Effect of grain refinement treatment on the microstructure of cast Al–7Si–SiCp composites

J.A. Garcia-Hinojosa[a,*], C. González R.[a], J.A. Juárez I.[b], M.K. Surrapa[c]

[a] *Metallurgy Engineering Department, Chemistry Faculty, UNAM, Circuito de los Institutos S/N, Cd. Universitaria, 04510 México DF, Mexico*
[b] *Department of Metallic and Ceramic Materials, Institute of Materials Research, UNAM, Circuito Exterior S/N, Cd. Universitaria, 04510 México DF, Mexico*
[c] *Department of Metallurgy, Indian Institute of Science, Bangalore 560012, India*

Abstract

An addition of Ti or Ti/B is an accepted technique to produce cast aluminum alloys having fine grain size and superior mechanical properties. Present investigation focuses on the role of grain refinement treatment on the SiC particle distribution in Al-7 wt.% Si-10 vol.% SiCp cast composites and also on the degree of refinement of matrix microstructure. Composites manufactured by vortex method were treated with three different commercial grain refiners namely; K_2TiF_6 salt, Al–6Ti and Al–5Ti–1B master alloys. Microstructural characteristics including nature of distribution of SiCp in the matrix, grain size and dendritic arm spacing have been studied. It was found that complete dewetting of the SiCp and consequently their rejection from the melt takes place when the composite was treated with K_2TiF_6 salt. Improved distribution of SiCp in the matrix of composites was observed when the melt was treated with either Al–6Ti or Al–5Ti–1B master alloy. Composite melt treated with Al–5Ti–1B master alloy show excellent combination of matrix grain refinement and uniform SiCp distribution.
© 2004 Published by Elsevier B.V.

Keywords: Grain refinement; Light weight composites; Al–SiCp composites; Al–Ti master alloys

1. Introduction

Presently aluminum matrix composites (Al MMCs) are finding increased acceptance owing to their interesting combination of engineering properties. Al MMCs possess superior wear resistance, higher specific stiffness and low co-efficient of expansion [1]. It is now well understood that the reinforcement content and nature of its distribution in the matrix of the composite have profound influence on the performance of composites.

Mechanical properties of particle reinforced metal matrix composites are mainly controlled by the nature of distribution of reinforcement particles and in this regard the main challenge is how to achieve the uniform distribution of particle reinforcements in the solidified composite. Phenomena of particle pushing during solidification leads to the segregation of the particles in the intergranular and interdendritic regions of the matrix [2–5]. In composites where matrix shows a dendritic structure, the microstructural features of the dendritic phase will play an important role on the particle distribution observed in the final product. It is common industrial practice to add inoculating agents to the monolithic Al–Si molten alloys to produce fine grained microstructure, in order to promote finer and more homogeneous distribution of the intergranular regions of the dendritic network, and achieve better distribution of eutectic, the intermetallics and the shrinkage porosity formed during the last stages of solidification. All these in turn will provide improved resistance to hot tearing and better pressure tightness. Hence, it is imperative to achieve smaller grain size and uniform particle distribution in cast composites. In the case of Al–Si monolithic alloys, chemical grain refinement has been a commercial practice for many years and the conventional and proven grain refiners have been titanium, boron or combination of both, which are added

* Corresponding author. Tel.: +52 55 56225239; fax: +52 55 56225228.

either as K_2TiF_6 salt or Al–Ti or Al–Ti–B master alloys to molten alloys prior to casting [6,7]. The purpose of this work is to explore the use of conventional grain refinement as a technique to improve the SiCp distribution in cast A356/SiCp composites and to refine the matrix microstructure.

2. Experimental

In the present study A356 Al alloy has been used as matrix alloy. Three grain refiners were considered in this work: K_2TiF_6 salt, Al–6Ti and Al–5Ti–1B master alloys. Experiments were focused with a view to:

1 to find the optimum amount of grain refiner needed to produce acceptable grain refinement (ASTM grain number 11 or higher) in the monolithic A356 Al alloy;
2 to fabricate A356 Al/10 vol.% SiCp composites with and without grain refinement treatment by employing techniques which are generally used to refine microstructure of monolithic aluminum silicon alloys;
3 to characterize the nature of SiCp distribution in the matrix in each of the above cases with a view to assess the role of grain refinement on the uniformity of SiC particle distribution in the composites.

