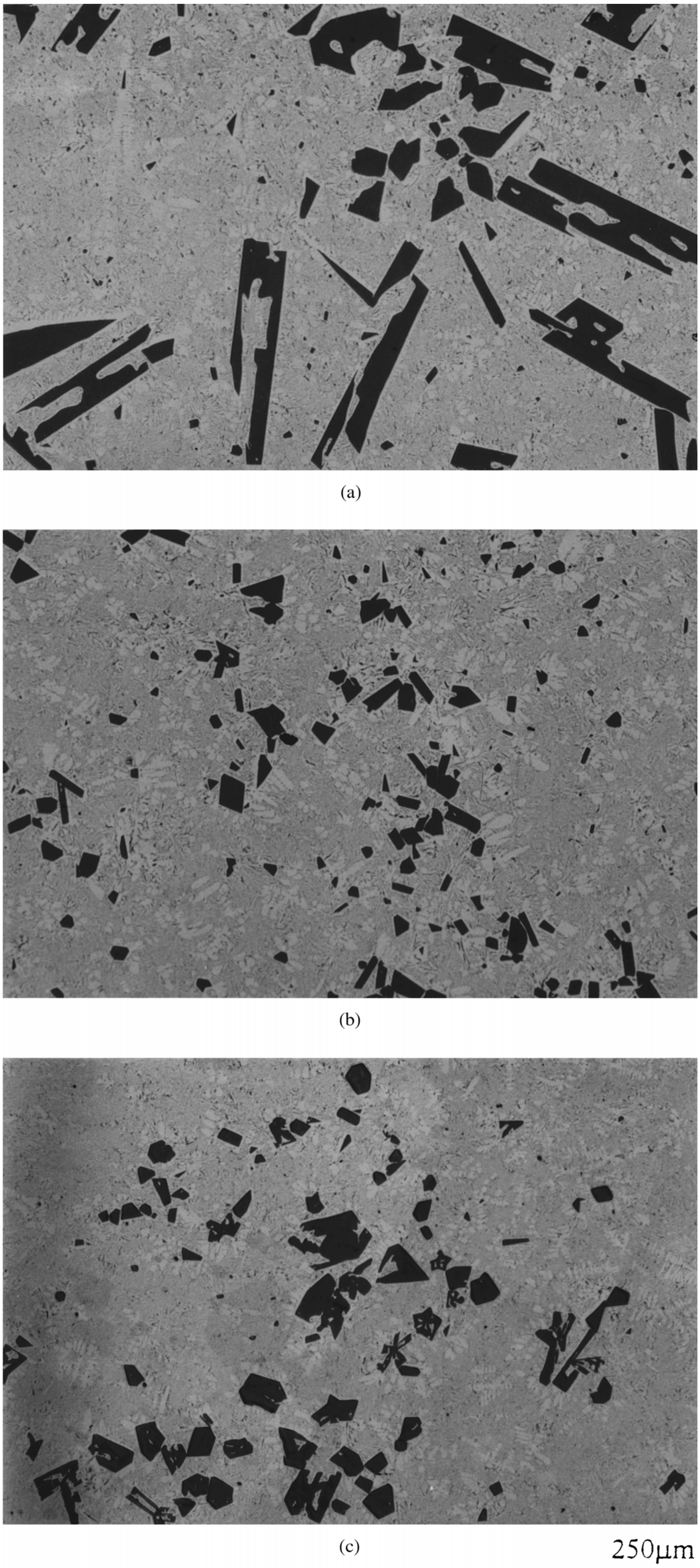
The use of phosphorus additions to refine primary silicon in hypereutectic Al-Si alloys has been traced [1] back to a patent by Sterner-Rainer [2] in 1933. Onitsch-Modl [3] in 1952 and Mascré [4] in 1953 reported on the silicon size-refining effects of PCl_5 and Cu-P alloy additions to an Al alloy containing between 17 and 23 wt%Si. The available information has been reviewed by Bates [5] in 1960, by Sigworth [1] in 1987 and by Tenekedjiev and Gruzleski [6] in 1990, and developments in this technology and in understanding of its mechanism continue to appear eg. refs [7–12]. Earlier work at Sheffield employed controlled velocity Bridgman solidification and TIG weld transversing to establish relationships between primary silicon particle number density N_A or λ and solidification process variables, front velocity V, temperature gradient G and cooling rate $\dot{T}$ [13–15]. The present contribution explores the effect of added phosphorus on N_A and λ for an Al-20 wt% Si alloy.

