

Eutectic Modification of Al-Si Alloys with Rare Earth Metals*¹

Kazuhiro Nogita*², Stuart D. McDonald and Arne K. Dahle

Division of Materials Engineering, The University of Queensland, Brisbane, Qld 4072 - Australia

The effects of different concentrations of individual additions of rare earth metals (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) on eutectic modification in Al-10 mass%Si has been studied by thermal analysis and optical microscopy. According to the twin-plane re-entrant edge (TPRE) and impurity induced twinning mechanism, rare earth metals with atomic radii of about 1.65 times larger than that of silicon, are possible candidates for eutectic modification. All of the rare earth elements caused a depression of the eutectic growth temperature, but only Eu modified the eutectic silicon to a fibrous morphology. At best, the remaining elements resulted in only a small degree of refinement of the plate-like silicon. The samples were also quenched during the eutectic arrest to examine the eutectic solidification modes. Many of the rare-earth additions significantly altered the eutectic solidification mode from that of the unmodified alloy. It is concluded that the impurity induced twinning model of modification, based on atomic radius alone, is inadequate and other mechanisms are essential for the modification process. Furthermore, modification and the eutectic nucleation and growth modes are controlled independently of each other.

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1. Introduction

Modification of the eutectic silicon phase in hypoeutectic Al-Si alloys is carried out extensively in industry to improve mechanical properties, particularly ductility. Modification results in a structural transformation of the silicon phase from a plate-like, to a fine fibrous morphology. The fibrous morphology can be achieved in two different ways; by addition of certain elements (chemical modification) or with a rapid cooling rate (quench modification). Several elements are known to cause chemical modification, although Sr and Na are the most commonly used in industry today. Addition of other alkali, alkaline earth and rare earth metals have also been reported to cause modification, although very limited data is available in the literature.¹⁻⁴⁾

It has been shown that the fibrous silicon phase in chemically modified alloys is heavily twinned. This impurity induced twinning has been explained by a model suggesting that atoms of the modifier are absorbed onto the growth steps of the silicon solid-liquid interface^{2,5)} creating a twin plane re-entrant edge (TPRE).⁶⁾ It has been calculated that a growth twin is formed at the interface when the atomic radius of the element relative to that of silicon (r/r_{Si}) exceeds 1.65.²⁾ Because the elements causing modification, including Na, Sr, Sb, Ba, Ca, Y, Yb and misch metals (mixture of Lanthanum, Cerium, Praseodymium and Neodymium), all have an atomic radius ratio close to 1.65, the theory is generally well accepted. Among the rare earth elements, Eu and Yb have the most optimal ratios with r/r_{Si} of 1.70 and 1.66, respectively, while other rare-earth elements have a ratio in the range of 1.48 (Lu) to 1.61 (La).

Even though the impurity induced twinning theory is well accepted, there are still some questions and contradictions that remain. Recent papers discussing the twin probability and TEM crystal morphology of eutectic silicon in alloys modified by Ba, Ca, Y, Yb⁴⁾ and misch metal⁷⁾ showed there was a low density of twinning, despite the structure being well modified. The aim of the present paper was therefore to investigate the individual effects of each rare earth element on the eutectic microstructure in an Al-10 mass%Si alloy. Furthermore, the effect of each elemental addition on the eutectic solidification mode and thermal arrest were studied by quenching and cooling curve analysis, respectively. Since, according to previous models, the two elements, Eu and Yb, have an atomic radius likely to induce impurity twinning, this paper concentrates on the effect of these additions.

2. Experimental

Hypoeutectic aluminium-silicon alloys of nominal composition aluminium-10 mass% silicon were used for experimentation. The composition of the base alloy is given in Table 1. The alloys were produced by placing approximately 1 kg commercial purity aluminium and silicon in a clay-graphite crucible and heating in an electric resistance furnace to a temperature of 760°C. Metallographic samples were taken of each melt before making additions of the metallic rare earth elements. Each addition was allowed 30 to 40 min for dissolution before sampling.

Thermal analysis and quenching experiments were performed in tapered stainless-steel cups coated with a thin layer of boron nitride as shown in Fig. 1. The cooling rate just prior

Table 1 Average composition of the nominal aluminium-10 mass% silicon alloys (mass%).

