

ON THE MECHANISM OF MODIFICATION OF THE ALUMINUM-SILICON EUTECTIC BY STRONTIUM: THE ROLE OF NUCLEATION

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Abstract

The purpose of this contribution is to demonstrate that the presence of strontium in hypoeutectic Al-Si alloys significantly influences the kinetics of nucleation of eutectic silicon; and therefore, contrary to current belief, a complete theory for the mechanism of modification of the eutectic phases in hypoeutectic

Al-Si alloys by strontium must address not only the Growth aspects of the process, but also its Nucleation aspects.

Keywords: eutectic phases, aluminum-silicon alloys, nucleation kinetics

Introduction

Formation of eutectic silicon in the later stages of solidification of hypoeutectic Al-Si alloys requires two processes; namely, Nucleation and Growth. The process of Nucleation involves the formation of very small silicon particles (nuclei), and the process of Growth involves the increase in size of these nuclei by further addition of silicon atoms from the eutectic liquid. The purpose of this correspondence is to demonstrate that the presence of strontium in hypoeutectic Al-Si alloys significantly influences the kinetics of nucleation of eutectic silicon; and therefore, contrary to current belief,¹ a complete theory for the mechanism of modification of the eutectic phases in hypoeutectic Al-Si alloys by strontium must address not only the Growth aspects of the process, but also its Nucleation aspects.

Nucleation of a solid phase in a liquid, such as the nucleation of eutectic silicon in molten Al-Si alloys, occurs due to thermal and/or compositional fluctuations within the bulk of the liquid that bring into existence clusters of silicon atoms with the right configuration. In the case of un-modified Al-Si alloys, nucleation of the eutectic silicon particles begins when two groups, each made up of a few silicon atoms arranged in a tetrahedron, combine to form what is typically referred to as an embryo.² The optimum shape of this embryo is dictated by surface energy considerations and an embryo bound by low energy facets of $\{111\}$ planes is the most thermodynamically stable.³ Calculation of the surface energy of various polyhedrons that can form from tetrahedrons show that a decahedron formed from five tetrahedrons in a twin relationship has the least surface energy.⁴ Hence the most stable silicon nucleus in un-modified hypoeutectic Al-Si alloys is a decahedron bound by $\{111\}$ facets as shown schematically in Fig. 1.

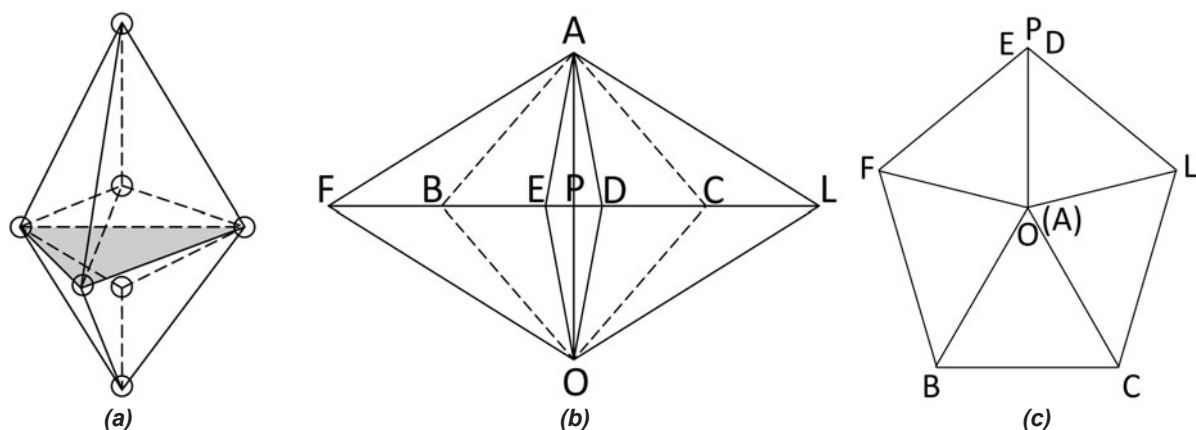


Figure 1. Schematic representations of (a) two tetrahedrons with the $\{111\}$ mirror plane (highlighted) act as a silicon embryo, (b) side view of the silicon nucleus, and (c) top view of the silicon nucleus showing the five tetrahedrons that make up the decahedron.