2. Experimental

The Al-Si alloy was supplied as ingot by KB alloys and had composition Al-20Si-0.30Fe-0.08Mn-0.06Mg with <0.02 Cu, Zn, Ni, Ti and Cr (wt%). Approximately 150 g samples were remelted in graphite crucibles so that additions corresponding to 100 ppm of phosphorus could be made to the melt. The additions were of Al-11.6Fe-4.1P-0.7Mn-0.4Si-0.1Ti supplied as billet 30 mm in diameter and an Al-18.8 Cu–1.18P alloy supplied as extruded rod. These were added to the melt at 850°C followed by stirring for approximately 10 seconds using a graphite rod. The melt was then held for 60 seconds at 850°C before casting into a split steel chill mould, which yielded on solidification a number of cast rods 7 mm in diameter. These were swaged and rolled down to 2.8 mm diameter in stages with 15 minute intermediate anneals at 500°C. The resulting rods were inserted into 3 mm bore alumina tubes for Bridgman processing. Remelting occurred in the Bridgman furnace described previously [16] with melt temperatures 850 and 930°C giving temperature gradients of 8 and 16 K/mm respectively during Bridgman solidification in the velocity range 0.1 to 1mm/s used. Control samples with no addition of phosphorus were also processed at the same velocities and temperature gradients. Resulting solidified samples were sectioned longitudinally and mounted in Bakelite for metallographic preparation and optical microscopy. Transverse sections were similarly prepared for some of the sample conditions. The number N_A of primary silicon particles per unit area was measured from photomicrographs, averaging at least 15 areas per sample condition.

3. Results and discussion

Fig. 1a–f show the effect of added Al-Fe-P on primary silicon for the representative growth velocities 0.1, 0.51 and 1.03 mm/s. Fig. 2a, b shows the equivalent effect of Al-Cu-P addition at 0.51 mm/s. The change from coarse plate-like to fine equiaxed primary silicon on increase in V and on addition of Al-Fe-P or Al-Cu-P is very evident. The corresponding measurements of N_A and equivalent $\lambda = N_A^{-1/2}$ are given in Table I and plotted in Figs 3 and 4 against solidification cooling rate $\dot{T} = GV$. The increase in N_A and decrease in λ with increasing $\dot{T}$ is consistent with the relationship $\lambda = N_A^{-1/2} = K\dot{T}^{-1/3}$[14] with $K = 256 \pm 24\mu\text{m}$ $(\text{K/s})^{1/3}$ for the alloy with no addition. This value of K is similar to $250 \pm 30\ \mu\text{m}\ (\text{K/s})^{1/3}$ found by Bayraktar *et al.* [14] for primary silicon in hypereutectic Al-Si alloys of a range of Si-contents (18 to 31wt%) and solidification cooling rates (0.02 to 10^6 K/s) obtained by a variety of solidification techniques. The factor of 3 increase in N_A and factor of 2 decrease in λ produced by

