

Refinement and modification of Silicon phases in Solidification of high purity hypereutectic Al-15Si alloy

Kawther Al-Helal^{1,a}, Ian Stone^{1,b} and Zhongyun Fan^{1,c}

¹The EPSRC Centre - LiME, BCAST, Brunel University,
Uxbridge, Middlesex, UB8 3PH, UK

^a Kawther.Al-helal@brunel.ac.uk, ^b Ian.Stone@brunel.ac.uk,
^c Fan.Zhongyun@brunel.ac.uk

Abstract

The effect of phosphorus and calcium content on the morphology of silicon phases in solidification of high purity Al-15Si alloy in comparison with commercial purity alloy was investigated. The optical micrographs show that typical microstructures of conventionally cast high purity Al-15Si consists of irregular coarse primary silicon particles with average particle size of approximately 68 μm dispersed in lamellar eutectic structure. While, typical microstructure of commercial purity Al-15Si consist of a perfect octahedron coarse primary Si with average particle size of approximately 34 μm and the eutectic matrix have a fibrous morphology. Adding 20 ppm P was quiet enough to refine primary silicon in high purity Al-15Si alloy and to reduce the average particle size to 20 μm . While, the same amount of P reduced the average particle size primary silicon in commercial purity Al-15Si alloy to 25 μm . Adding 30 ppm of Ca to the high purity Al-15Si modify the eutectic Si to a fibrous structure with shifting the apparent eutectic position such that no primary silicon is evident.

Key words: Hypereutectic Al-Si alloys, refinement, modification, High purity Al-Si alloys, Calcium effect.

1 Introduction

Hypereutectic Al-Si alloys are currently the most widely used aluminium-based alloys in aerospace and military industry, particularly in parts such as brake rotors, engine blocks and cylinder liners, pistons, gears, etc. [1]. The increasing importance of Al-Si alloys is due to their excellent mechanical and casting properties such as good corrosion resistance, outstanding abrasion, low thermal expansion and high strength-to-weight ratio [2]. The machinability of unrefined and unmodified hypereutectic Al-Si alloy is worse due to the presence of coarse primary silicon and long needle like eutectic silicon matrix. Usually, in real casting practice, fine particles of primary Si with uniform distribution in modified eutectic structure are desired. To increase the industrial applicability of hypereutectic Al-Si alloys, various methods have been used to refine and modify the silicon phases. Microstructure control using minor element addition has been the most popular

method due to its simplicity. Apart from the small amount of coexisting elements in Al-Si alloy, some elements are added into the Al-Si melt to a significant quantity so that the alloy's sensitivity to heat treatment and microstructure is changed. Alloying elements can form fine precipitates, modify silicon phase morphology, refine grain size and reduce the effects of defects and thus can usually increase both fatigue and wear resistance. Thus alloying has become an effective method to improve the microstructure and mechanical properties of Al-Si alloy. Alloying elements used in the Al-Si alloy often include Fe, Mg, Cu, Mn, Ni, Zn, Pb, P, Na, Sb and Sr [3]. Generally, Na, Sr, Ca or Sb are the typical modifiers of the highly twinned Si structures to produce fibrous eutectic structure while phosphorus can refine primary Si more effectively due to the nucleation of AlP, leading to an optimum particle size of 15~20 μm .

Suzuki and Oshir [4] have invented an efficient method of eliminating P from molten aluminium by addition of Ca at a temperature of 923 to 1123K followed by blowing chlorine gas or a chloride flux to remove calcium phosphide with the forming dross to improve modification of hypoeutectic Al-Si alloys with Sr.

The objective of this research is to investigate the effect of Ca and P content on morphology of silicon phases in solidification of high purity Al-15Si alloy in comparison with solidification of commercial purity Al-15Si alloy.

