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Effect of $TiAl_3$ particles size and distribution on their settling and dissolution behaviour in aluminium

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Abstract The effect of $TiAl_3$ particle size and distribution on their settling and dissolution behaviour in molten aluminium during grain refinement has been studied. For this purpose Al–5Ti master alloys containing blocky $TiAl_3$ particles of different size and distribution are synthesised at reaction temperatures 750, 800 and 850 °C for 60 min and used for grain refinement. The extent of fading and the recovery due to stirring is calculated from the measured grain size and used to judge the dissolution and settling behaviour of $TiAl_3$ in molten Al, which is greatly attributed to its size and distribution in Al–5Ti master alloy. Fine $TiAl_3$ particle dissolve faster in the melt and cause fading. Larger size $TiAl_3$ particles exist for longer time in molten Al and act as a nucleating site even when added in hypoperitectic concentration (0.05 wt% Ti).

Introduction

Aluminium and its alloys are usually grain refined by Al–Ti and Al–Ti–B master alloys, which provide heterogeneous nucleation sites such as $TiAl_3$ and TiB_2 particles [1, 2]. In certain areas like foil and electrical applications the presence of boron in found to be detrimental due to the presence of TiB_2, which is known to reduce the formability and electrical conductivity of aluminium [1]. In such critical application Al–Ti master alloys has been used extensively as an alternative to Al–Ti–B grain refiner. $TiAl_3$ particle in Al–Ti grain refiner is a powerful nucleant for α-Al, than any other heterogeneous nucleating particles [2–7]. The mechanism of grain refinement in aluminium by $TiAl_3$ is not much doubted and explained by acting $TiAl_3$ as heterogeneous nucleating site [8] as well as by the peritectic theory [9]. The difficulty behind using Al–Ti master alloys as a grain refiner for Al, is the dissolution behaviour of $TiAl_3$ particles in molten Al when present at hypoperitectic concentration, which cause significant fading on long holding [1, 2]. Adding $TiAl_3$ particles at hyperperitectic concentrations can efficiently grain refine Al [10]. However, for aluminium industries it is not cost-effective solution. Therefore developing Al–Ti grain refiners for effective grain refinement of Al at hypoperitectic additions are on focus in recent years [11, 12].

Dissolution of intermetallic particles in metallic melt causes serious problem, when employing them as nucleating agents or as reinforcement particles in metal matrix composites. The dissolution behaviour of particles seem to be depends on number of factor including the holding temperature, holding time and the composition of the melt. Increasing the holding temperature cause AlP particles to dissolve in hypereutectic Al–Si melt and cause poor refinement of primary Si [13]. Similarly prolong holding cause dissolution of B_4C particles in Al melt, which affects the fluidity of the composite due to the formation of unwanted reaction products [14]. In some cases dissolution of intermetallic particles are beneficial, like dissolution of Al–Mn compound in Mg alloy AZ91 melt, which helps homogenous precipitation of $Mg_{17}A_{12}$ in the alloy [15].

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The presence of Al–Mn compound is also considered to be detrimental to the strength of the AZ91 alloy [15].

The dissolution of $TiAl_3$ particles in Al melt was studied by number of researchers both experimentally and theoretically which was well recorded in the reviews of Murty et al. [1] and Easton and John [2]. The differences in the dissolution times reported by several investigators could be partly attributed to the differences in $TiAl_3$ particle sizes and the presence of alloying elements/impurities, which are expected to have a strong influence on the dissolution kinetics. Li et al. [11] and Venkateswarlu et al. [12] have shown that size, morphology and distribution of $TiAl_3$ particles have significant difference in their grain refining efficiency. In addition to dissolution contribution to fading, the grain refining literatures suggest that the settling of nucleating particles in the molten Al on longer holding is also responsible for fading [1, 16]. The density difference between heterogeneous nucleating particles and the molten Al is the cause for settling. A $TiAl_3$ particle has a density of $3.13\ g\ cm^{-3}$ [17], which is greater than the molten Al, which is $2.38\ g\ cm^{-3}$ at 720 °C [18]. Ideally all $TiAl_3$ particles would settle on longer holding in molten Al. However, the dissolution behaviour of $TiAl_3$ makes the settling study complex and therefore much attention was not given on studying the settling behaviour. In our present work the dissolution and settling behaviour of $TiAl_3$ particle is studied in a way that the results of one phenomenon can explain the other. And we have shown that the dissolution and settling behaviour of $TiAl_3$ particles in molten Al is greatly attributed to its size and distribution in their respective master alloys. The study also presents an Al–5Ti master alloy, which can effectively grain refine Al even at hypoperitectic addition level (0.05 wt% Ti), due to the reduced dissolution tendency of $TiAl_3$ particles in molten Al.

