# Effect of solidification cooling rate and phosphorus inoculation on number per unit volume of primary silicon particles in hypereutectic aluminium—silicon alloys

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Collected data on derived number per unit volume $\bar{N}_V$ of primary silicon particles in hypereutectic Al-Si alloys show a power relationship with solidification cooling rate $\dot{T}$ of the form $\bar{N}_V = A\dot{T}^n$ where typically $n \sim 1$ and $A \simeq 130$ mm$^{-3}$ (K/s)$^{-1}$ in the absence of phosphorus and $A \simeq 720$ mm$^{-3}$ (K/s)$^{-1}$ in its prescence. Significantly lower apparent values of $\bar{N}_V$ from one set of results appear to stem from measurement of a mean long dimension rather than diameter of particle sections as well as lower measured undercoolings than in Bridgman experiments at similar $\dot{T}$. 

Size refinement of primary silicon in hypereutectic Al-Si base alloys is a key requirement for meeting property targets [1–4] and can be achieved by inoculation with phosphorus, as is routinely applied in conventional foundry practice [5], or by increasing the cooling rate during solidification, which has been applied, for example, in the development of improved performance in alloys processed by spray forming [6], and other rapid solidification technologies [8]. Arnold and Prestley [9] showed micrographs indicating size refinement of primary silicon in Al-16 wt%Si with increase of solidification cooling rate $\dot{T}$ in the range 0.6 to 1.5 K/s, but the results were not quantified. Sulzer [10] reported refinement of primary silicon size from 27 ± 4 $\mu$m at 3 K/s to 15.5 ± 1.5 $\mu$m at 70 K/s for Al-20Si-1Cu-1Mg (wt%) base alloy with 0.16 wt% P addition. Kaneko *et al.* [11] determined average size and number per unit area of section $\bar{N}_A$ of primary silicon in Al-19 wt%Si-0.02 wt%P alloy over the range of $\dot{T}$ between 0.02 and 2 K/s, and obtained a linear relationship between logarithm of derived number of particles per unit volume $\bar{N}_V$ and log $\dot{T}$, with a slope of ∼1.4. Moir and Jones [12] combined their own measurements of $\bar{N}_A$ versus solidification growth velocity V for two different temperature gradients $G$ (Bridgman solidification and tungsten inert gas weld traversing) with measurements by Pierantoni *et al.* [13] for laser surface melt traversing to show a linear relationship between log $\bar{N}_A$ and log $(G\sqrt{V})$ with a slope of unity. Bayraktar *et al.* [14] combined all these results with additional Bridgman measurements to show $\lambda\ \dot{T}^{1/3}$=250 $\mu$m (K/s)$^{1/3}$ over the range 0.02< $\dot{T}$<10$^6$ K/s where $\lambda = \bar{N}_A^{-1/2}$ is a measure of the primary silicon interparticle spacing. Mandal *et al.* [4] reported mean particle size $\bar{D}_A$ of primary silicon versus $\dot{T}$ in the range 15 to 31 K/s for Al-17, 22 and 27 wt%Si with 0.1 and 0.2 wt% P additions. Ohmi *et al.* [15, 16] reported $\bar{D}_A$ (*but see below*) of primary silicon and associated nucleation undercooling $\Delta T_m$ for Al-22 and 32 wt%Si for solidification cooling rates in the range 11 to 260 K/s, and showed particle size decreasing linearly with increase in undercooling and increasing with increased cooling rate (results show a reasonable fit with $\Delta T_m = A\dot{T}^n_{K/s}$ with A = 3.5 K (K/s)$^{-n}$ and $n$ = 0.6). Liang *et al.* [17] measured $\bar{N}_A$ and $\bar{D}_A$ together with formation temperature $T_f$ of primary silicon versus V and $G$ in Bridgman in solidification of Al-18.3 wt%Si for comparison with model predictions for steady state heterogeneous nucleation of the primary silicon from the bulk melt. The experimental results show $N_v \propto \dot{T}^{1.2}$ and that nucleation undercooling increases from ∼35 to ∼52 K over the range 1 < $\dot{T}$ < 20 K/s, consistent with the model prediction for a nucleation contact angle $\theta$ increasing from 26 to 36 deg over the same range of $\dot{T}$. Most recently Kyffin *et al.* [18] reported the effect of phosphorus inoculation on $\bar{N}_A$ of primary silicon for the range 0.8 < $\dot{T}$ < 16.5 K/s for comparison with the results of Sulzer [10] for 3 < $\dot{T}$ < 70 K/s, Kaneko *et al.* [11] for 0.02 < $\dot{T}$ < 2 K/s and Mandal *et al.* [4] for 15 < $\dot{T}$ < 30 K/s.