2 Experimental procedures

A series of high purity Al-15Si and Al-15Si-Ca alloys, with and without P additions, were prepared by using 4N purity Al (supplied by Hydro Aluminium High Purity GmbH, Grevenbroich, Germany) as well as 5N purity Si (supplied by Aldrich). The P content in the 4N Al was determined by glow discharge mass spectroscopy at Evans Analytical Group (Tournefeuille, France) and was 0.4 ± 0.08 ppm [5]. P was added in the form of CuP shot (Supplied by Aura Metals Ltd) and Ca added as 99.9% Ca powder (supplied by Riedel-de Haen). The aluminium was cleaned in NaOH solution followed by distilled water and the silicon cleaned in methanol. The aluminium and silicon were melted under argon atmosphere in an electrical resistance furnace, and held at 800 °C for 30 min to ensure a homogeneous melt. For Al-15Si-P and Al-15Si-Ca alloys, Ca powder and CuP shot were wrapped in aluminium foil and inserted into the Al-15Si melt. After 15-20 min of addition, samples were taken by using a preheated steel mould which was then water cooled at approximately 15 K/s. The same experiments were repeated to prepare commercial purity Al-15Si, Al-15Si-P and Al-15Si-Ca alloys by melting and diluting an Al-50Si master alloy with commercial purity aluminium LM0 at 1100 °C for 3 h in a clay crucible. The compositions of raw materials are listed in Table 1.

Table 1 Aluminium alloys composition wt%

Alloy	Cu	Mg	Si	Fe	Mn	Ni	Zn	Pb	Sn	Ti	Cr	Al
LM0	0.03	0.03	0.30	0.40	0.03	0.03	0.07	0.03	0.03	-	-	Bal.
Al-50Si	0.08	0.28	51.0	0.32	0.02	0.01	0.02	0.02	0.01	0.09	0.03	Bal.

Longitudinal sections of resulting samples were prepared by the standard technique of grinding with SiC abrasive papers and polishing with 1 μ m diamond suspension followed by silica suspension. The chemical composition for all alloys was analysed using a “Worldwide Analysis System (WAS) AG, Foundry master”. Microstructure characterization was accomplished using an optical microscope (Carl Zeiss Axioskop 2 MAT) equipped with image analysis software.

3 Results and discussion

3.1 Solidification of inoculated/unmodified high purity and commercial purity Al-15Si alloy

Figure 1 show the optical micrographs of unmodified/unrefined high purity Al-15Si alloy. It consists of irregular coarse primary silicon particles, 68 μ m in size, and dispersed in lamellar eutectic structure. Figure 2 show the typical micrographs of commercial purity Al-15Si which consist of a perfect octahedron coarse primary Si with average particle size of approximately 34 μ m and the eutectic Si had a mostly fibrous morphology.

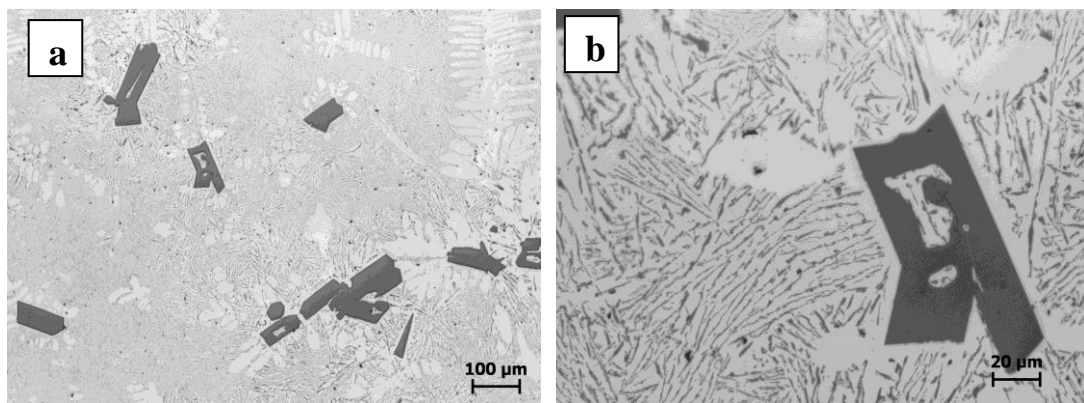


Figure 1 Optical micrograph of high purity Al-15Si (4N Al+5N Si) solidified from 800°C. (a) low magnification and (b) high magnification.