Experimental details

The Al–5Ti grain refining master alloys are synthesised by the reaction of molten commercial pure Al (99.97% purity) with K_2TiF_6 salt at three different reaction temperatures 750, 800 and 850 °C for 60 min The master alloys are characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) microanalysis. The master alloys are also subjected to wet chemical analysis for Ti pickup. The $TiAl_3$ particle size distribution in the master alloys is done using optical microscopy and Leica image analyser. For grain refinement, 200 g of commercial pure Al (99.97% purity) is melted in a graphite crucible using a pit type resistance furnace under a cover flux; 1.0 wt% (0.05 wt% Ti) of Al–5Ti master alloy is added to the melt at 720 °C. The melt is stirred for 60 s immediately on addition of the grain refiner and no further stirring is carried out. After a particular holding time a part of the melt is poured in water cooled copper mould. The remaining melt is also stirred and poured at the same interval in order to recover the settled $TiAl_3$ particles. The samples thus obtained are designated as HT (holding time) and HTS (holding time with stirring), respectively. The tests are conducted for different interval say 2, 5, 30, 60 and 120 min. At every interval the remaining melt is stirred and poured. The grain refined samples are metallographically polished and etched using Keller's reagent for grain size measurements, using linear intercept method as mentioned in ASTM E112-96 standard.

Results and discussion

Figure 1a–c shows the SEM photomicrographs of Al–5Ti master alloy produced at 750, 800 and 850 °C for 60 min reaction time. It is clear from the photomicrographs that an increase in reaction temperature significantly increases the $TiAl_3$ particles sizes. However, in all cases the $TiAl_3$ particles are blocky in shape and uniformly distributed throughout the Al matrix. The highest reaction temperature of Al–5Ti is set to 850 °C, while beyond that temperature the morphology of $TiAl_3$ is platelet or needle shape, which cannot act as nucleating sites [11, 12]. The nominal and actual Ti concentration in the Al–5Ti master alloys produced at three different reaction temperatures for 60 min is shown in Table 1. The particles size distribution has been performed for all three Al–5Ti master alloys using quantitative metallographic technique described elsewhere [19]. The size distribution of particles was obtained by performing particle size analysis on the optical micrographs using Leica image analyser. The shape of particles is assumed to be spherical; thus, the cross sections are in the shape of a circle. Particles in each specimen were divided into 7 groups according to their sizes. The number of particle in each group was counted. Table 2 shows the details of particles size distribution measurements conducted for the master alloys and Fig. 1d shows the particle size distribution curve for the Al–5Ti master alloys as a function of reaction temperature. Three major conclusions can be drawn from the Fig. 1d. Firstly, the minimum particle size is found to be more or less the same (2 μm) for all the reaction temperatures studied. Secondly the maximum particle size and hence the range of particles sizes continued to increase with the increase in reaction temperature and the number of finer particles (<20 μm) decrease with increase in reaction temperature.

Figure 2 shows the photomicrograph of Al grain refined using 1.0 wt% of Al–5Ti master alloy produced at 750 °C