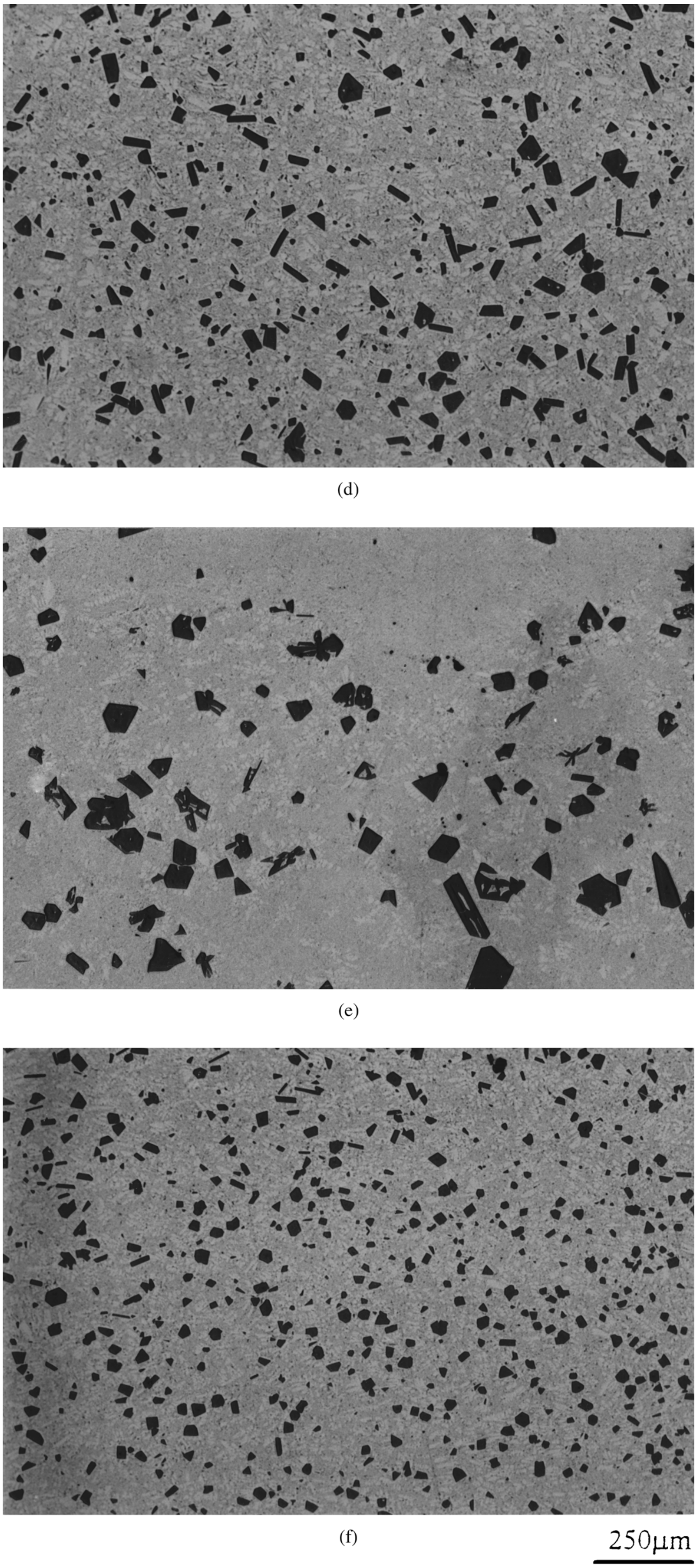


(a)

(b)

(c)

Figure 1 Effect of Al-Fe-P addition on primary silicon in Bridgman solidified Al-20 wt%Si (a, b) $G = 8$ K/mm, $V = 0.1$ mm/s; (a) no addition; (b) with Al-Fe-P addition (c, d) $G = 16$ K/mm, $V = 0.51$ mm/s; (c) no addition; (d) with Al-Fe- P addition (e, f) $G = 16$ K/mm, $V = 1.03$ mm/s; (d) no addition (f) with Al-Fe-P addition. (*Continued.*)



(d)

(e)

(f)

Figure 1 (*Continued.*)

the Al-Fe-P and Al-Cu-P reflects the effect of phosphorus in nucleating octahedral primary silicon under the conditions of Bridgman solidification studied. P-rich particles, presumed to be AlP, which is isomorphous with Si, have been found within or associated with nucleated silicon particles in several studies [16–21], although the expected epitaxial fit at the AlP/Si interface has yet to be demonstrated, for example, by High

TABLE I Number of primary silicon particles per unit area N_A and corresponding interparticle spacing $\lambda(=N_A^{-1/2})$ versus conditions in Bridgman solidification, for Al-20 wt%Si without and with additions of Al-Fe-P or Al-Cu-P