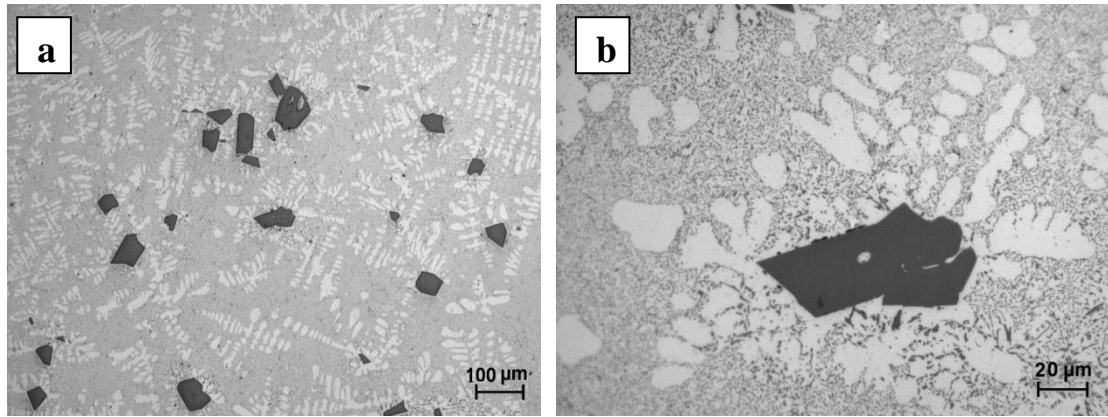


Figure 2 Optical micrograph of commercial purity Al-15Si solidified from 800°C. (a) low magnification and (b) high magnification.

The chemical composition for commercial purity Al-15Si alloy analysed using a “Worldwide Analysis System (WAS) AG, Foundry master” showed that Ca content is more than 200 ppm and P content is less than 20 ppm. Hence, the fibrous structure of eutectic Si in solidified commercial purity Al-15Si alloy is due to the presence of Ca in amount enough to modify the eutectic matrix and restrict the growth of primary silicon. It is well established that calcium and phosphorus are among the various trace elements reported to be exist in commercial Al-Si alloys. The origin of Ca impurity in Al-Si alloys is mainly from the commercial purity silicon [6]. The source of phosphorus in Al-Si alloy is its raw materials which include the phosphorus content of painted and inked aluminium scrap and the phosphorus content of metallic silicon [7].

In solidification of inoculated and unmodified high purity Al-15Si alloy, the mechanism for homogeneous nucleation of primary silicon and modification of eutectic silicon are as follows:

3.1.1 Homogeneous nucleation and growth mechanism of primary silicon in inoculated hypereutectic Al-Si alloys

During solidification of inoculated hypereutectic Al-Si alloys, Si atoms will arrange themselves in the form of tetrahedrons when close to their freezing point. Then, the silicon nucleates on embryos that form by the coalescence of these tetrahedrons. The optimum shape of these embryos is determined by surface energy considerations. An embryo bound by low energy facets of {111} planes is the most thermodynamically stable. Thus, the most stable silicon nucleus is a decahedron bound by {111} facets. This formed nucleus grows at locations with multiple twins by the Twin Plan Re-entry Edge (TPRE) mechanism. Hence, primary silicon nucleates on equiaxed, twinned embryos and grows into different morphologies [8]. The most commonly observed primary silicon morphologies are massive primary silicon, which is also known as polygonal silicon, and star-like primary silicon [9].

Xu *et al.* [10] suggested different sequences of crystal growth of octahedral primary silicon in inoculated hypereutectic Al–Si alloys as shown in Figure 3.

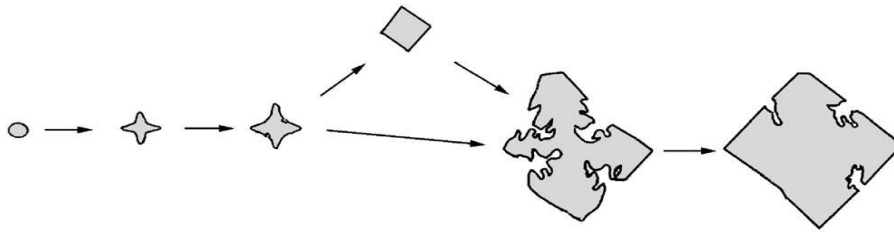


Figure 3 A schematic illustrating the different growth sequences of octahedral primary silicon in unmodified Al–Si alloys [10].

According to the vector relationship for silicon crystal, illustrated in Figure 4, they suggested that at the initial stage, primary silicon crystal along [100] direction will rapidly grow to a stable first branching. As a result, growth is suppressed in all directions except the high-mobility [100] direction due to the strong faceting tendency of the growing primary silicon crystal. They found that:

- The primary silicon crystal will grow as a perfect octahedron when $V_{[100]}/V_{[111]} = 1.5$ as observed in solidification of commercial purity Al–Si alloys and shown in Figure 2.
- If $V_{[100]}/V_{[111]} < 1.5$, the primary silicon crystal will grow as other irregular morphologies which occurs in solidification of high purity Al–Si alloys and as shown in Figure 1.