In the case of Al-Si alloys modified with strontium, at the beginning of nucleation of the eutectic phases, the concentration of strontium atoms in the liquid is quite low (about 0.02 wt% in an optimally modified Al-7%Si alloy)¹⁴ moreover, the solubility of strontium in silicon is negligible.^{5, 6} Therefore the probability that strontium atoms interfere with the stacking of silicon atoms during formation of the nucleus to the extent that it alters the shape of the nucleus is negligibly small and, for all practical purposes, the shape of the silicon nucleus in strontium-modified Al-Si alloys is the same as that in the un-modified alloys.

Once formed, the stability of the solid embryos in the liquid alloy depends on surface energy considerations because their formation leads to the creation of an interface between them and the liquid. Creation of this interface causes a positive energy contribution to the total free energy of the system. For this reason, nucleation of the solid in the liquid requires a certain degree of under-cooling in order to provide the additional driving force that is needed to overcome this energy barrier. The preceding analysis is known as the classical theory for homogeneous nucleation⁷ and may be represented mathematically by Eq. (1)

$$\Delta G_{Hom} = V\Delta G_B + A_S\gamma \quad \text{Equation 1}$$

In Eq. (1), ΔG_{Hom} is the total free energy of the system (liquid + solid), V is the volume and A_S is the surface area of the solid nucleus, ΔG_B is the free energy of the bulk which is equal to the difference between the free energy of the solid and the free energy of the liquid, and γ is the solid/liquid interfacial energy. For five conjoined tetrahedrons each of edge length a , Eq. (1) gives

$$\Delta G_{Hom} = \frac{5}{\sqrt{72}}a^3\Delta G_B + 5\sqrt{3}a^2\gamma \quad \text{Equation 2}$$

The presence of a catalytic surface in the Al-Si melt, e.g., pre-existing solid particles such as oxide bi-films,⁸ phosphorous-rich particles,⁹ or pre-eutectic iron-rich particles,^{10, 11} may aid nucleation by providing surfaces on which silicon can easily form. In this way, the positive energy contribution of the surface that is created by the silicon embryo can be reduced. This is known as heterogeneous nucleation⁷ and may be represented mathematically by Eq. (3)

$$\Delta G_{Het} = \left[\frac{5}{\sqrt{72}}a^3\Delta G_B + 5\sqrt{3}a^2\gamma \right] f(S) \quad \text{Equation 3}$$

In Eq. (3), $f(S)$ is some function of S where $S = \cos \delta$ and δ is the wetting angle of the liquid alloy on the catalytic particle. For an effective catalytic particle, $f(S)$ is less than 1. Differentiating Eq. (3) with respect to a , and equating the result to zero allows determination of the critical nucleus size, a^*

$$a^* = -4\sqrt{6}\frac{\gamma}{\Delta G_B} \quad \text{Equation 4}$$

Substituting the critical nucleus size into Eq. (3) allows determination of the energy barrier to heterogeneous nucle-

ation of the eutectic silicon particles, ΔG^*

$$\Delta G^* = 160\sqrt{3}\frac{\gamma^3}{(\Delta G_B)^2}f(S) \quad \text{Equation 5}$$

Song et al.¹² measured the effect of strontium on the interfacial energy (γ) between an Al-Si eutectic melt and solid silicon and reported that strontium significantly decreases γ . Similarly, Nakae¹³ reported that the interfacial energy between the Al-Si eutectic liquid and solid silicon decreases upon addition of strontium. Therefore, and according to Eq. (5), strontium significantly lowers the energy barrier (ΔG^*) and aids nucleation of eutectic silicon particles in hypoeutectic Al-Si alloys. In Eq. (5) ΔG^* depends on γ and ΔG_B . However, the interfacial energy of liquids, γ , is only a weak function of temperature¹⁵ so when it comes to temperature-dependency, we can write

$$\Delta G^* \propto \frac{1}{\Delta G_B^2} \equiv \frac{1}{(G_S - G_L)^2} \quad \text{Equation 6}$$