Bridgman conditions			No P addition			Al-Fe-P			Al-Cu-P				
V mm/s	G K/mm	$\dot{T}$ K/s	N_A mm^{-2}	λ μm	$\lambda\dot{T}^{1/3}$ μm^{-} (K/s)$^{1/3}$	N_A mm^{-2}	λ μm	$\lambda\dot{T}^{1/3}$ μm (K/s)$^{1/3}$	N_A mm^{-2}	λ μm	$\lambda\dot{T}^{1/3}$ μm (K/s)$^{1/3}$	N_A (Al-Fe-P) ÷ N_A (No addn)	N_A (Al-Cu-P) ÷ N_A (No addn)
0.10	8	0.8	*15 ± 4	260 ± 35	241	67 ± 10	122 ± 6	113	-	-	-	4.5	-
0.10	16	1.6	†23 ± 8	210 ± 30	246	87 ± 22	107 ± 11	125	73 ± 12	117 ± 9	137	3.8	3.2
0.34	8	2.7	†35 ± 6	169 ± 12	235	99 ± 11	101 ± 5	141	-	-	-	2.8	-
0.51	8	4.1	†43 ± 8	153 ± 13	245	106 ± 16	97 ± 6	155	93 ± 14	104 ± 7	166	2.5	2.2
0.34	16	5.4	†50 ± 9	142 ± 12	249	131 ± 15	87 ± 4	153	-	-	-	2.6	-
0.51	16	8.2	†54 ± 16	136 ± 17	274	182 ± 25	74 ± 5	149	160 ± 21	79 ± 5	159	3.4	3.0
1.03	16	16.5	•71 ± 14	119 ± 11	303	237 ± 19	65 ± 3	165	200 ± 19	71 ± 3	181	3.3	3.3
Means					**256 ± 24**			**143 ± 18**			**161 ± 18**	**3.3 ± 0.7**	**2.9 ± 0.5**

*predominantly plate-like.
†Mixed plate-like + polyhedral.
•Predominantly polyhedral. Otherwise polyhedral.

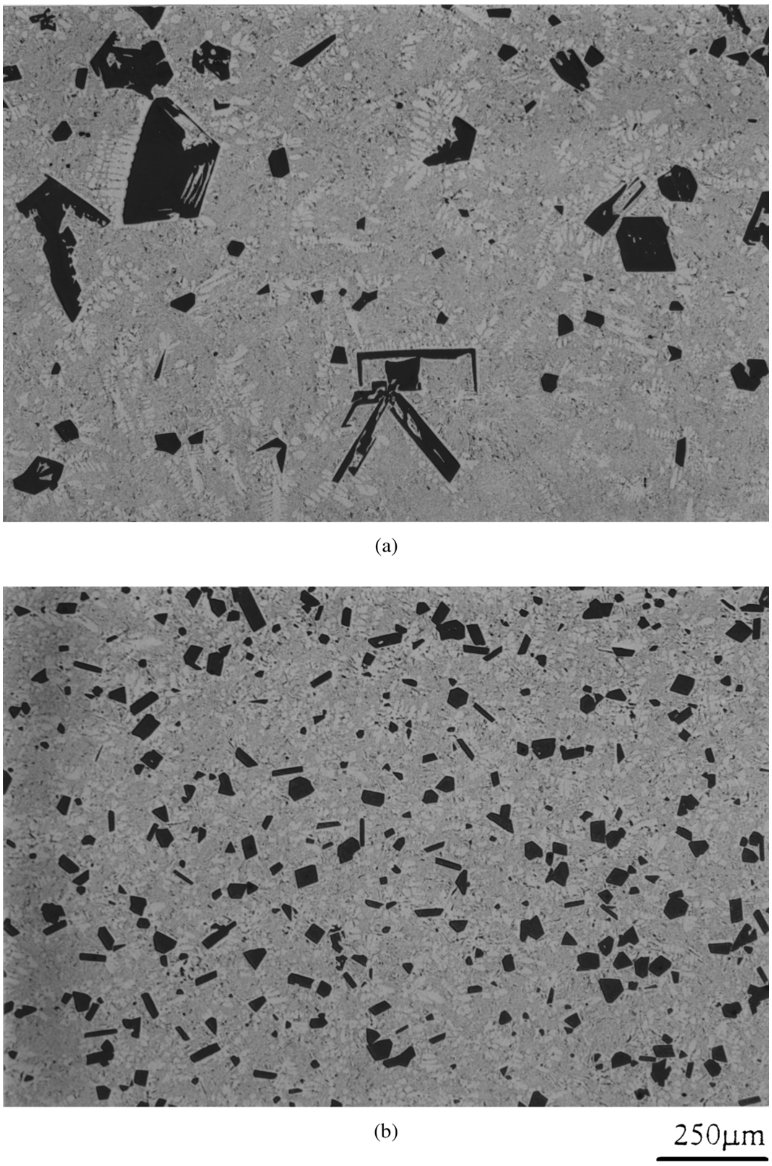


Figure 2 Effect of Al-Cu-P addition on primary silicon in Bridgman solidified Al-20 wt%Si (a, b) $G = 8$ K/mm, $V = 0.51$ mm/s (a) no addition; (b) with Al-Cu-P addition.

