Abstract

The present work deals with the fading and poisoning phenomena that are observed during grain refinement of Al and Al-7Si alloy. The grain refining inoculants commonly used for aluminium and its alloys are usually Al-Ti, Al-B, Al-Ti-B and Al-Ti-C master alloys, which provide nucleating particles such as AlB_2, $TiAl_3$, TiB_2, and TiC either individually or in combination as the case may be. Several theories have been proposed about their role on nucleating α-Al. However, the role of these intermetallic particles is still not clearly understood. The grain refining efficiency, fading and poisoning behaviour of these nucleation particles in Al and Al-7Si both individually and in combination have been studied in detail. For this purpose indigenously developed binary Al-3B, Al-5Ti, Al-5TiB_2 and Al-5Ti-1.2C master alloys which contain AlB_2, $TiAl_3$, TiB_2 and TiC particles, respectively, have been used. The ternary Al-1Ti-3B, Al-5Ti-1B and Al-5Ti-0.8C master alloys contain mixture of AlB_2+TiB_2, $TiAl_3$+TiB_2 and $TiAl_3$+TiC particles, respectively. Although several types of grain refiners are commercially available, their grain refining efficiencies differ widely. In most cases, the grain refiners are found to be efficient in converting the columnar grain structure to fine equiaxed grains on short holding after the addition of the same to the molten alloy. In certain cases, however, such effects on the addition of the grain refiners are lost on prolonged holding. This is due to the dissolution and settling behaviour of $TiAl_3$ and TiB_2 particles in the melt on prolonged holding resulting in increase in grain size. This phenomenon is commonly known as "fading". However, no systematic study was done in the past to understand the dissolution and settling behaviour of nucleation particles, which causes fading.

Most aluminum alloys respond favourably to grain refinement by Al-5Ti-1B master alloy. The Al-Si alloy containing Si in excess of 3% respond poorly to grain refinement by the conventional addition of 0.2% of Al-5Ti-1B master alloy due to a phenomenon called "Poisoning". It is believed that Si interacts with the nucleating particles like $TiAl_3$ and TiB_2 and makes them impotent. However, the mechanism of poisoning is not well understood. This detailed and systematic study is taken up with a

view to achieve an understanding the role of intermetallic particles on nucleating α-Al and the fading and poisoning phenomenon occurring during grain refinement of Al and Al-7Si alloy. The specific objectives of the present work are:

- To achieve an understanding of the grain refining potency of different nucleating particles on Al and Al-7Si alloy.
- To bring out clearly the causes for the fading phenomenon in the grain refinement of Al with different nucleating particles / master alloys.
- To reveal the mechanism of poisoning of the heterogeneous nucleating particles by Si in Al-7Si alloy.

The Al-3B, Al-5Ti, Al-5TiB$_2$, Al-5Ti-1B and Al-1Ti-3B master alloys have been made by the reaction of K_2TiF_6 and/or KBF_4 salts with molten Al. The Al-5Ti-0.8C and Al-5Ti-1.2C master alloy have been made by the reaction of K_2TiF_6 and graphite powder with molten Al. In particular three different Al-5Ti master alloys have been prepared at three different reaction temperatures 750, 800 and 850^{o}C for the reaction time 60 min. The master alloys have been characterised by chemical analysis, particle size analysis, XRD and SEM/EDX microanalysis and X-ray mapping.

The grain refining behaviour of the master alloys have been studied by their addition at different addition levels to liquid Al, Al-7Si and LM25 alloys at 720^{o}C. The grain refined samples were subjected to macroscopic examination, grain size analysis using linear intercept method. The grain refining efficiency and the fading and poisoning tendency has been evaluated for all nucleating particles individually as well as in combination with the help of macroscopy and grain size analaysis. In the case of Al, TiC particles exhibits better grain refining efficiency and lesser settling and dissolution tendency than that of $TiAl_3$, TiB_2 and AlB_2 particles at all addition levels and at all holding time. Similarly, the combined $TiAl_3$+TiB_2 particles exhibit better grain refining efficiency and lesser settling and dissolution tendency than that of $TiAl_3$+TiC and AlB_2+TiB_2 particles at all addition level and at all holding time. AlB_2 particles and the combined AlB_2+TiB_2 particles exhibit better grain refining efficiency in Al-7Si alloy. AlB_2 particle shows zero poisoning effect when compared to $TiAl_3$,