Al	Si	Cu	Fe	Mg	Zn	Cr	Ni	Mn	Ti	Sr	Zr	P
Balance	9.86	<0.01	0.10	<0.01	<0.01	<0.005	<0.01	<0.01	0.007	<0.001	<0.005	<0.002

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*²Corresponding author: E-mail: K.Nogita@minmet.uq.edu.au

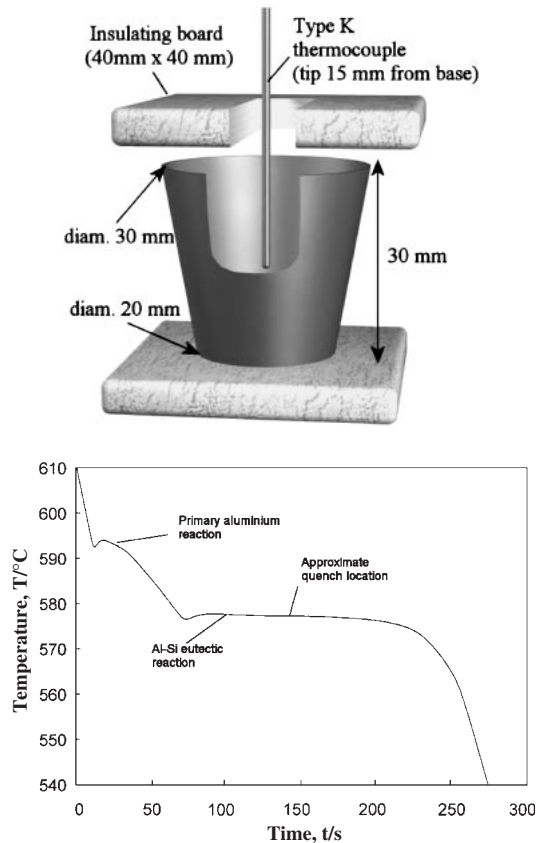


Fig. 1 A schematic (cut-away and exploded for clarity) of the experimental set-up for thermal analysis. Two samples were taken simultaneously, one with and one without a thermocouple, the cup without a thermocouple was quenched approximately half-way through eutectic solidification. An example cooling curve showing the approximate quench location is also shown.

to nucleation of the aluminium dendrites was about 1 K/s. Two samples were taken in parallel, one with and one without a thermocouple, by submerging the stainless steel cups into the clay-graphite crucible. During solidification the cooling curve from the thermocouple was monitored on a real-time display and the sample without a thermocouple was quenched at a desired stage during solidification. Although it is acknowledged that solidification will not proceed identically in both cups, this method prevents the thermocouple from interfering with solidification or from damaging the microstructure during quenching.

Two characteristic temperatures were determined for each reaction detected on the cooling curves according to the method of Tamminen.⁸⁾ These temperatures were the nucleation temperature, T_n , defined as the first noticeable change on the derivative of the cooling curve, and the growth temperature, T_g , defined as the maximum reaction temperature reached after recalescence. Solidification of the quenching samples was interrupted at a desired time during the eutectic reaction by plunging the sample into water at room temperature. Each thermocouple was calibrated prior to experimentation using commercial purity aluminium.

Samples were prepared for microscopy using standard techniques with the final polishing stage being produced by 0.05 μm colloidal silica. Macrostructures were captured using a high resolution flatbed scanner after etching for 60 seconds

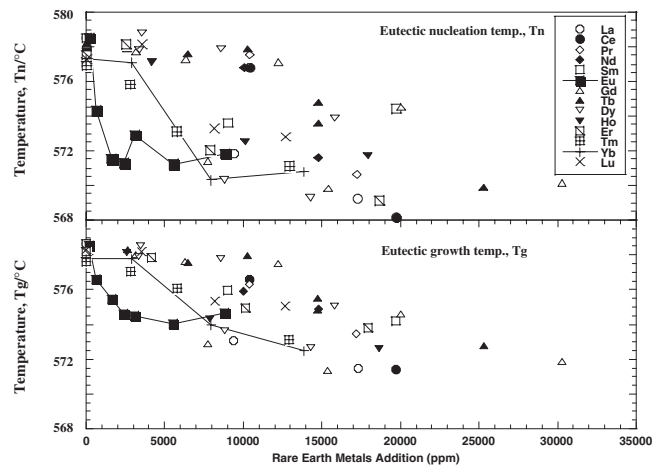


Fig. 2 Eutectic nucleation (above) and growth (below) temperatures vs. rare earth metals addition.

at room temperature in a mixture of 60 ml water, 10 g sodium hydroxide and 5 g potassium ferricyanide (Modified Murakami reagent). Optical micrographs were taken of both unetched and etched samples.

3. Results

3.1 Thermal analysis and silicon modification

Figure 2 is a plot of the eutectic nucleation (T_n) and growth temperature (T_g) with respect to each addition level of the elements.