The chemical composition of the A356 Al alloy, the matrix material used is shown in the Table 1. To begin with to arrive at the optimum grain refiner needed to achieve refined microstructure corresponding to ASTM grain number 11 in the monolithic A356 alloy, different amounts of grain refiners were tried. Effective Ti content in these different amounts of grain refiners varied from 0.05 to 0.15 wt.% Ti for Al–5Ti–1B master alloy and 0.15–0.25 wt.% Ti for K_2TiF_6 salt and Al–6Ti master alloy. The maximum melt temperature was 750 °C and the grain refinement treatment temperature was 730 °C. The melt was degassed with Ar and the alloys were poured into cast iron moulds to obtain cylindrical samples of 2.5 cm diameter and 20 cm height. Macrograin size was measured as per the ASTM E112 procedure [8].

In order to evaluate the role of the grain refinement on the SiCp distribution in cast A356/10 vol.% SiCp composites, three sets of composite samples were made with and without grain refinement treatment. The composites were manufactured by the melt–stir technique in an electric furnace under argon atmosphere. Average size of SiC particles was 40 ± 8 μm. Known quantities of grain refiners (obtained based on experiments done on monolithic alloy) were mixed with SiCp and incorporated into the melt. The liquid slurry was degassed by bubbling argon for 10 min, with a gas flow rate of 1.5 l/min. During bubbling care was taken to avoid any turbulence in the melt. The dross was skimmed and the composite slurry was poured into a cast iron mould. The cast billets were cut transversally at the mid height and prepared by conventional metallographic practice. The first section was used to determine the average grain size by etching the sample with 20 vol.% $CuCl_2$ solution, followed by rinsing with 1:6 $HF:HNO_3$ concentrated solution and finally washed with cold water. The second section was examined without etching in order to measure the number of SiC particles and SiCp clusters per unit area using quantitative metallographic techniques. A minimum of 20 measurements were made randomly across the cross section of each sample. Finally this section was etched using 1 vol.% HF solution for revealing the microstructural features, including secondary arm spacing (SDAS), size of eutectic and the nature and distribution of eutectic Si particles and SiC particles in the matrix.

3. Results and discussion

Unreinforced A356 Al alloy cast without grain refinement shows grains having two types of morphologies; columnar grains located at the peripherial zone of the sample and. coarse equiaxed grains in the central region with average ASTM grain size between 7.5 and 9.0 (2600–1600 μm in diameter). This structure is very common in cast Al based alloys without grain refinement and it is normally known as ingot structure. This characteristic structure features a boundary layer adjacent to the mold wall, formed by small equiaxed crystals with random orientations, referred to as chill zone; followed by a band of elongated crystals aligned parallel to the directions of heat flow extraction, known as columnar zone; and finally a central region of equiaxed grains known as equiaxed zone. The chill crystals nucleate on or near the mould wall and begin their growth. There is competitive growth between crystal growing from the chill zone in such a way that those with the steepest thermal gradient (parallel to the dendrite arm axis direction) grow more rapidly than their less favorably oriented neighbors, giving place to the columnar zone. The development of the equiaxed zone is due to the following causes: (a) the formation of equiaxed crystals during the initial chill near the mold wall which are drifted by the growing columnar dendrites to the central zone of the cast where they become equiaxed grains, (b) to the multiplication of grains by the melting off of the arms of growing columnar dendrites due to thermal fluctuations due to convection of the liquid alloy, and (c) to the equiaxed nuclei formed at the free surface of the ingot and settled into the liquid ahead of the columnar zone [9]. The macroetched sample is shown in Fig. 1a. The average value of secondary dendrite arm spacing (SDAS) was 26 ± 5 μm and the eutectic silicon showed acicular morphology (Fig. 1b).