Resolution Electron Microscopy. The effect of a further increase in phosphorus addition can be demonstrated by comparing the present data with those of Mandal *et al.* [23] who added 0.1 and 0.2 wt%P. Their results (Table II) are for particle diameter d of primary silicon in Al-17, 22 and 27 wt%Si for cooling rates between 15 and 30 K/s. Assuming that d represents the average diameter of silicon particles in a uniform cubic array, it follows that particle separation $\lambda = (\frac{\Pi}{6f})^{1/3} d$, so allowing $K = \lambda\dot{T}^{1/3}$ to be obtained for each condition in

TABLE II Diameter d of primary silicon particles in Al-17, 22 and 27 wt%Si cast into rods 12 mm diameter in different moulds [23]

Addition 0.1 wt%p						Addition 0.2 wt%p					
Expt No	Wt%Si	$\dot{T}$ k/s	d μm	Equiv. λ μm	$\lambda\dot{T}^{1/3}$ μm (K/s)$^{1/3}$	Expt No	Wt%Si	$\dot{T}$ K/s	d μm	Equiv. λ μm	$\lambda\dot{T}^{1/3}$ μm (K/s)$^{1/3}$
2	17	16.2	18.3	38.4	97	3	17	16.0	21.4	44.0	11
4	22	16.0	27.1	45.3	114	5	22	15.7	19.3	32.0	81
7	27	19.2	32.8	47.9	128	9	27	22.4	28.9	42.2	119
10	17	31.4	18.2	37.5	118	12	17	30.6	13.2	27.2	85
14	22	20.9	24.5	40.9	113	15	22	21.7	21.3	35.6	99
16	27	18.5	19.7	28.8	76	17	27	15.9	18.0	26.3	66
19	17	30.1	16.1	33.2	103	20	17	26.3	16.2	33.4	99
22	22	25.4	13.1	21.0	64	24	22	23.3	17.9	29.9	85
26	27	20.1	29.4	42.9	117	27	27	14.9	20.3	20.3	50
					Mean:103 ± 21						Mean:88 ± 22

Equiv. $\lambda = (\Pi/6f)^{1/3}\,d$ where f is estimated volume fraction of primary silicon (0.06, 0.11 and 0.17 for 27, 22 and 27 wt%Si).

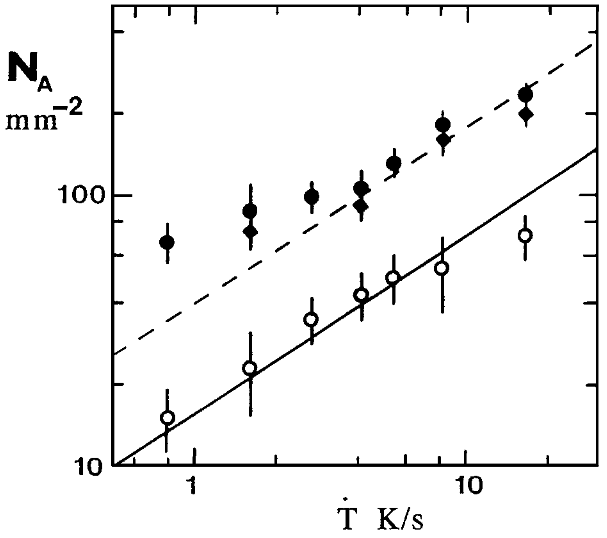


Figure 3 Number of primary silicon particles per unit area N_A versus cooling rate $\dot{T}$ for Bridgman solidified Al-20 wt% Si ○ without addition ● with Al-Fe-P addition ◆ with Al-Cu-P addition. Full line represents $N_A\dot{T}^{-2/3} = 15.3$ mm^{-2} (K/s)$^{-2/3}$. Dashed line is a factor of 3 higher.