TiB_2 and TiC particles. TiB_2 and TiC has more poisoning tendency than $TiAl_3$. Higher addition level of $TiAl_3$+TiB_2 or $TiAl_3$+TiC shows better grain refining efficiency in Al-7Si due to a decrease in the poisoning tendency of both TiB_2 and TiC particles in the presence of $TiAl_3$. The grain refining efficiency of Al-5Ti-0.8C and Al-5Ti-1.2C master alloy at the 0.1% addition level is equal to that of Al-3B and Al-1Ti-3B master alloy at 1.0% addition level in LM25 alloy.

The effect of solute Ti on the grain refining potency of TiB_2 particles on Al and Al-7Si was studied. The Al and Al-7Si alloy have been grain refined using different addition levels of Al-5TiB_2 master alloy with and without solute Ti. In the absence of solute Ti the studies showed marginal grain refinement with Al-5TiB_2 master alloy, and not as good as that obtained usually with Al-5Ti-1B ternary master alloy. No significant improvement on grain refinement was obtained at higher addition levels of Al-5TiB_2 master alloy. Similarly in the absence of solute Ti, Al-5TiB_2 master alloy could not grain refine Al-7Si alloy due to poisoning effect of Si. The experiments were conducted by addition solute Ti at 0.001, 0.01 and 0.05% along with Al-5TiB_2 grain refiner for both Al and Al-7Si. Here Ti was added in form of Al-5Ti binary master alloy. The present results show that with even 0.001% of Ti addition, a drastic decrease in grain size was found (in presence of TiB_2) when compared to without Ti addition for both Al and Al-7Si alloy. The grain size decreased further at higher addition level of Ti. This investigation involves a detailed microstructural study of the grain refined alloys and discusses the possible mechanism for the role of Ti in improving the grain refining efficiency of TiB_2. In conclusion, the results of this section indicate that solute Ti makes Al-TiB_2 master alloy a more effective refiner, by reducing the agglomeration and settling tendency of TiB_2 particles and hence the fading effect. In the case of Al-7Si alloy even with smaller solute Ti addition the poisoning effect of Si decreases to great extent. Increasing the solute Ti addition level decrease the grain size of Al-7Si alloy grain refined with different addition level of Al-5TiB_2 master alloy at all holding times. The present result clearly shows that Ti reduces the settling tendency of TiB_2 even in Al-7Si alloy. In the presence of solute Ti, the poisoning by Si of TiB_2 and formation of titanium silicide coating over TiB_2 particles is highly reduced, which not only improves the grain refining efficiency of Al-TiB_2 master alloy but also reduces the agglomeration and hence the settling tendency of TiB_2 particles.

In order to understand the fading phenomenon the dissolution behaviour of $TiAl_3$ and the settling behaviour of $TiAl_3$, TiB_2, TiC and AlB_2 particles has been studied in detail. To investigate the dissolution behaviour of $TiAl_3$ particles, Al has been grain refined using 1.0% (0.05%Ti) of Al-5Ti master alloy prepared at three different reaction temperatures (750, 800 and 850°C), which provides $TiAl_3$ particles of different sizes. In all cases the $TiAl_3$ particles are blocky in shape and uniformly distributed throughout the matrix. The particles size analysis has been performed on all the three binary (Al-5Ti) master alloys using quantitative metallographic technique. The minimum particle size was observed to be more or less the same (2μm) for all the reaction temperatures studied. The maximum particle size and hence the range of particle sizes continued to increase with the increase in reaction temperature and the number of finer particles (<20μm) decrease with increase in reaction temperature. Al-5Ti master alloy produced at 850°C shows better grain refinement at all holding time. Fading is also less up to 120 min. of holding in case of master alloys prepared at higher temperatures (800 and 850°C) as compared to the one prepared at 750°C. Further, recovery after stirring is also more in case of master alloys prepared at higher reaction temperatures suggesting that $TiAl_3$ particles settled became active on stirring. The present results indicate that even $TiAl_3$ particles settle down, if they have larger particle sizes. Interestingly, in an earlier section it was shown that $TiAl_3$ particles do not have strong settling tendency. This was due to the fact that the Al-5Ti master alloy used in that study was prepared at the reaction temperature of 750°C with smaller particle size.