Table 1
Chemical composition of the metal matrix alloy (A356)

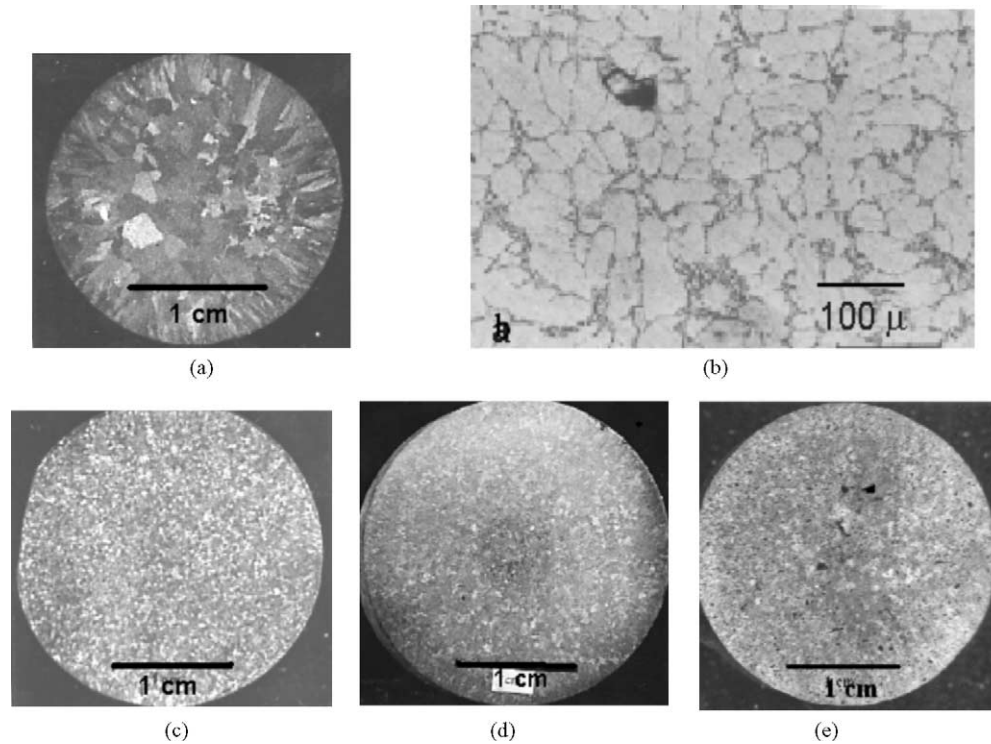| Alloy	wt.%
Si	6.9
Mg	0.25
Cu	0.48
Na	0.009
Ti	0.04
Fe	0.40
Al	Balance

Sr content: less than 0.0005 wt.%.

Fig. 1. Macrostructures of A356 monolithic alloy (a) unrefined, (b) microstructure of A356 unreinforced matrix shown acicular Si located in the interdendritic region (c) refined with 0.15 wt.% Ti with K_2TiF_6 salt, (d) refined with 0.20 wt.% Ti with Al–6Ti master alloy and (e) refined with 0.15 wt.% Ti–0.03 wt.% B with Al–5Ti–1B master alloy.

Grain size values of monolithic alloy treated with the three different grain refiners are listed in Table 2. It can be observed that the amounts of grain refiners needed to obtain the required grain size (ASTM 11) are: 0.15 wt.% of Ti for the K_2TiF_6 salt, 0.2 wt.% Ti for the Al–6Ti master alloy and 0.15 wt.% Ti for the Al–Ti–B master alloy. Secondary dendrite arm spacing in these samples were not affected by the grain refinement treatment. Further, microstructure show acicular eutectic Si, similar to that shown in Fig. 1b. The macrostructures of the three grain refined monolithic alloys are shown in Fig. 1c–e.

The macroetched samples of the composites without grain refinement shows grains having two types of morphologies;

Table 2
Relationship between ASTM grain size-refiner amount-refiner material for the Al–7Si monolithic alloy

Amount of Ti or Ti/B (wt.%)	Refiner material/ASTM[a] grain size (average size μm)		
	K_2TiF_6	Al–6Ti master alloy	Al–5Ti–1B master alloy
0.15	13 (400)	8.5 (1900)	–
0.20	15 (200)	13 (400)	–
0.25	15.5 (160)	15 (200)	–
0.01/0.002	–	–	8.5 (1900)
0.05/0.01	–	–	8.5 (1900)
0.10/0.02	–	–	9.0 (1600)
0.15/0.03	–	–	11.5 (650)

[a] ASTM E112 [5].