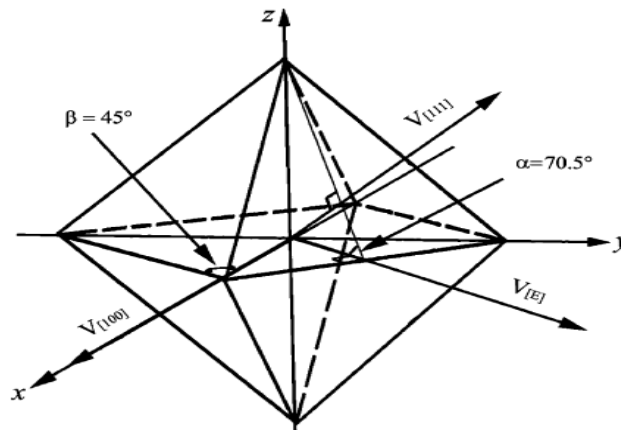


Figure 4 A schematic illustrating the vector relationship between the growth rate $V_{[100]}$ normal to the [100] growth direction, growth rate $V_{[E]}$ normal to the edges and the growth rate $V_{[111]}$ normal to the {111} facets [10].

Some investigations have been made to study the octahedral morphologies of primary silicon in inoculated hypereutectic Al–Si alloys. Wang *et al.* [11] have investigated the relationships between the morphologies and growth mechanisms of primary silicon and believed that octahedral primary silicon can be formed primarily by layer growth, which was the generation of repeated parallel

{111} planes on {111} facets. At the same time, they derived a general equation for stable faceted growth of the silicon, and indicated that no evidence of the Twin Plan Re-entry Edge (TPRE) growth mechanism was found in the growth of the octahedral-type crystals. However, they also suggested that the dislocation mechanism provided a major source for layer growth of the primary silicon crystal by the observation of dislocation spirals on {111} facets [12].

3.1.2 Modification mechanism of unmodified eutectic Si in Al-Si alloy

In the Al-Si system, silicon is a non-metal with directed covalent bonds. It tends to grow anisotropically into faceted crystals and hence it requires more undercooling for its growth than the isotropic aluminium phase. Therefore, the coupled region in the Al-Si system is asymmetric. Coupled regions represent fields within the phase diagram where the two phases of the eutectic are organized in the solid in such a way as to allow diffusion in the liquid to occur effectively at a duplex solid/liquid front.

The morphology of unmodified eutectic Si is typically coarse and flaky and is usually observed in slowly cooled foundry alloys and when no chemical modifiers are added.

Wagner [13] proposed a Twin Plan Re-entry Edge (TPRE) growth mechanism of the eutectic silicon in un-modified Al-Si alloys. The unmodified plate like form of Si can grow easily only in the $\langle 112 \rangle$ crystallographic direction, and when the crystal structure of Si is taken into account, this implies that the large flat faces of the crystal are $\langle 111 \rangle$ planes. A very important feature of Si crystallization is that twins are easily formed and hence unmodified Si occurs basically in an unbranched, flat-plate morphology.

Crosley and Mondolfo [14] suggested that the needle-like silicon particles observed in unmodified alloys must be flakes or sheets. Now, with the availability of electron microscopy, it is confirmed that silicon in unmodified Al-Si eutectics has the flake-like structure.

3.2 Solidification of Al-15Si alloy refined with P

The effect of adding P on the morphology of silicon in solidification of high purity and commercial purity Al-15Si alloy was studied. It is clear from the optical micrograph that adding 20 ppm P was quiet enough to refine primary silicon and to reduce the average particle size from 68 μm to 20 μm as shown in Figure 5. While, adding 20ppm P to commercial purity Al-15Si refine the primary silicon and reduce the average particle size from 34 μm to 25 μm as shown in Figure 6. The eutectic Si structure in solidification of high purity and commercial purity Al-15Si+20ppm P alloys was lamellar structure.

In heterogeneous nucleation of primary silicon, the added phosphorus combines with molten aluminium to form tiny, insoluble AIP particles. Aluminium phosphide (AIP) particles are often suggested to be the nucleation site for silicon phases in Al-Si alloys. The crystal structure and lattice

parameter of AIP are close to that of silicon, with mismatch less than 1% [15]. These particles are suspended in the melt and act as potent sites for epitaxial nucleation and growth of primary silicon. At the same time these AIP particles are responsible for the nucleation of Si in the eutectic matrix [16]. In using commercial Al-15Si, the amount of P required to refine primary silicon to less 20 μm should be more than 50 ppm.