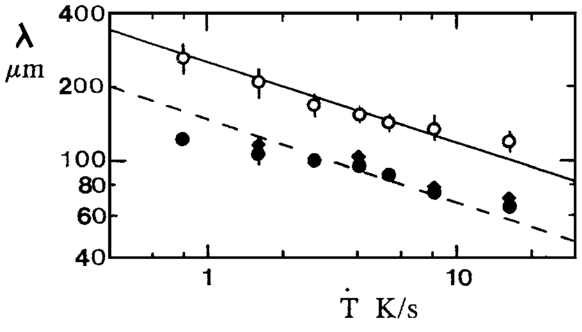


Figure 4 Spacing λ between primary silicon particles versus cooling rate $\dot{T}$ for Bridgman solidified Al-20 wt%Si. Key as for Fig. 3. Full line represents $\lambda\dot{T}^{1/3} = 256\,\mu$m (K/s)$^{1/3}$. Dashed line is a factor of $\sqrt{3}$ lower.

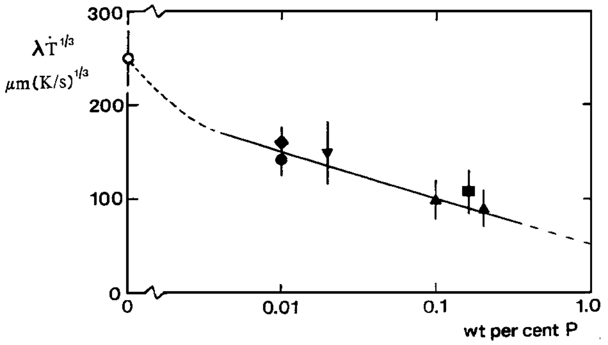


Figure 5 $\lambda\dot{T}^{1/3}$ for primary silicon in Al-18 to 31 wt%Si versus wt% added phosphorus. ○ Bayraktar *et al.* [14] and present work (PW) ● PW, Al-Fe-P ◆ PW, Al-Cu-P, ▲ Mandal *et al.* [23] ■ Sulzer [24] ◄ Kaneko *et al.* [25].

Table II, as was done in Table I. A similar approach was used for the more limited results of Sulzer [24] for 0.16 wt%P addition to Al-17 wt%Si and of Kaneko *et al.* [25] for 0.02 wt%P addition to Al-19 wt% Si. Fig. 5 shows that mean $\lambda\dot{T}^{1/3}$ from Tables I and II plus the results of Sulzer and of Kaneko *et al.* decreases continuously from 250 μm (K/s)$^{1/3}$ with no addition of phosphorus to 88 ± 22 μm (K/s)$^{1/3}$ at 0.2 wt%P addition, for the ranges of cooling rates involved (0.8 to 16.5 K/s in the present work, 15 to 30 K/s in that of Mandal *et al.*, 3 to 70 K/s for Sulzer and 0.02 to 2 K/s for Kaneko *et al.*). The results in Fig. 5 are well represented by $\lambda\dot{T}^{1/3} = 250$–$215\,(\text{wt\%P})^{0.17}$ where λ is in μm and $\dot{T}$ is in K/s.

4. Conclusions

1. Addition of 100 ppm P by means of Al-Fe-P or Al-Cu-P inoculants to Bridgman solidified Al-20 wt%Si base alloy gave polyhedral primary silicon with three times the number of particles per unit area obtained in the absence of phosphorus, corresponding to a factor of 2 decrease in interparticle spacing λ.

2. Mean interparticle spacing of primary silicon in the absence of phosphorus conformed to the relationship $\lambda\dot{T}^{1/3} = 256 \pm 24\,\mu$m (K/s)$^{1/3}$ over the range of cooling rate $\dot{T}$ from 0.8 to 16.5 K/s in good agreement with data collected earlier by Bayraktar *et al.*

3. Combining the present results with those of Mandal *et al.* [23], Sulzer [24] and Kaneko *et al.* [25] for additions of 0.02 to 0.2 wt%P to Al-17 to 27 wt% Si, and those of Bayraktar *et al.* [14] shows a continuous decrease in $\lambda\dot{T}^{1/3}$ for primary silicon to 90 ± 20 μm (K/s)$^{1/3}$ at 0.2 wt%P addition, showing a good fit with the relation $\lambda\dot{T}^{1/3} = 250$–$215\,(\text{wt\%P})^{0.17}$ where λ is in μm and $\dot{T}$ is in K/s.

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