fine columnar grains located at the peripheral zone of the sample and fine equiaxed grains in the central region with an ASTM number 9.5–10 (1300–1100 μm) (Fig. 2a). This sample showed an average of 90 ± 12 SiC particle/mm^2 and the distribution was very non-uniform. SiCp clusters were observed in the matrix. Microstructure of the sample showed presence of SiC particles in free form as individual particle and also as clusters. On the average, there were 10 clusters/mm^2 and also it was observed that SiC particles appear to be decorating the grain boundaries of the primary phase (Fig. 2b). Reinforcement particles are generally segregated to the last freezing zone as a result of pushing particles by moving solid–liquid interfaces (particle pushing phenomena [2–5]). The absence of nucleation of α-Al on SiCp in hypoeutectic Al–Si alloys has been explained as a result of the high interfacial energy associated with the aluminium/SiC interface [10]. In Al–Si/SiCp composites it has been found [3] that both rejection and engulfment of SiC can occur as a result of interactions with the solid–liquid (S/L) interface during solidification. The engulfment/rejection behavior significantly depends on the S/L interfacial velocity and the engulfment occurs only at high interfacial velocities (over 14,800 μm/s for Al–7Si/5SiC) typical for rapid solidification processing [11]. For the conditions commonly found in conventional solidification, like those present in this work, SiC is pushed by the S/L interface. Preferential nucleation of eutectic Si was observed around SiCp clusters (Fig. 2c), while average SDAS size was 25 ± 6 μm, indicating that the presence of
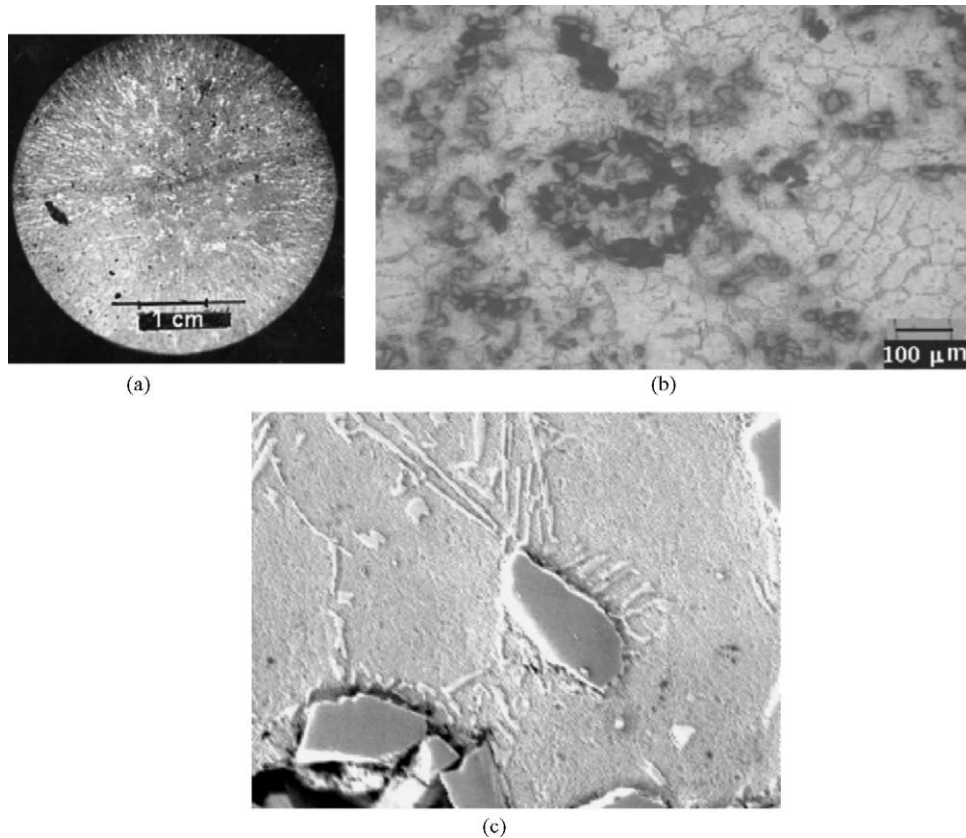
Fig. 2. Unrefined cast composite (a) macrostructure, (b) microstructure with non-uniform distribution of SiCp and (c) preferential nucleation of Si eutectic around of SiC particles.

SiCp in the A356 Al matrix does not affect this parameter significantly.