The effects of increasing the concentration of rare earth elements on T_n and T_g are clearly observed in Fig. 2. All rare earth elements caused a decrease in the eutectic nucleation and growth temperature and, in general, the magnitude of this reduction increased steadily with the concentration of the rare earth element. The element europium is an important exception, and the decrease in the eutectic nucleation and growth temperature occurs at much lower concentrations compared with the other rare earth elements. Additions of Eu resulted in a significant decrease of T_n and T_g at levels below 5000 ppm, while the other elements required more than 10000 ppm.

Figures 3(a)–(o) show optical micrographs of fully solidified (uninterrupted) samples at the addition level corresponding to maximum modification (most refined silicon) observed for the specified element; (a) unmodified, (b) 17300 ppm La, (c) 19700 ppm Ce, (d) 17200 ppm Pr, (e) 14800 ppm Nd, (f) 19700 ppm Sm, (g) 600 ppm Eu, (h) 30300 ppm Gd, (i) 25300 ppm Tb, (j) 14300 ppm Dy, (k) 18700 ppm Ho, (l) 17900 ppm Er, (m) 12900 ppm Tm, (n) 13900 ppm Yb, and (o) 12700 ppm Lu. As expected, a coarse plate-like silicon morphology was observed in all unmodified samples. At high concentrations, all elements used in this research resulted in some changes in the appearance of the eutectic silicon. With the exception of Eu, the structural transition was limited to a refinement of the coarse plate-like silicon structure to a finer, but still plate-like, morphology. Europium additions resulted in a fully modified, fibrous silicon structure, and modification was complete with additions of 600 ppm Eu, i.e. a fine fibrous eutectic morphology was observed throughout the entire sample.

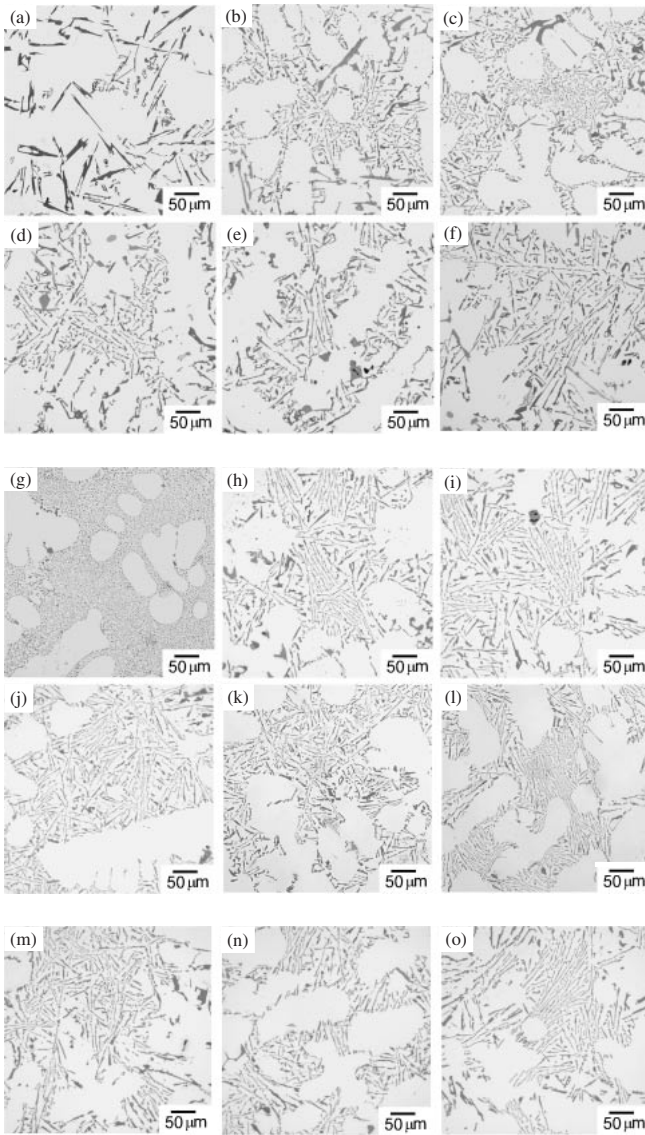


Fig. 3 Optical micrographs of fully solidified samples at the addition level corresponding to the maximum modification for the specified element; (a) unmodified, (b) 17300 ppm La, (c) 19700 ppm Ce, (d) 17200 ppm Pr, (e) 14800 ppm Nd, (f) 19700 ppm Sm, (g) 600 ppm Eu, (h) 30300 ppm Gd, (i) 25300 ppm Tb, (j) 14300 ppm Dy, (k) 18700 ppm Ho, (l) 17900 ppm Er, (m) 12900 ppm Tm, (n) 13900 ppm Yb, and (o) 12700 ppm Lu.