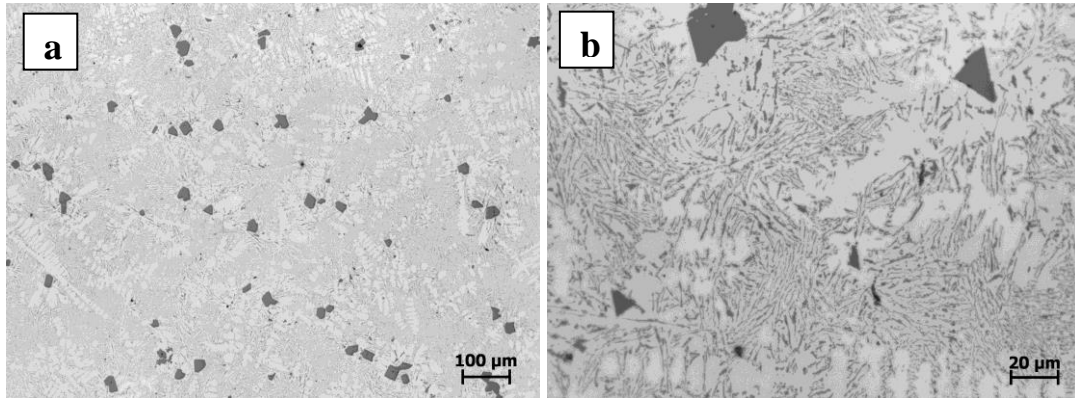


Figure 5 Optical micrograph of high purity Al-15Si+20ppm P solidified from 800 $^{\circ}\text{C}$.

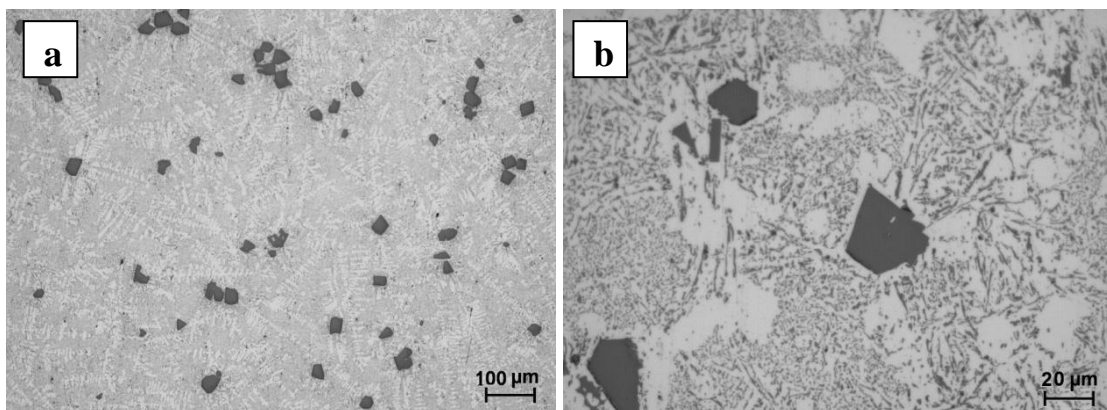


Figure 6 Optical micrograph of commercial purity Al-15Si+50ppm P solidified from 800 $^{\circ}\text{C}$.

It has been proved that high Ca content can lead to P refinement inefficiency. This phenomenon is due to the formation of Ca_xP_y compounds, which are more stable than AIP in the Al-Si melt [6]. The estimated free enthalpy of the formation of Ca_3P_2 (-506 kJ mol^{-1}) is much less than that of the AIP phase ($-111.66 \text{ kJ mol}^{-1}$) [17]. Hence, with the presence of elements with more negative enthalpy of phosphide formation, the AIP will deplete. It is important to point out that the lack of AIP phase results in an increased particle size of primary silicon.

3.3 Solidification of Al-15Si alloy modified with Ca

Figure 5 show that adding 30 ppm of Ca to the high purity Al-15Si has a significant modification effect on the eutectic Si. It is clear that, the modified high purity Al-15Si alloy contains no primary silicon particles, i.e. there was a shift in the apparent eutectic position with the addition of Ca. The

eutectic matrix in commercial purity Al-15Si alloy which contain more than 200ppm Ca, is already modified as shown in Figure 2.