Composites treated with K_2TiF_6 refiner salt (0.15 wt.% Ti) show a predominantly columnar structure with a few coarse equiaxed grains in the central region with an ASTM number 6.5–8 (3500–2200 μm), as shown in Fig. 3a and the absence of SiC particles through the entire sample (Fig. 3b). This implies that Ti additions in the form of salt did not produce grain refinement of the matrix in the composite. Absence of refinement may be attributed to the adsorption of Ti on the SiC particles (which were eventually rejected by the melt),

reducing the concentration of Ti and $TiAl_3$ particles required for promoting fine equiaxed grains by heterogeneous nucleation. Reason for coarsening of the grain of the composites treated with K_2TiF_6 is not clear at this stage.

On the other hand, the ceramic reinforcements underwent complete dewetting and got rejected from the melt. Another microstructural characteristic was the presence of acicular eutectic Si in the matrix (Fig. 3b).

The complete dewetting and flotation of SiC particles in the composite samples treated with K_2TiF_6 salt, could be attributed to the liberation of elemental potassium and AlF_3 due
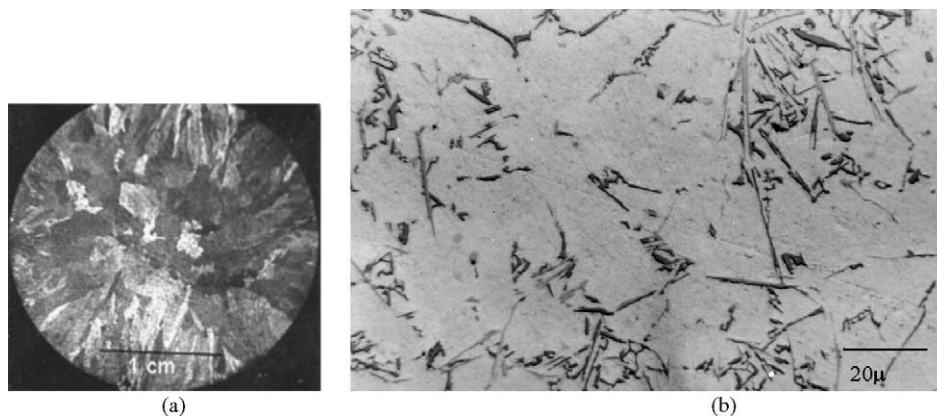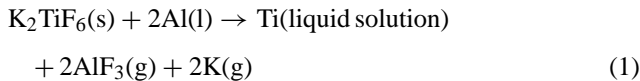

Fig. 3. Composites with 0.15 wt.% Ti treated with K_2TiF_6 refiner salt (a) macrostructure and (b) microstructure showing denude SiCp matrix.

to the decomposition of the K_2TiF_6, based on the following reaction:

$$K_2TiF_6(s) + 2Al(l) \rightarrow Ti(liquid\ solution)$$
$$+ 2AlF_3(g) + 2K(g) \tag{1}$$

The presence of potassium at the SiC particles–matrix interface changes the wetting properties by altering the interfacial tension, based on surface energy values expressed in terms of the work of adhesion, W_{ad} as:

$$W_{ad} = \gamma_{Al} + \gamma_{SiC} - \gamma_{Al-SiC} \tag{2}$$

where γ_{AL} is the surface tension of the molten Al alloy, γ_{SiC} is surface energy of SiC particles and γ_{Al-SiC} is the interfacial surface tension between Al and SiCp. Presence of flux and stirring in the composite provide large surface area for adsorption of potassium, and this condition promotes dewetting of SiCp. Similar results have been reported by Liu [12] in Al–Si–Mg/10p/SiCp composite when a flux containing alkali chlorides were added. Composites treated with 0.20 wt.% Ti (using Al–6Ti master alloy) show presence of fine equiaxed grains (280 μm in diameter.) having ASTM grain size of 14 (Fig. 4a). This sample showed an average of 125 SiC particles/mm^2 and had an average cluster density of 5 cluster/mm^2. Distribution of SiCp in the matrix in the sample was found to be better compared to the unrefined composite, see Fig. 4b. In this figure it can be observed that SiCp present in the interdendritic and intergranular regions of the metal matrix were pushed by the growing dendrites. Taking into account the measured SDAS (25 ± 6 μm) of the metal matrix and the average size of SiCp (40 ± 8 μm), it can be concluded that SiCp have been pushed mainly to the intergranular regions and mechanically entrapped. With a finer and more uniform distribution of the intergranular regions (grain refinement) produces a better distribution of SiCp, as can be observed by comparing Figs. 2b and 4b.

