

MODIFICATION AND REFINEMENT OF CAST Al-Si ALLOYS

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Abstract

In the Al-Si system, minor additions of metallic impurities, Na, Sr and others, modify the microstructure of eutectic and primary silicon by inducing a high twin density, causing a morphological transition from flake-like to fibrous or spherical shapes. This modification should be distinguished from the inoculation or refining effects of other minor impurities, notably of phosphorous. The modified structural transition can be entirely explained in terms of growth kinetics modified by impurity induced twinning for the silicon phase and numerical modelling of the cooling curves shows that there need be no change in the nucleation behavior. The presence of elements such as phosphorous complicates the picture because in contrast to the former growth controlled process, the latter probably do alter the nucleation kinetics.

Introduction

Two common melt treatments concerned with the silicon phase of Al-Si cast alloys are frequently used in foundry practice, modification and refinement. Both of these treatments produce a finer scale of silicon phase and subsequently improve the mechanical properties of the alloys, but the microstructural effects are very different.

- **Modification:** a dramatic morphological change of silicon phase from coarse flake-like to fine fibrous structure.
- **Refinement:** silicon flakes (eutectic) or parti-

cles (hypereutectic) are refined to a smaller scale and distribution without significant change in shape.

The modification of cast aluminum silicon alloys was discovered by accident arising from a change of flux some 75 years ago^[1] and was subsequently attributed to trace additions of sodium, at levels around 0.01 wt.%^[2]. Since that time the metallurgical literature has abounded with contributions concerned with practical control of the process, with the use of alternative additions and, throughout, with attempts to explain the mechanism(s) which operates^[3-5]. Metallic additions of strontium, barium, calcium, europium, lanthanum, cerium, praseodymium, neodymium and ytterbium etc. are also reported to have a similar modification effect^[6], but may not be as immediately efficient as sodium. In the case of refinement, phosphorous, and arsenic or antimony are reported to be effective^[4].

The Al-Si system is of simple eutectic form, Fig. 1. The aluminum phase is non-faceted and in hypoeutectic alloys is dendritic, the minor silicon phase, in pure binary alloys, occurs typically as faceted flakes, either as the primary phase or as the finer eutectic constituent. The shapes of the silicon in the untreated alloys can be described in terms of facets on the close packed {111} faces of the diamond cubic structure, generally combined with a few twins on the same planes. TEM examination also shows that silicon flakes have a <211> preferred growth direction. Fig. 2 summarizes these features. The twin spacing is around 0.4 - 1.0 μm on a typical

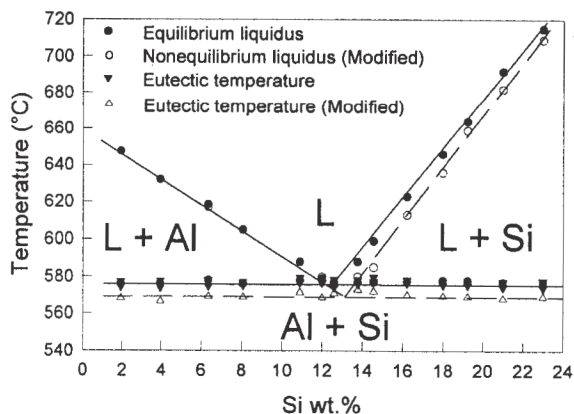


Figure 1 Summary of thermal analysis' results for unmodified and sodium modified Al-Si alloys.

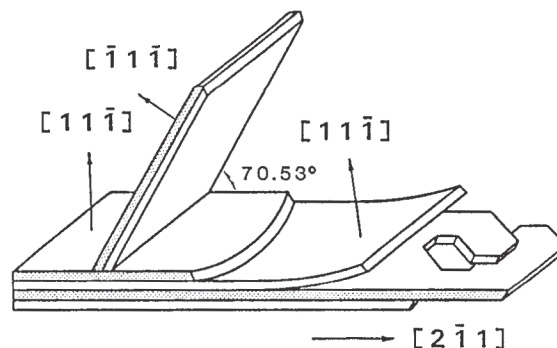


Figure 2 Schematic model of eutectic Si flakes with twin configuration shaded.

cross section^[7]. The duplex solid-liquid growth front of the eutectic is very irregular with silicon flakes projecting ahead of the metal matrix in a nearly random array, although they are widely interconnected in three dimensions^[8]. These features are illustrated in Figs. 3 (a-c) by optical, SEM and TEM micro graphs. It is almost impossible to identify a eutectic grain or cell structure on a typical section. In the present paper, the modification effect and mechanisms are the major concern and these are compared with the refinement in terms of nucleation and growth kinetics.