In Eq. (6) G_S and G_L are the free energy of the solid and the liquid, respectively so that $(G_S - G_L)$ is the under-cooling of the system. Eq. (6) states that the energy barrier for nucleation decreases sharply with increased under-cooling. Table I shows that addition of strontium to an Al-Si hypoeutectic alloy is accompanied by significant under-cooling which supports the fact that strontium changes the nucleation environment of eutectic silicon. Experiments by Bian et al. with high temperature x-rays confirm the presence of Si-Si covalent bonds in liquid Al-Si alloys.¹⁶ More importantly, Bian et al. show that addition of strontium to these alloys decreases the number of these Si-Si covalent bonds. Since small aggregates of covalently bonded silicon atoms are potential nuclei of silicon (i.e., embryos), it follows that the presence of strontium in liquid Al-Si alloys reduces the number of silicon nuclei in the melt, and hence under-cooling always accompanies solidification of strontium-modified alloys. Similarly, recent synchrotron radiation x-ray micro-diffraction experiments by Shankar et al.¹⁷ show that addition of strontium to hypoeutectic and near-eutectic Al-Si alloys reduces the average coordination number of silicon atoms, increases the average Si-Si inter-atomic distance, and changes the Si-Si-Si bond angle. All these changes in the structure of the liquid Al-Si alloy confirm Bian et al.'s assertion that strontium reduces the number of silicon nuclei during solidification of the eutectic phases in hypoeutectic Al-Si alloys. Further evidence that strontium reduces the number of silicon nuclei during solidification of the eutectic phases comes from McDonald et al. who found that adding strontium to hypoeutectic Al-Si alloys significantly increases the size of the eutectic grains (which suggests that strontium decreases the number of nucleation events of eutectic silicon).¹⁸

Hence, the presence of strontium in hypoeutectic Al-Si alloys has two opposing effects: (1) It aids nucleation of eutectic silicon by decreasing the interfacial energy of the liquid alloy; and (2) it hinders nucleation of eutectic silicon by decreasing the number of potential silicon

Table 1. Undercooling Caused by Addition of Strontium to an Al-7%Si Alloy¹⁹

Strontium (wt %)	Eutectic Nucleation Temperature (C)	Undercooling (C)
< 0.0001	577.7	-
0.015	573.3	4.42

embryos in the liquid. The significant undercooling that accompanies solidification of these alloys when they are properly modified with strontium suggests that the second effect dominates.

As solidification progresses, strontium is continuously rejected into the eutectic liquid ahead of the solid/liquid interface because of its low solubility in both silicon^{5,6} and aluminum^{10,21}, and as the end of nucleation approaches and growth begins, a large fraction of the strontium atoms would have been rejected into the continuously diminishing eutectic liquid. These strontium atoms (now at a relatively high concentration in the eutectic liquid) poison the growth of the atomic silicon layers by becoming adsorbed onto the surface steps and kinks. The adsorbed strontium atoms induce twinning in the silicon crystals by altering the stacking sequence of the atomic layers as the newly added layers seek to grow around the adsorbed strontium atoms. This is the well known Twin Plane Re-entrant Edge (TPRE) mechanism which was first introduced by Hamilton and Seidensticker to explain the growth of germanium dendrites²² and was later adopted by Lu and Hellawell to explain the growth of eutectic silicon in chemically-modified Al-Si alloys.²³