3.2 Eutectic solidification modes

The microstructures of quenched samples of unmodified, Eu and Yb addition samples are shown in Fig. 4. The samples were quenched mid-way through eutectic solidification. The dark areas in each macrograph are a combination of primary aluminium dendrites and aluminium-silicon eutectic that solidified prior to quenching, while the lighter areas were liquid at the time of quenching. There is a well-developed network of primary aluminium dendrites in all samples. In the unmodified alloy in Fig. 4(a) there is a high density of small eutectic grains, the majority are of the order of 100-200 μm in their longest dimension. As shown in the micrograph (inset), each of these grains are not spherical, but have the typical rough morphology of an unmodified eutectic interface. Many of the samples to which the rare earth elements were added displayed completely different eutectic grain structures compared to the unmodified alloy and typical examples, for Eu and Yb additions, are observed in the macrographs in Figs. 4(b) and (c). In these alloys, the nucleation of eutectic grains has been suppressed and there are a small number of large eutectic grains, up to several millimetres in diameter, with a globular appearance. There does not appear to be a fixed relationship between the eutectic grain structure and the eutectic morphology; for instance, the eutectic morphology in the Eu modified alloy is fibrous, while that in the Yb modified sample (b) is plate-like, although both display large eutectic grains.

4. Discussion

The fine fibrous eutectic structure that was obtained with Eu additions is typical of that obtained with conventional modifiers such as sodium and strontium.⁹⁾ Modification improves with increasing additions of Eu until a fully modified eutectic structure is obtained at 600 ppm Eu. As is commonly observed with Sr and Na, modification with Eu results in a significant depression of the eutectic nucleation and growth temperatures.

Large additions of Yb and other rare earth elements (besides Eu) did not modify the eutectic silicon and only resulted in a small refinement of the plate-like morphology. Lu and Hellowell²⁾ reported significant eutectic modification with Yb, documenting results for an addition level of 5000 ppm. On the contrary, our results indicate that even at

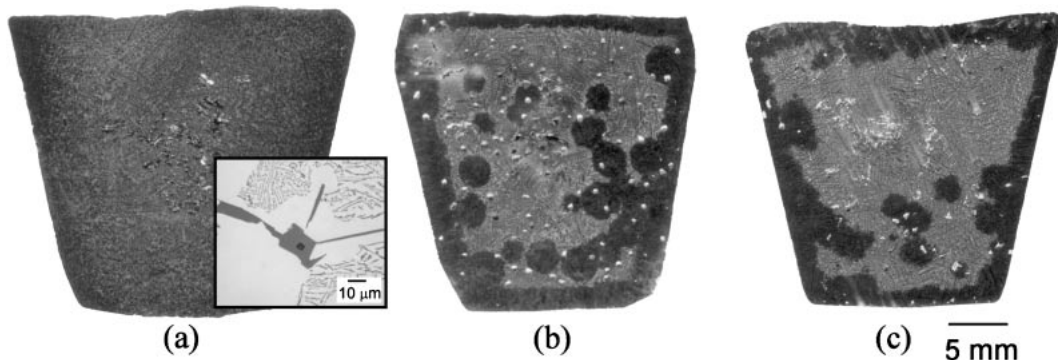


Fig. 4 Macrographs of the aluminium-10 mass% silicon castings that have been quenched during solidification (etched). (a) unmodified, (b) 600 ppm europium and (c) 13900 ppm ytterbium. The dark areas are a mixture of primary aluminium dendrites and aluminium-silicon while the lighter areas were liquid at the time of quenching.

additions of 13500 ppm Yb, modification does not occur and the silicon is still plate-like, although somewhat refined. The behaviour of the majority of rare earth elements is therefore more similar to that of Sb than Sr or Na.

In modified alloys, the heavily twinned Si fibres are suggested to be crystallographically very imperfect and able to bend, curve and split to give a fine microstructure.⁵⁾ All of the elemental additions studied in this paper, fall within the atomic radius range proposed by Lu and Hellawell²⁾ to cause twinning. The observation that elements within this range of radii behave differently suggests that the criterion is insufficient on its own to determine and predict the effectiveness of a modifying element. It should be noted, however, that the mechanisms causing refinement of the silicon phase as opposed to modification are, as of yet, undetermined and further developments of the modification mechanism are required.