Finally, in the case of composite treated with 0.15 wt.% Ti/0.03 wt.% B (using Al–5Ti–1B ternary master alloy) shows fine equiaxed grains (450 μm in diameter) having ASTM grain size 12.5 (Fig. 5a). As shown in the Fig. 5a this sample has better distribution of SiCp throughout the matrix and the density of SiC clusters has further reduced to about 3 clusters/mm^2. On the average there were 135 SiCp particles/mm^2 in the matrix.

Table 3 shows the comparison of grain size for monolithic alloy and composites for the grain refiners additions used in this work. It can be seen from Table 3 that composites exhibit lower grain sizes than the monolithic alloy for the same level additions of Al–6Ti and Al–5Ti–1B master alloys. This suggests that the presence of SiCp promote the activation of more nucleation sites. This must be due to a dendritic growth restriction associated with the presence of reinforcement which in turn promotes further nucleation events to occur.

It is interesting to note that the grain size of composites treated with Al–6Ti is smaller compared to those treated with Al–5Ti–1B master alloy. This could be due to the lower level of grain refiner used in the case of Al–5Ti–1B which in the monolithic alloy produced a coarser grain (650 μm) as compared with Al–6Ti (400 μm), where effective Ti addition to the melt was 0.20 %, results on number of SiC particles and clusters per unit area suggest that Al–5Ti–B have better performance than Al–6Ti as grain refiner of the composites studied in this work.

From the grain refining theory of Al–Ti–B master alloys, it is well established that TiB$_2$ and TiAl$_3$ provide nucleation sites during solidification of molten Al alloy treated with Al–Ti–B master alloy. These particles allow formation of new primary aluminum crystals ahead of the growing front and these new crystals will prevent the growth of columnar grains from the mould wall. Further, these particles are also present throughout the composite slurry promoting nucleation of a large number of small embryos of α-Al primary phase and generate a finer equiaxed cast structure. Finer solidification structure leads to more uniform distribution of SiC reinforce-
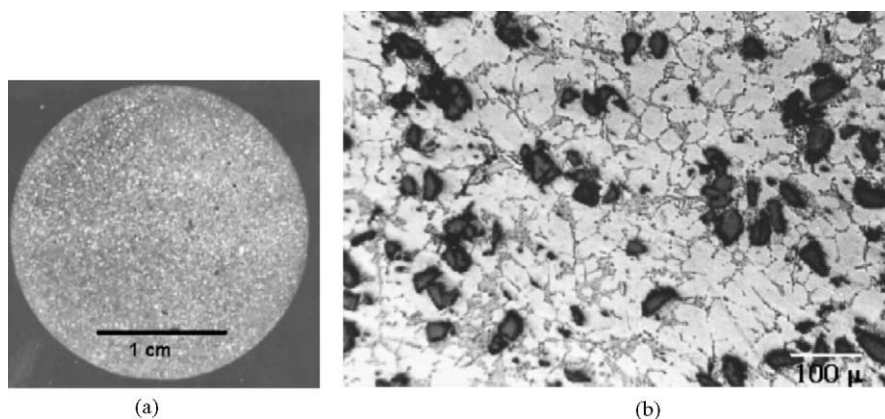

(a)   (b)

Fig. 4. Composite refined with 0.20 wt.% Ti using Al–6Ti master alloy (a) macrostructure and (b) microstructure showing the distribution of SiCp into the matrix.
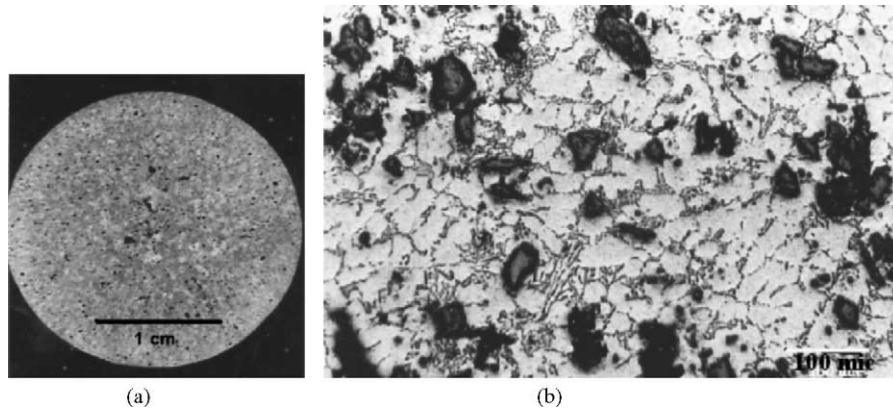
Fig. 5. Composite refined with 0.15 wt.% Ti/0.03 wt.% B using Al–5Ti–1B (a) macrostructure and (b) microstructure showing the distribution of SiCp into the matrix.