Modification

Modification effect can be achieved in two ways:

- *Chill modification*: with rapid cooling rates - growth rates around 1 mm s⁻¹ or larger - the silicon becomes correspondingly finer and changes to a fibrous form^[6, 9].
- *Impurity modification*: with low concentrations of sodium in the melt and slightly higher concentrations of the alkaline earth metals (Sr, Ca, Ba) or selected rare earth metals (La, Ce, Pr, Eu and Yb) the eutectic flakes are modified to branched fibers and primary flakes assume more nearly spherical shapes.

Although these two methods may result in apparently the same fibrous eutectic silicon, the internal structures of the two are very different. Chill modified fibers are very smooth in a non-faceted form. The twin density does not appear to change significantly and the fibres are branched and interconnected^[7], Fig. 4. The impurity modified fibers and spherical primary silicon are still faceted on microscale but have very high twin densities^[6, 7], Fig. 5. This observation indicates that two different mechanisms are involved in modification.

Sodium is the most effective modifier, although the effect fades rapidly, and in the eutectic fibers the twin spacing is as low as ≈ 10 nm, or only some 30 interplanar, {111} spacings. These fibers are also faceted on a very fine scale and show a principle <100> growth direction with possible branches in four fold <211> directions due to {111} multiple twinning. Intermediate levels of modification occur

at lower concentration of the additions. Sodium, in excess of ≈ 0.015 wt.% causes "overmodification" bands at which the duplex eutectic front is briefly arrested and overgrown by a film of aluminum. The duplex eutectic growth front is no longer jagged and irregular but becomes more nearly planar. These modification features are summarized in Table I.

Precise location of the minor additions within the microstructure is very difficult at the low levels concerned. In the case of sodium, limited evidence from Auger analysis and from selective chemical analysis of the phases, indicates that sodium is associated with the silicon^[6], as the dramatic rise in twin density would suggest. The modification is not limited to castings and also occurs in long unidirectionally solidified samples at a continuously advancing growth front, far removed from any nucleation events. These observations suggest that it is the growth of silicon which is affected, rather than a modified nucleation process.

There is no evidence that the aluminum matrix phase is directly influenced by the modifying additions. The appearance of aluminum dendrites in modified alloy of nominal eutectic composition is explicable in terms of retarded growth for primary or eutectic silicon, depressing the freezing point and so shifting the effective eutectic point to higher silicon levels, Fig. 1. Rapid cooling rates have a similar effect and skew the coupled growth regime in the same way.

It seems reasonable to conclude that the impurity modification process is linked to the promotion of twinning in the silicon, induced by some sort of adsorption on the silicon liquid interface. Inspection of those elements which promote twinning reveals that they have large atomic radii relative to silicon, the values lying in a band within a radius ratio between 1.54-1.85. If such atoms were adsorbed at atomic growth steps on the {111} faces of silicon, they could induce twinning by physical displacement of subsequent growth steps, so that it is possible to rationalize the effect in this way, although there are clearly other contributory factors related to vapor pressures and oxide formation^[6]. Sodium is also a special case because the

Table I: Summary of Experimental Evidence due to Modification

		Unmodified	Modified		Ref.
			Minor Additions	Chill	
Microstructure	Shape	Faceted flakes	Microfaceted fibers	Smooth fibers (Nonfaceted)	6
	Growth Direction	<211>	<100>	Uncertain	7
	Internal Structure (twin spacing)	Very few twins (0.4 - 1 μ m)	Heavily twinned (0.005 - 0.1 μ m)	Few twins	6 7
	Growth Undercooling	Relatively Small	Large	Very large	8
	Growth Interface	Irregular	Near planar	Uncertain	8
Modifier	Distribution	N/A	Within Si phase	N/A	6
	Atomic Size (Radius Ratio, r^*/r_{Si})	N/A	Large (1.54 - 1.85)	N/A	6