REFERENCES

- Granger D. and Elliott R., ASM Metals Handbook, 9th ed., ASM Int., Metals Park, OH, vol. 15, p 162 (1988).
- Bernal J.D., Nature, "A Geometrical Approach to the Structure of Liquids", vol. 183, Issue 4655, pp 141-147 (1959).
- Kobayashi K. and Hogan L.M., "The Crystal Growth of Silicon in Al-Si Alloys" Journal of Materials Science, vol. 20, no. 6, pp 1961-1975 (1985).
- Ino S. and Ogawa S., "Multiply Twinned Particles at Earlier Stages of Gold Film Formation on Alkali Halide Crystals" Journal of the Physical Society of Japan, vol. 22, no. 6, pp 1365-1374 (1967).
- Okamoto H., Journal Phase of Equilibria and Diffusion, vol. 27, no. 2, p 204 (2006).
- Itkin V.P. and Alcock C.B., Bulletin of Alloy Phase Diagrams, vol. 10, no. 6, p 630 (1989).
- Turnbull D. and Fisher J.C., Journal of Chemical Physics, vol. 17, p 71 (1949).
- Campbell J., International Journal of Cast Metals, vol. 3, no.1, p 65 (2009).
- Crosley P.B. and Mondolfo L.F., Modern Castings, vol. 46, p 89 (1966).
- Shankar S., Riddle Y.W., and Makhlof M.M., "Nucleation Mechanism of the Eutectic Phases in Aluminum-Silicon Hypoeutectic Alloys" Acta Materialia, vol. 52, Issue 15, pp 4447-4460 (2004).
- Liu L., Ph.D. Thesis, "Paramètres Métallurgiques Contrôlant L'évolution Microstructurale Dans Les Alliages De Fonderie Al-Si-Mg and Al-Si-Cu" University of Quebec at Chicoutimi, p 248 (2003).
- Song K., Kikuchi T., Yoshida M., and Nakae H., Nippon Kinzoku Gakkaishi, vol. 58, no. 12, p 1454 (1994) (in Japanese).
- Nakae H., in "Solidification and Casting", B. Cantor and K. O'Reilly eds., Institute Of Physics Publishing, Bristol, UK, p 326 (2003).
- Gruzleski J.E and Closset B.M., "The Treatment of Liquid Aluminum-Silicon Alloys," American Foundry Society, Des Plaines, IL, p 31 (1990).
- Verhoeven J.D., Fundamentals of Physical Metallurgy, John Wiley and Sons, New York, NY, p 225 (1975).
- Bian X., Wang W., and Qin J., Materials Science Forum, vol. 331, p 349 (2000).
- Shankar S., Prakash S.V., Malik M., Jeykumar M., Walker M.J, and Hamed M., Proceedings of 113th TMS Annual Meeting, San Francisco, CA, p 173 (2009).
- McDonald S.D., Dahle A.K., Taylor J.A, and St. John D.H., "Eutectic Grains in Unmodified and Strontium-Modified Hypoeutectic Aluminum-Silicon Alloys", Metallurgical and Materials Transactions A, vol. 35, no. 6, pp 1829-1837 (2004).
- Makhlof M.M., Proc. of the Int. Summer School on High Integrity Die Casting, WPI, Worcester, MA (2008).
- Closset B., Dugas H., Pegguleryuz M., and Gruzleski J.E., The Aluminum-Strontium Phase Diagram, Metallurgical and Materials Transactions A, vol. 17, no. 7, p 1250-1253 (1986).
- Alcock C.B. and Itkin V.P., Bulletin of Alloy Phase Diagrams, vol. 10, no. 6, p 614 (1989).
- Hamilton D.R. and Seidensticker R.G., Journal of Applied Physics, vol. 31, p 1165 (1960).
- Lu S. and Hellawell A., "The Mechanism of Silicon Modification in Aluminum-Silicon Alloys: Impurity Induced Twinning", Metallurgical and Materials Transactions A, vol. 18, no. 10, pp 1721-1733 (1987).

Technical Review & Discussion

On the Mechanism of Modification of the Aluminum-Silicon Eutectic by Strontium: The Role of Nucleation

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Reviewer: There was a long discussion published on this subject in previous issues of the IJMC. Does this contribution add to that earlier discussion?

(Editors note: the original paper, *The Modification of Al-Si Casting Alloys: Important Practical and Theoretical Aspects*, G.K. Sigworth, Alcoa Primary Metals, Rockdale, Texas was published in IJMC Spring 2008; Vol. 2 Issue 2 and the subsequent technical discussion was published in IJMC Winter 2009; Vol. 3 issue 1)

Author: *The current paper is different from the earlier discussion that appeared in IJMC. The current paper focuses on the role that strontium plays in the nucleation of the eutectic phases irrespective of what the catalyst for nucleation is. The discussion that the reviewer refers to focused on the nature of the nucleant and was initiated by Dr. Campbell's suggestion that oxide films are potent nucleants for the eutectic phases. The current paper draws on the Classical Nucleation Theory and highlights the role that strontium plays in altering the environment in which the eutectic phases form.*

Reviewer: The author refers to an article (ref. 1) in the old edition of the ASM Metals Handbook on Casting. This chapter has been changed in the new edition of the handbook and is now very similar to the previous IJMC articles.

Author: *The article in the old edition of the ASM Metals Handbook represents persisting beliefs, and I reference it only as a preamble to establishing the fact that a complete theory for the mechanism of modification of the eutectic phases in hypoeutectic Al-Si alloys must address not only the Growth aspects of the process, but also its Nucleation aspects.*

Reviewer: The author should discuss briefly some of the evidence for the role of P (or AlP) as nucleant, and how Sr might change that nucleation.

Author: *The nature of the nucleant is not the concern of this paper and that is why I do not discuss the role of P in as much as I do not discuss the role of oxide bi-films, or pre-eutectic iron-rich particles. I do not dispute that the known modifiers of eutectic silicon (e.g., Na, Sr, Ca, etc.) react with P (when P is present in the melt) and as a consequence they have the capability to neutralize AlP particles and thus affect the nucleation of the eutectic phases. However, I intentionally do not go in this detail as it may distract the reader from the purpose of the paper. Instead I say in the body of the article: "it [meaning Sr] hinders nucleation of eutectic silicon by decreasing the number of potential silicon embryos in the liquid." And I provide ample evidence for this assertion from the published literature.*