The present purpose is to investigate the possible generality of the relationships between $\bar{N}_V$ and $\dot{T}$ obtained by Kaneko *et al.* [11], Ohmi *et al.* [15, 16] and Liang *et al.* [17]. The available experimental data are summarised in Table I and plotted in Fig. 1 as log $\bar{N}_V$ versus log $\dot{T}$. The results for phosphorus-free samples fall into two groups. Results from Bridgman solidification, TIG weld traversing and laser surface melt

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TABLE I Summary of data on $\bar{N}_V$ versus $\dot{T}$ for primary silicon in hypereutectic Al-Si alloys

| Alloy composition wt% | Solidification technique | Range of cooling rate $\dot{T}$, K/s | Resulting $\bar{N}_V$ mm$^{-3}$ | $\bar{N}_V/\dot{T}$, mm$^{-3}$ (K/s)$^{-1}$ | Reference |
|---|---|---|---|---|---|
| Al-16Si + 0 to 0.17P | Sand and chill casting | 0.56 to 15.3 | – | – | Arnold and Prestley 1961 [9] |
| Al-20Si-1 Cu-1Mg based + 0.16P | Chill casting | 3 to 70 | $^*4\times10^3$ to $2\times10^4$ | $730\pm490$ | Sulzer 1961 [10] |
| Al-19Si – 0.02P | Cooled in a container | 0.017 to 1.67 | $^‡2.5$ to 1250 | $390\pm270$ | Kaneko *et al.* 1978 [11] |
| Al- 17.1, 18.2, 24.8, +30.7Si | TIG and Bridgman | 7.7 to 3690 | $^†740$ to $7\times10^5$ | $140\pm80$ | Moir and Jones 1991 [12] |
| Al-26Si | Laser surface melt traversing | $1.6\times10^4$ to $10^6$ | $^†5\times10^6$ to $1.8\times10^8$ | $250\pm100$ | Pierantoni *et al.* 1992 [13] |
| Al-18.4Si | Bridgman | 0.9 to 15.5 | $^†64$ to 866 | $107\pm39$ | Bayraktar *et al.* 1992 [14] |
| Al-17, 22, 27Si | Chill casting | 16 to 31 | $^*5\times10^3$ to $5\times10^4$ | $640\pm560$ | Mandal *et al.* 1991 [4] |
| +0.1 or 0.2 P | – | – | – | $780\pm540$ | |
| Al-22 +32 Si | Crucible cooling, chill casting | 10 to 220 | $^*14$ to 430 | $1.2\pm0.5$ | Ohmi *et al.* 1991, 1994 [15, 16] |
| Al-18.3Si | Bridgman | 1.0 to 18.9 | $^†90$ to 1260 | $77\pm21$ | Liang *et al.* 1995 [17] |
| Al-20Si | Bridgman | 0.8 to 16.5 | $^†150$ to 520 | $160\pm40$ | Kyffin *et al.* 2001 [18] |
| Al-20Si + 0.1P | – | – | $^†1390$ to 9270 | $840\pm380$ | |