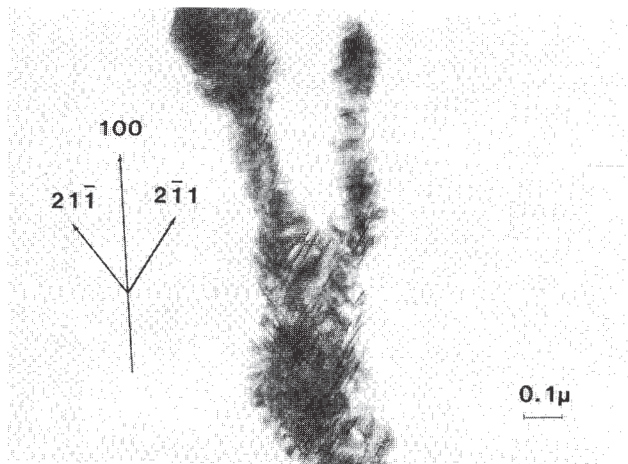
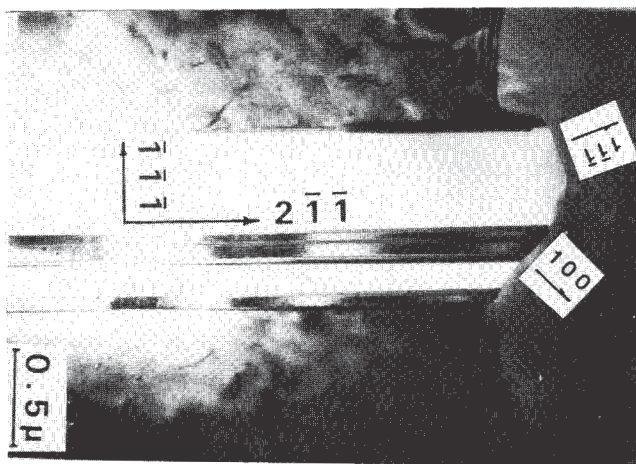
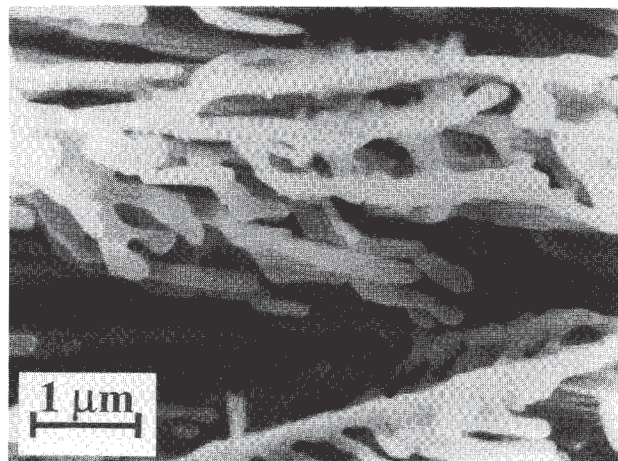
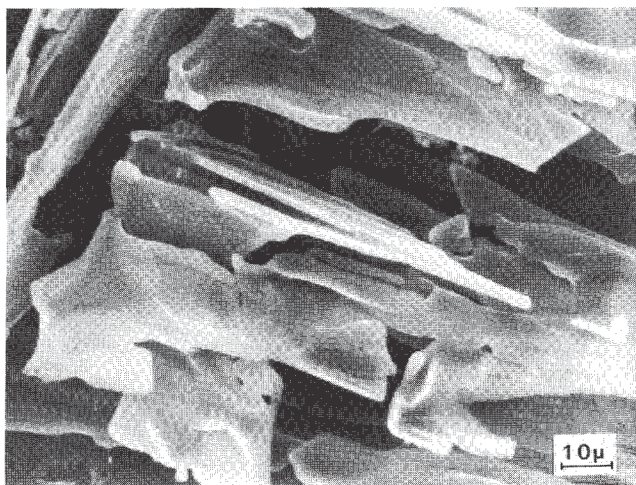
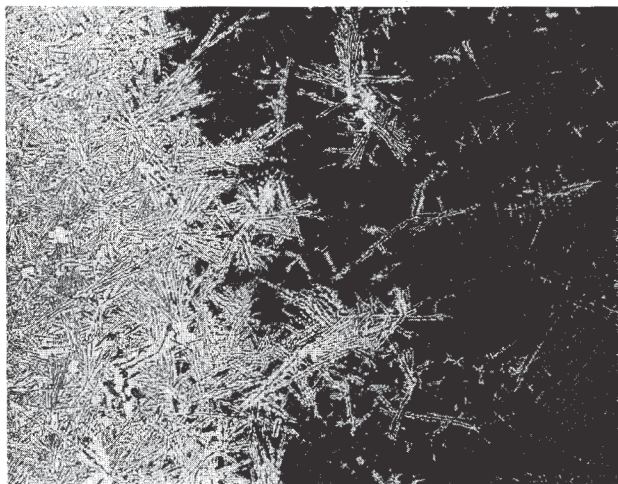