The settling behavior of heterogeneous nucleation particles like $TiAl_3$, TiB_2 and TiC has been studied through vertical section experiments. Al was grain refined using Al-5Ti, Al-5Ti-2C, Al-5TiB_2 and Al-3B master alloys. For grain refinement Al was melted at 720°C in a cylindrical graphite crucible of 2.5 cm diameter and 10 cm height. All experiments were conducted by placing the grain refiner chips at the top surface of the melt and no stirring were carried out after the addition of grain refiner. The experiments were carried out for different holding times (0, 2, 5, 30, 60, 120 and 180 min.) and the melt was allowed to solidify in the crucible itself by air-cooling. The castings were sectioned vertically for macrostructural, microstructural and grain size analysis studies. The experimental results obtained were correlated with the mathematical calculation derived using Stoke's Law. The demonstration of settling behaviour of $TiAl_3$, TiB_2 TiC and AlB_2 particles clearly shows that all particles settles in the melt due to their density difference with the molten Al. However the settling tendency of TiC and TiB_2 particles are more because of their higher density than molten aluminium and their clustering behaviour. However the agglomeration tendency of TiC particles is less compared to the TiB_2 and the former can grain refine Al efficiently even they settle very early in the melt. The present study also confirms the settling of undissolved $TiAl_3$ particles in the melt.

In order to understand mechanism of poisoning, the Al-7Si alloy has been grain refined with, Al-5Ti ($TiAl_3$), Al-5TiB_2 (TiB_2), and Al-5Ti-1.2C (TiC) master alloys at equal Ti addition level. The samples have been analysed using scanning electron microscopy (SEM), energy dispersive X-ray (EDX) microanalysis, scanning electron probe microanalysis (SEPMA) and ATEM in order to observe the possible reaction of Si with the nucleating particles, which causes poisoning. The SEM/EDX microanalysis studies of Al-7Si with $TiAl_3$, TiB_2 and TiC particles clearly revealed reaction of Si with the particles, which makes the nucleation particles impotent. The EPMA elemental mapping of Al-7Si alloy with TiC particles showed Ti in the α-Al solid solution and C in the grain boundaries at both 5 min and 120 min. holding indicating TiC dissolves in Al-7Si. The EDX line scanning over the TiB_2 cluster and TiC cluster shows a prominent titanium silicide coating. These results clearly established reaction of the nucleating particles with Si.

In summary, the present work led to the followings:

- A clear understanding of the grain refining efficiency, fading and poisoning tendency of different nucleation particles in Al and Al-7Si and LM25 alloy.
- An understanding of the effect of solute Ti on increasing the grain refining efficiency of TiB_2 particles in Al and Al-7Si alloy by overcoming the fading and the poisoning effect.

- Understanding of dissolution behaviour of $TiAl_3$ particles and settling behaviour of $TiAl_3$, TiB_2, TiC and AlB_2 particles in the Al melt.
- Understanding of the reaction of Si with the $TiAl_3$, TiB_2 and TiC particles in Al-7Si alloy
- Development of Al-Ti-C master alloys, which are effective grain refiners for Al, Al-7Si and LM25 alloys

The following observations have not been understood and need further investigation:

- The marginal grain refinement of Al-3B and Al-1Ti-3B master alloy in Al at higher addition levels (0.05 and 0.1%B).

- The simultaneous dissolution and settling behaviour of $TiAl_3$ particle in liquid Al makes the situation rather complex to draw any specific conclusion regarding its fading tendency.

- How the settled $TiAl_3$ particles in Al-7Si melt that were made impotent by silicide coating could become effective nucleating sites on stirring of the melt after 120 min. of holding.

- Why LM25 alloy shows poor grain refinement on increasing the addition level of Al-Ti-C master alloy beyond 0.1%.

Key words: Grain refinement, Al and Al-Si alloys, Al-Ti, Al-B, Al-Ti-B and Al-Ti-C master alloys, Fading, Poisoning.