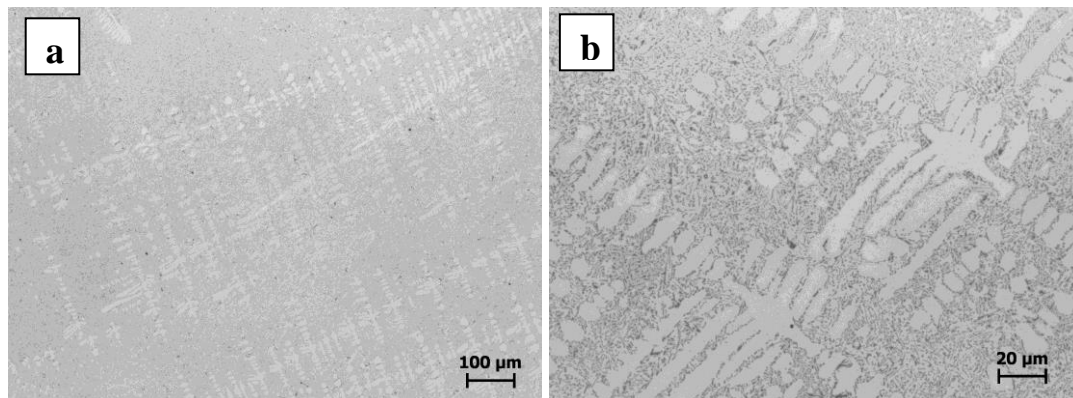


Figure 5 Optical micrograph of high purity Al-15Si+30ppm Ca alloy solidified from 800 °C.

It is well established that alloys within a few percent of the usual eutectic composition of 12.6% silicon are sensitive to the presence of a refiner such as phosphorus or a modifier such as sodium or strontium. Alloys containing 11-12% silicon easily develop numerous primary silicon particles in the presence of phosphorus, and alloys containing around 14% silicon will contain no primary silicon in the presence of sufficient sodium or strontium [18]. The addition of Ca decrease the undercooling required for lamellar-fibrous transition and this is accompanied by a complete suppression of primary silicon precipitation. It is notable that Ca modification has no effect on the incidence of primary α dendrites.

Jenkinson *et al.*[19] investigated the effect of adding Sr to high purity Al-Si alloys and they found that in the presence of 0.02% Sr no primary silicon appears in any alloy up to 17%Si. They concluded that the apparent shift of the eutectic point can be attributed to the shape of the coupled region boundary, and the suppression of primary silicon.

The typical unmodified Al-Si eutectic is closer to a lamellar structure than to a fibrous one. This structure is usually attributed to the strong anisotropy of growth of silicon and to the relatively low interfacial energy between silicon and aluminium [9]. Trace amounts of Ca can effectively modify the eutectic Si shape, just similar to that with sodium or strontium under the same melting and casting conditions. Knuutinen *et al.* [20] reported that Ca can cause a depression of the eutectic arrest and result in fibrous eutectic Si. In conclusion, due to the low level of P content in high purity Al-15Si (less than 1 ppm), the modification with 30 ppm Ca was very efficient. The optimum amount of Ca used to modify eutectic Si in commercial Al-Si alloy should be more than 50 ppm [21].

4 Summary

The conclusions from above results are:

- 1- High purity Al-15Si alloy, cast in steel mould with cooling rate 15K/s, consists of irregular coarse primary silicon particles, 68 μm in size, and dispersed in lamellar eutectic structure. While, commercial purity Al-15Si alloy consist of a perfect octahedron coarse primary Si with average particle size of approximately 34 μm and the eutectic Si had a mostly fibrous morphology.
- 2- Typical unmodified eutectic Si is closer to a lamellar structure. This is usually attributed to the strong anisotropy of growth of silicon and to the relatively low interfacial energy between silicon and aluminium.
- 3- Adding 20 ppm P was quiet enough to refine primary silicon in high purity Al-15Si alloy and to reduce the average particle size from 68 μm to 20 μm . While, the same amount of P refine primary silicon in commercial Al-15Si alloy and reduce the average particle size from 34 μm to 25 μm .
- 4- Adding 30 ppm of Ca to the high purity Al-15Si can modify the eutectic matrix to fibrous structure with no primary silicon is evident, i.e. the apparent eutectic position is shifted.