Figure 3 Microstructures of Si flakes in unmodified Al-Si eutectic alloy: a) optical, also shows an irregular growth front; b) SEM, deep etched removing metal matrix; c) TEM, shows a few {111} twins and growth orientation.

Figure 4 Microstructure of Si fibers in sodium modified Al-Si eutectic alloy: a) Optical, also shows a near planar growth front; b) SEM, deep etched removing metal matrix; c) TEM, shows a high density of multiple twinning and growth orientation.

Al-Na phase diagram is of monotectic form with low solubility of sodium in liquid aluminum (at 0.18 wt.%) which would cause a very rapid, local concentration rise at the duplex growth front. Overmodification by sodium is probably a result of this and is unique. With regard to the atomic concentrations of the minor additions, if all the add-atoms were located in the silicon phase, the level would be $\approx 1:10^3$ for sodium or perhaps as high as $\approx 1:10^2$ for the other modifiers. It is suggested that an efficient modifier should satisfy the following criteria:

- Large atomic size with a value of the radius ratio to Si atom being 1.54 - 1.85. This is a principle requirement to induce twinning in silicon crystal.
- Surface active, causing adsorption of modifiers at the growth fronts of silicon crystal.
- Low melting point or chemically reactive, which promotes a rapid dissolution in the melt.
- High vapor pressure, which promotes a very rapid distribution in the melt but may also result in a quick fade (e.g. sodium).
- Lower free energies of oxide formation relative to aluminum, which prevent their removal in combined form.

Refinement

Refinement should be distinguished from modification effect. This is brought about by low concentrations of phosphorus (arsenic or antimony) at around 0.015 wt.%^[3,4]. Here, the change, in most cases, concerns hyper-eutectic, silicon rich alloys, up to 20 wt.% Si, in which the primary silicon particles are refined into smaller faceted shapes, although the eutectic remains essentially unchanged⁴ (see Fig.5) It is known that phosphorus addition reacts first with aluminum in the melt and forms compound AlP which is thought to be a good substrate for heterogeneous nucleation of silicon crystal. In this process, nucleation kinetics rather than growth kinetics are probably altered.

Since metallic modifiers react in a melt with phosphorus, the resultant microstructure depends on that which remains in excess after phosphide formation. It is not possible to produce simultaneous modification and refinement: the processes are quite separate.

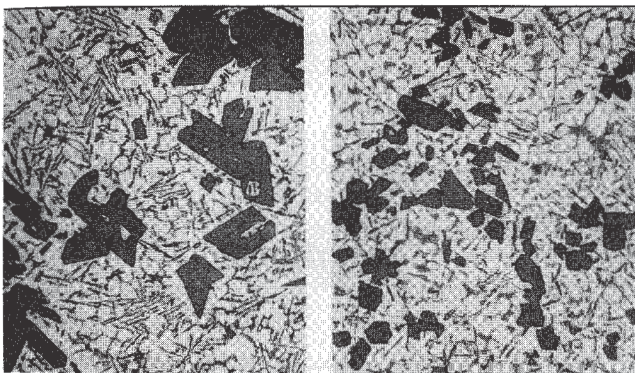


Figure 5 Effect of phosphorus refinement on primary silicon particles in hyper-eutectic Al-Si alloys: a) without phosphorus addition, b) with phosphorus addition^[3].

Nucleation and Thermal Analysis

It has been argued that modification mechanism also involves nucleation kinetics. The supporting evidence seems to be that (a) for commercial Al-Si alloys modification process brings about a change in solidification mode from equiaxed to columnar growth, which indicates the nucleation sites in the melt are eliminated by modifiers such that the nucleation kinetics is altered; (b) the cooling curve of modified Al-Si eutectic alloy shows a large supercooling before recalescence and this was considered as an indication of reduced nucleation events. It will be seen, however, in the following context that this evidence can not actually support the argument.