Note: $^*\bar{N}_V$ calculated from reported mean sectioned diameter $\bar{D}_A$ using $\bar{N}_V = \frac{4}{\pi}(\frac{2}{3})^{1/2} f/\bar{D}_A^3$ with f as volume fraction of primary silicon.
$^†\bar{N}_V$ calculated from reported number $\bar{N}_A$ of primary silicon particles per unit area on sections using $\bar{N}_V = (\pi/6f)^{1/2}\bar{N}_A^{3/2}$.
$^‡\bar{N}_V$ calculated by Kaneko *et al.* from $\bar{N}_A/\bar{D}_V$ with $\bar{D}_V = \pi\bar{D}_A/2$, where $\bar{D}_V$ is true mean volume diameter.

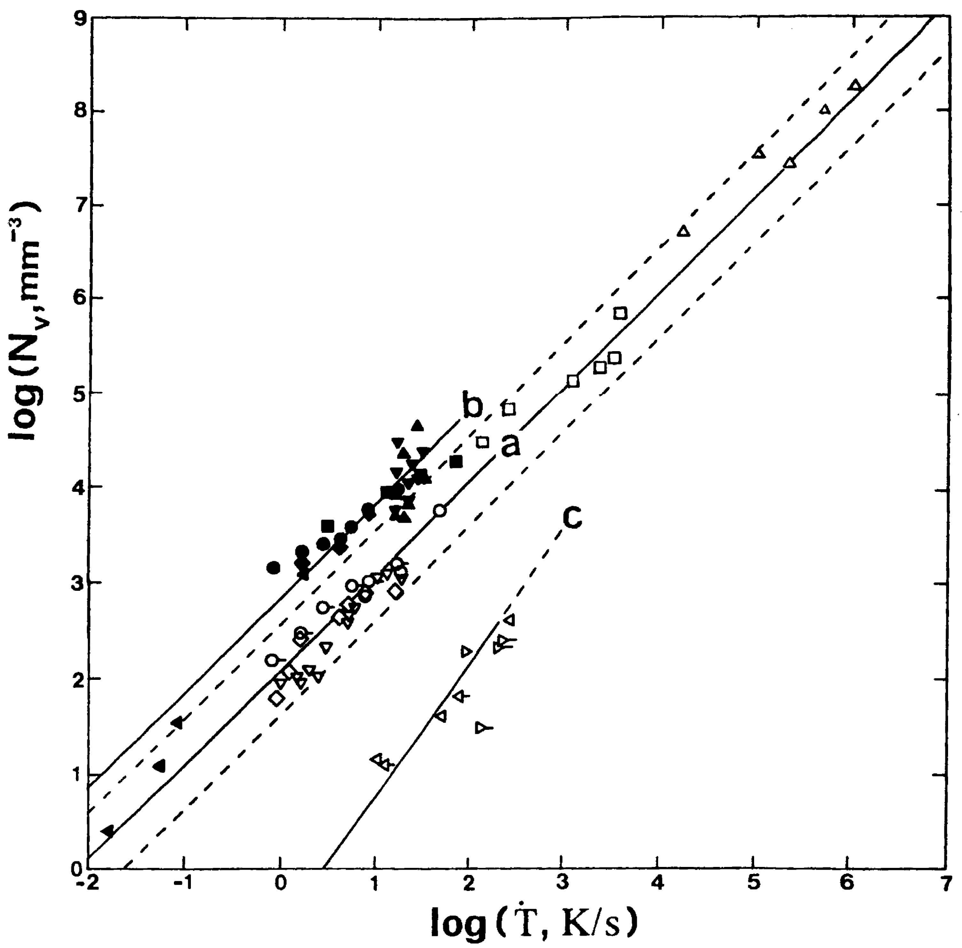


*Figure 1* Mean number $\bar{N}_V$ of primary silicon particles per unit volume in hypereutectic Al-Si alloys versus solidification cooling rate $\dot{T}$. Key: Experimental data ■ Sulzer [10], ◀ Kaneko *et al.* [11],□ ○ Moir and Jones [12] TIG and Bridgman, △ Pierantoni *et al.* [13], ◇ Bayraktar *et al.* [14], ▲▽Mandal *et al.* [4] 0.1 and 0.2 wt%P, ◁▷Ohmi *et al.* [15, 16] crucible cooling and chill casting ▽Liang *et al.* [17], • • ♦ Kyffin *et al.* [18] 0.0P, 0.1P (Al-Fe-P) and 0.1P(Al-Cu-P). Filled points indicate inoculation with phosphorus. Further details of conditions are in Table I. Line a represents fit of the phosphorus-free data to Equation 1 with $n = 1$ and $A = 130$ mm$^{-3}$ (K/s)$^{-1}$, with factor of 3 scatter band indicated. Line b represents fit of results with phosphorus present to Equation 1 with $n = 1$ and $A = 720$ mm$^{-3}$ (K/s)$^{-1}$. Line c is the prediction of model B of Ohmi *et al.* [19] giving $n = 1.44$ and $A = 0.21$ mm$^{-3}$ (K/s)$^{-1.44}$ in Equation 1

traversing show a good fit (within a factor of 3 in $\bar{N}_V$) with

$$\bar{N}_V = A\dot{T}^n \quad (1)$$

with $n = 1$ and $A = 130$ mm$^{-3}$ (K/s)$^{-1}$. The results of Ohmi *et al*. [15, 16] for crucible cooling and chill casting, in contrast, show values of $\bar{N}_V$ some two orders of magnitude below the Bridgman and surface melting results. At least part of this discrepancy arises because it now appears that Ohmi *et al*. reported the mean long dimension of their primary silicon particles from sections rather than the mean diameter. Correction for this would move their data