Acknowledgement

The financial support from Engineering and Physical Sciences Research Council (EPSRC), UK is acknowledged with gratitude.

References

1. Choi, H., Konishi, H. and Li, X., *Al₂O₃ nanoparticles induced simultaneous refinement and modification of primary and eutectic Si particles in hypereutectic Al–20Si alloy*. J. Mater. Sci. Eng.: A, 2012. **541**: p. 159-165.
2. Dai, H.S. and X.F. Liu, *Optimal holding temperatures and phosphorus additions for primary silicon refinement in Al–high Si alloys* Materials Science and Technology, 2009. **25**(10): p. 1183-1188.
3. Ye, H., *An overview of the development of Al-Si alloy based material for engine applications*. J. Mater. Eng. Perf., 2003. **12**(3): p. 288-297.
4. Suzuki, T. and N. Oshiro, *US Pat. No. 6, 336, 955*. 2002.
5. Zarif , M., B. Mckay, and P. Schumacher *Study of Heterogeneous Nucleation of Eutectic Si in High-Purity Al-Si Alloys with Sr Addition*. J. Metal. Mater. Trans. : A, 2011. **42**: p. 1684-1691.
6. Qiao, J., X. Liu, and X. Bian, *Relationship between microstructures and contents of Ca/P in near-eutectic Al-Si piston alloys*. J. Mater. Lett., 2005. **59**(14-15): p. 1790-1794.

7. Mayuki, M., *Sources of Phosphorus and Shrinkage Characteristics of Al-Si Alloy*. Journal of Japan Foundry Engineering Society, 2002. **74**(6): p. 383-387.
8. Bernal, J.D., *Geometrical approach to the structure of liquids* Nature, 1959. **183**(4655): p. 141-147.
9. Makhlouf, M.M. and H.V. Guthy, *The aluminum-silicon eutectic reaction: mechanisms and crystallography*. Journal of Light Metals, 2001. **1**(4): p. 199-218.
10. Xu, C.L., et al., *Growth of octahedral primary silicon in cast hypereutectic Al-Si alloys*. J. Crys. Grow., 2006. **291**(2): p. 540-547.
11. Wang, R.Y., Lu, W.H. and Hogan, L.M. , *Twin Related Silicon Crystal in Al-Si Alloys and Their Growth Mechanism*. J. Mater. Sci. Technol., 1995. **11**: p. 441-449.
12. Wang, R.Y., W.H. Lu, and L.M. Hogan, *Faceted Growth of Silicon Crystals in Al-Si Alloys*. J. Met. Mater. Trans. :A, 1997. **28**: p. 1233-1243.
13. Wagner, R.S., *On the growth of germanium dendrites*. Acta Metallurgica, 1960. **8**(1): p. 57-60.
14. Crosley, P.B. and L.F. Mondolfo, *The modification of Aluminum-Silicon alloys*. Mod. Cast, 1966. **46**(March): p. 89-100.
15. Nogita, K., et al., *Aluminium phosphide as a eutectic grain nucleus in hypoeutectic Al-Si alloys*. Journal of Japanese Society of Microscopy, 2004. **53**(4): p. 361-369.
16. Campbell, J. and M. Tiryakioglu, *Review of effect of P and Sr on modification and porosity development in Al-Si Alloys*. J. Mater. Sci. Technol., 2010. **26**(3): p. 262-268.
17. Li, J.H. and P. Schumacher, *Effect of Y addition and cooling rate on refinement of eutectic Si in Al-5 wt-%Si alloys*. International Journal of Cast Metals Research, 2012.
18. Jorstad, J. and D. Apelian, *Hypereutectic Al-Si Alloys: Practical Casting Considerations*. International Journal of Metalcasting, 2009. **3**(3): p. 13-36.
19. Jenkinson, D.C. and L.M. Hogan, *The modification of aluminium-silicon alloys with strontium*. Journal of Crystal Growth, 1975. **28**(2): p. 171-187.
20. Knuutinen, A., et al., *Modification of Al-Si alloys with Ba, Ca, Y and Yb*. Journal of Light Metals, 2001. **1**(4): p. 229-240.
21. Kumari, S., R.M. Pillai, and B.C. Pai, *Role of calcium in aluminium based alloys and composites*. Int. Mater. Rev., 2005. **50**(4): p. 216-238.