As mentioned earlier, metallic modifiers are very active in a melt and would first clean up the existing phosphide etc. which could be potential nucleation sites in the liquid for equiaxed growth. This side effect is more pronounced in "dirty" commercial alloys that contain various impurities but it does not affect pure Al-Si alloys in which modification is achieved without change in overall solidification pattern. Other convincing evidence is the case of complete modification of unidirectionally solidified casting, where the possibility of nucleation of silicon in the liquid is removed.

Thermal analysis is instructive but requires some care with interpretation. Referring to the measured cooling curves for nominal eutectic composition with a cooling rate, $\epsilon = 4 \text{ Kmin}^{-1}$, Fig.6(a)^[6], unmodified alloy shows 1-2K of supercooling and a well defined horizontal arrest, while with modification the eutectic arrest is depressed by some 5-6K at the same cooling rate, with similar relative supercooling and recalescence and with a small arrest at the extended aluminum liquidus, corresponding to the aforementioned primary dendrites. The corresponding heating curves show only a small depression of the melting point, $\approx 1\text{K}$, which could be attributed partly to the form of the Al-Na phase diagram and monotectic reaction therein. On either side of the eutectic composition, the aluminum liquidus is unaffected by modification but the silicon liquidus is depressed, as previously mentioned and shown in Fig. 1, where the equilibrium and kinetic boundaries are distinguished.

The cooling curve data are entirely compatible with a modification mechanism based on modified growth kinetics, rather than one involving the nucleation kinetics, even though there is supercooling and recalescence in both cooling curves. It is a common fallacy to suppose that supercooling must automatically imply delayed nucleation, because retarded growth kinetics can produce the same or a similar thermal effect. Simple calculations illustrate the relative influences of modified growth versus modified nucleation kinetics. In Fig. 6(b), the calculated cooling curves are based on a simple model for nucleation and spherical growth without impingement, assuming two arbitrary densities of nucleation sites, $N_1 = 10 \text{ mm}^{-3}$ and $N_2 = 2 \times 10^{-6} \text{ mm}^{-3}$, combined with two rather extreme growth rate dependencies of the form $V = A\Delta T^n$, where larger A and smaller n values correspond to relatively rapid radial growth rates, V, at low undercooling, ΔT , and vice versa (see Figure 7). Combining these alternatives, curve #1 is for normal growth from many sites, $N_1 = 10 \text{ mm}^{-3}$ and $V = A_1\Delta T^2$, and is numerically similar to the unmodified arrest of Fig. 6(a). Curve #2 corresponds to the same number of nucleation sites but with a growth equation which might match with modified molecular attachment kinetics, $V = A_2\Delta T^5$; it fits

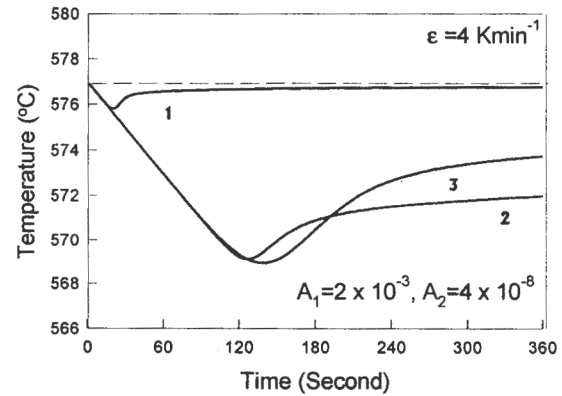
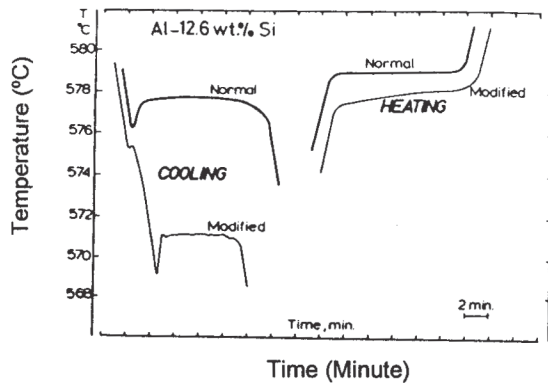