points in Fig. 1 closer to the other $\bar{N}_V$ measurements plotted there. Predictions of their nucleation model B [19] give $n = 1.44$ with $A = 0.21$ mm$^{-3}$ (K/s)$^{-1.44}$ in Equation 1 at $\dot{T} < 200$ K/s in good accord with their measurements but exhibits plateaus in $\bar{N}_V$ at $\dot{T} > 200$ to $10^3$ K/s depending on superheat. A further significant difference from the Bridgman results of Liang *et al*. was that Liang *et al*.'s associated measured nucleation undercoolings $\Delta T$ were relatively larger, e.g. 43 K at 13 K/s compared with 16 K at this cooling rate reported by Ohmi *et al*., indicative of operation of heterogeneous nucleation at lower undercoolings in their work compared with the Bridgman studies. Fig. 1 also includes results for phosphorus inoculated samples (filled points). Except for the results of Kaneko *et al*. at 0.018 and 0.056 K/s, these lie mostly above the scatter band of the main body of results from phosphorus free samples, showing a fit of $\bar{N}_V$ within a factor of 3 of Equation 1 with $n = 1$ and $A = 720$ mm$^{-3}$ (K/s)$^{-1}$, i.e. a factor of 5.5 higher $\bar{N}_v$.

In conclusion, collected data for number per unit volume $\bar{N}_V$ of primary silicon particles in hypereutectic Al-Si alloys, derived from measurements of number $\bar{N}_A$ per unit area or mean diameter $\bar{D}_A$ on sections, show a power relation with solidification cooling rate $\dot{T}$ of the form $\bar{N}_V = A\dot{T}^n$, where typically $n \sim 1$ and $A \simeq 130$ mm$^{-3}$ (K/s)$^{-1}$ in the absence of inoculation with phosphorus and $A \simeq 720$ mm$^{-3}$ (K/s)$^{-1}$ in the presence of phosphorus. The significantly lower values of $\bar{N}_V$ from the results of Ohmi *et al*. appear to be associated with measurement of mean long dimension rather than mean diameter of particle sections as well as nucleation at much lower measured undercoolings in their experiments compared with the undercoolings measured in the experiments of Liang *et al*., which were associated with $\bar{N}_V$ values more typical of the majority of measurements.

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