Table 3
Comparison of grain size for monolithic alloy and composites for the grain refiners additions used in this work

Grain refiner	Amount added (wt.%)	Grain size, ASTM number (μm)
Monolithic alloy		
Non refined	–	7.5–9 (2600 a 2300 μm)
K_2TiF_6 salt	0.15 Ti	13 (400 μm)
Al–6Ti master alloy	0.20 Ti	13 (400 μm)
Al–5Ti–1B master alloy	0.15 Ti/0.03 B	11.5 (650 μm)
Cast composites		
Non refined	–	9.5–10 (1300–1100 μm)
K_2TiF_6 salt	0.15 Ti	6.5–8 (3500–2200 μm)
Al–6Ti master alloy	0.20 Ti	14 (280 μm)
Al–5Ti–1B master alloy	0.15 Ti/0.03 B	12.5 (450 μm)

ment in the composites. In this case, the effectiveness of the heterogeneous nucleation is attributed to presence of TiB_2 particles together with $TiAl_3$ particles, which are not segregated at the matrix–SiC interface.

Finally, experimental results show that Al–6Ti and Al–%Ti–1B master alloys were able to promote heterogeneous nucleation efficiently and create large number of primary α-Al grains required for the grain refinement of Al–Si/10SiCp promoting a better distribution of the reinforcement.

4. Conclusions

In the present work Al-7 wt.% Si-10 vol.% SiCp particle cast composites were grain refined using Ti salt (K_2TiF_6), Al–6Ti and Al–5Ti–1B master alloys in order to evaluate the role of grain refinement treatment on the SiC particles distribution on the matrix The results of the investigation reveal:

1 Additions of salt based grain refiner such as K_2TiF_6 leads to complete dewetting of SiC particles and subsequently complete rejection of SiC particles from the melt. Hence, it is not recommended for use as grain refiner in A356 Al–SiCp cast composites.

2 Al–6Ti and Al–5Ti–1B master alloys have proved to be suitable grain refining agents for the A356 Al–SiCp composites leading to more uniform distribution of SiC particles in the matrix.

Acknowledgements

References

[1] D. Weiss, B. Chamberlain, R. Bruski, Justifying metal matrix composites in an era of cost reduction, Mod. Casting 90 (2) (2000) 58–60.
[2] Y. Wu, H. Liu, E.J. Lavernia, Acta Metal. Mater. 42 (3) (1994) 825–837.
[3] M.K. Surappa, P.K. Rohatgi, J. Mater. Sci. 16 (1981) 562.
[4] J.K. Kim, P.K. Rohatgi, Acta Mater. 46 (4) (1998) 1115–1123.
[5] J.K. Kim, P.K. Rohatgi, Metal. Mater. Trans. A 29 (1) (1998) 351–358.
[6] B.S. Murty, S.A. Kori, M. Chakraborty, Int. Mater. Rev. 47 (1) (2002) 3–29.

[7] D.G. Mc Cartney, Int. Mater. Rev. 34 (5) (1989) 247–269.

[8] ASTM Designation E112 in Annual Book of ASTM Standard, Part 3, V. 03.03, Philadelphia, PA, 1984, p. 120.

[9] G.J. Davies, Solidification and Casting, Applied Science Publishers, London, 1973.

[10] J.K. Kim, P.K. Rohatgi, Metal. Mater. Trans. 31A (2000) 1295–1304.

[11] M. Gupta, F.A. Mohamed, E.J. Lavernia, Int. J. Rapid Solid. 6 (3–4) (1991) 247–284.

[12] H. Liu, F.H. Samuel, AFS Trans. 101 (1993) 739.