All elemental additions studied in this work cause a depression of the eutectic arrest to lower temperatures with increased addition level. The eutectic growth temperature is often used as a reference for describing modification level and it has been suggested that a modification rating can be determined automatically from this temperature without microstructural analysis. Figure 2 (below) shows a plot of the eutectic growth temperature as a function of addition level for the elements studied. The figure shows that all elements decrease the growth temperature, and that the growth temperature for most of the higher addition levels is in the range of 571–574°C. Although all elements are found to reduce the growth temperature, only additions of Eu result in a fibrous, well-modified eutectic. This indicates that there is not a direct relationship between silicon morphology/modification rating and eutectic growth temperature. Therefore, although a low eutectic growth temperature is characteristic of a well-modified structure, it would not alone be a significant predictor of modification for an unknown addition.

With reference to Fig. 4, it can be seen that additions of Yb and Eu greatly reduce the number of eutectic grains compared to the unmodified alloy. There is not a large difference between the number of eutectic grains in the Yb and Eu containing samples. In a study of eutectic solidification mechanisms in hypoeutectic Al-Si alloys, Dahle *et al.*^{10,11)} proposed three possible solidification modes. The three modes are:

Mode I: nucleation and growth opposite the thermal gradient;
 Mode II: nucleation on the dendrites; and
 Mode III: heterogeneous nucleation of eutectic grains in the interdendritic liquid.

While unmodified alloys solidify according to Mode II, many of the rare earth additions promote nucleation and growth according to Mode III, or often a combination of Mode I and III. The quenching results show clearly that the samples containing additions of Eu and Yb display eutectic growth that appears to be a combination of modes I and III.

Modification is therefore not only causing alterations in the morphology of the eutectic silicon, but also differences in the nucleation behaviour. It has previously been shown that

additions of the conventional modifying elements strontium and sodium both result in a transition in the silicon morphology and a reduction in the number of eutectic grains that nucleate.^{12,13)}

5. Conclusions

(1) The modifying action of many rare earth metals in an Al-10 mass% Si alloy has been investigated. All rare-earth elements had some effect on the eutectic silicon. Of all elements tested, Europium was the only element to cause a fully modified, fine fibrous silicon. The other elements only resulted in a minor refinement of the plate-like silicon morphology.

(2) All elements studied are within the atomic radii range predicted by previous models to be effective in producing growth twins on the silicon and therefore to modify. However, despite being of similar atomic diameter as Eu and having an atomic ratio of r/r_{Si} close to the ideal ($r/r_{\text{Si}} = 1.65$), Yb additions did not cause a flake-fibrous transition. This indicates that the ratio of atomic radii of a potential modifying element is not itself capable of predicting a fibrous transition in the eutectic silicon.

(3) The eutectic solidification modes were determined by metallographic observations of samples quenched during the eutectic arrest. The results show that many of the rare earth elements, including Eu and Yb additions, promote alterations in the eutectic nucleation and growth mode. There does not appear to be a fixed relationship between the nucleation and growth modes and the eutectic silicon morphology, indicating they are controlled by independent mechanisms.

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REFERENCES

- 1) S. T. Chiu: *Z. Metallkde.* **57** (1966) 396–401.
- 2) S. Z. Lu and A. Hellawell: *Metall. Trans. A* **18A** (1987) 1721–1733.
- 3) J. Chang: *J. Mater. Sci. Lett.* **20** (2001) 1305–1307.
- 4) K. Nogita, J. Drennan and A. K. Dahle: *Mater. Trans.* **44** (2003) 625–628.
- 5) L. M. Hogan and M. Shamsuzzoha: *Mater. Forum* **10** (1987) 270–277.
- 6) R. S. Wagner: *Acta Metall.* **8** (1960) 57–60.
- 7) J. Y. Chang and H. S. Ko: *J. Mater. Sci. Lett.* **19** (2000) 197–199.
- 8) J. Tamminen: *Doctoral Dissertation, Thermal analysis for investigation of solidification mechanisms in metals and alloys*, (Stockholm University, 1988).
- 9) J. E. Gruzleski: *Trans. Am. Foundry. Soc. (AFS Trans.)* **100** (1992) 673–683.
- 10) A. K. Dahle, K. Nogita, J. W. Zindel, S. D. McDonald and L. M. Hogan: *Metall. Mater. Trans. A* **32A** (2001) 949–960.
- 11) A. K. Dahle, J. Hjelen and L. Arberg: *Proc. 4th Decennial Int. Conf. on Solidification Processing*, Eds. J. Beech and H. Jones, University of Sheffield, Sheffield, UK (1997) 527–530.
- 12) K. Nogita and A. K. Dahle: *Mater. Trans.* **42** (2001) 207–214.
- 13) K. Nogita, S. D. McDonald, J. W. Zindel and A. K. Dahle: *Mater. Trans.* **42** (2001) 1981–1986.