Figure 6 Comparison of measured cooling curves with modelling results for Al-Si eutectic alloy. a) Measured cooling/heating curves of both unmodified and sodium modified alloys; b) Modelling results: 1 - Unmodified, $N_1 = 10 \text{ mm}^{-3}$ and $V=A_1\Delta T^2$, 2 - Change in growth mechanism: $N_1 = 10 \text{ mm}^{-3}$ and $V=A_2\Delta T^5$, 3 - Change in nucleation densities: $N_2 = 2 \times 10^{-6} \text{ mm}^{-3}$ and $V=A_1\Delta T^2$.

reasonably well with the measured curve of Fig. 6(a) and the supercooling has nothing to do with nucleation changes. Curve #3 is for the same growth rate equation as for curve #1, but with the density of nucleation sites reduced sufficiently ($N_2 = 2 \times 10^{-6} \text{ mm}^{-3}$) to produce the same maximum supercooling as curve #2, and since the growth rate is not reduced, the temperature continues to rise at longer times. However, in order to simulate the same supercooling as that observed experimentally, it was necessary to assume that nucleation sites were improbably remote, at nearly 100 mm apart! Modified nucleation does not appear to offer a reasonable alternative to modified growth and indeed, attempts to identify the eutectic cell or grain size by delineation with a third component, namely copper^[10], do not indicate any significant difference between the modified and unmodified material, as far as eutectic cell or grain sizes are concerned. In contrast, the supercooling before recalescence for the phosphorus refined alloys is almost eliminated entirely, which is compatible with the increase of nucleation sites due to the formation of phosphide in the melt^[3].

It remains to understand how the modified growth actually works to yield the fibrous rather than flake morphology. The clue seems to lie in the dramatic rise in twin density and suppressed growth temperature. We have to suppose that the modifier must be adsorbed on the silicon-liquid interface

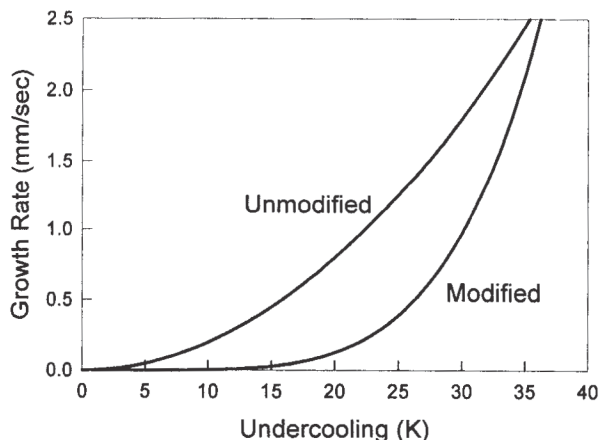


Figure 7 Relationships between growth rate and undercooling in the numerical model for unmodified and modified Al-Si eutectic alloys; Unmodified: $V = A_1\Delta T^2$ ($A_1=2 \times 10^{-3}$), Modified: $V = A_2\Delta T^5$ ($A_2=4 \times 10^{-8}$).

and poisons the growth, by blocking the movement of growth steps. This has two consequences, firstly, it depresses the temperature for an equivalent growth rate, causing the eutectic silicon to fall back at the duplex front, until it is more nearly level with and surrounded by the aluminum matrix and, secondly, the induced twinning offers almost a continuum of equivalent growth directions. The overall growth pattern is no longer anisotropic but becomes effectively isotropic, except on a scale of a few tens of interplanar spacings, where fine microsteps and facets occur. Whether or not the reentrant steps arising from twinning are important as atomic attachment sites remains an open question. Growth at rapid rates does not appear to depend upon the presence of twins, atoms deposit on the growth interface so rapidly that intrinsic step sources are obscured by the atomic/molecular deluge and growth becomes truly isotropic.

Conclusion

1. modification by a minor addition is to be distinguished from refinement by traces of elements in Group VB. Microscopic evidence and thermal analysis are compatible with a modified growth rather than a nucleation mechanism.
2. The result of numerical modelling of cooling curves shows that high supercooling before recalescence should not necessarily mean a reduced nucleation events but be a result of reduced growth rate.

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