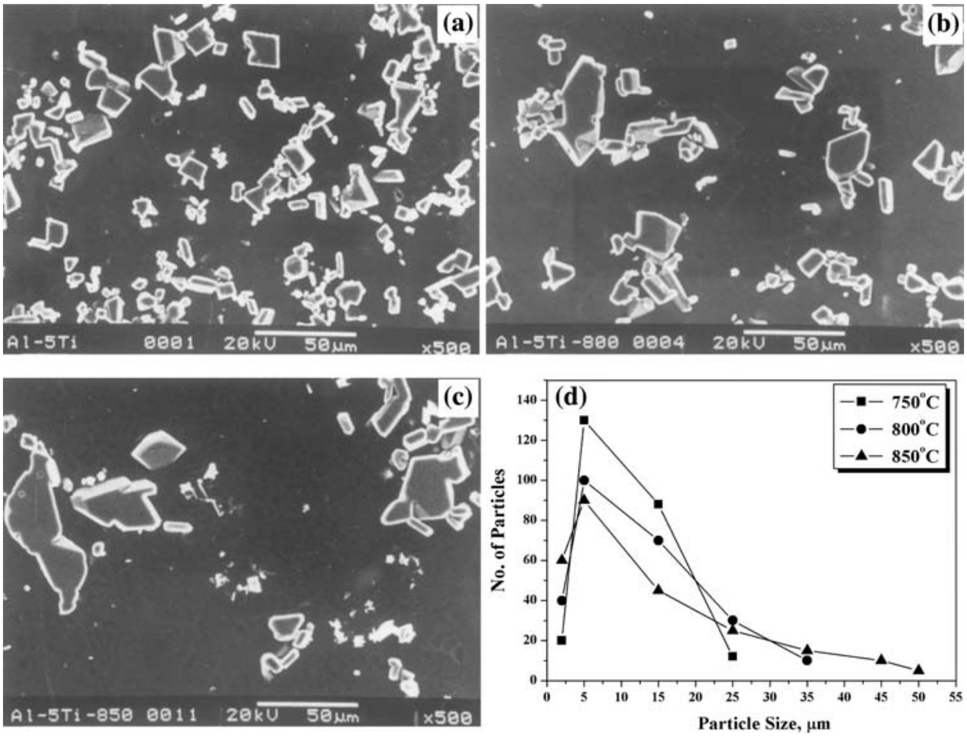


Fig. 1 SEM photomicrograph of Al–5Ti master alloy produced at different reaction temperature **a** 750 °C, **b** 800 °C and **c** 850 °C for 60 min and **d** corresponding particle size analysis

Table 1 Titanium analysis of Al–5Ti master alloy through wet chemical analysis

Alloy	Reaction temperature (°C)	Reaction time (min)	Nominal Ti (wt%)	Actual Ti (wt%)
Al–5Ti	750	60	5	4.65
Al–5Ti	800	60	5	4.74
Al–5Ti	850	60	5	4.90

at both HT and HTS conditions. The microstructure of 2HT sample confirms the columnar to equiaxed transition occurred immediate after the addition of grain refiner. The microstructure of the 2HTS sample also shows similar fine equiaxed grain structure suggesting that no particles settling has occurred at that short duration. Similar grain structure is observed for 5HT and 5HTS sample. The microstructure of 30HT sample shows little coarsening in the grain structure indicating fading. Interestingly the microstructure of 30HTS sample shows finer grain structure than that of 2HT sample. This clearly suggests particle settling within 30 min holding. Stirring the melt activates the settled $TiAl_3$ particles which recovers the fading. On further holding the melt to 60 and 120 min fading becomes larger, which is evident from the coarse grains observed for 60HT and 120HT samples. The 60HTS and 120HTS samples also show similar microstructure as 60HT and 120HT indicating that stirring could not recover the grain structure. This could be attributed to dissolution of $TiAl_3$ particles which cause fading. In such as case fading is unrecoverable, as the Ti is in equilibrium to the solution. Figure 3 shows the photomicrographs of Al grain refined using 1.0 wt% of Al–5Ti master alloy produced at 800 °C at both HT and HTS conditions. The grain structure observed in this case is similar to that of the previous one (Fig. 2). Recovery of fine grain structure due to stirring can be observed for both 30HTS and 60HTS sample suggesting that the $TiAl_3$ particles in this case take little longer time to dissolve in molten Al due to the presence of larger size $TiAl_3$ particle >25 µm. Figure 4 shows the photomicrograph of Al grain refined using 1.0 wt% of Al–5Ti master alloy produced at

Table 2 $TiAl_3$ particle size analysis of Al–5Ti master alloys prepared at different reaction temperature for 60 min

Alloy	Preparation condition (°C)	Statistical data				Particles less than 20 µm (%)
		Mean (µm)	Std. Dev (µm)	Range (µm)		
				Min	Max	
Al–5Ti	750	11	4.44	2	25	95.05
Al–5Ti	800	15	6.06	2	35	82.27
Al–5Ti	850	17	9.36	2	50	73.08

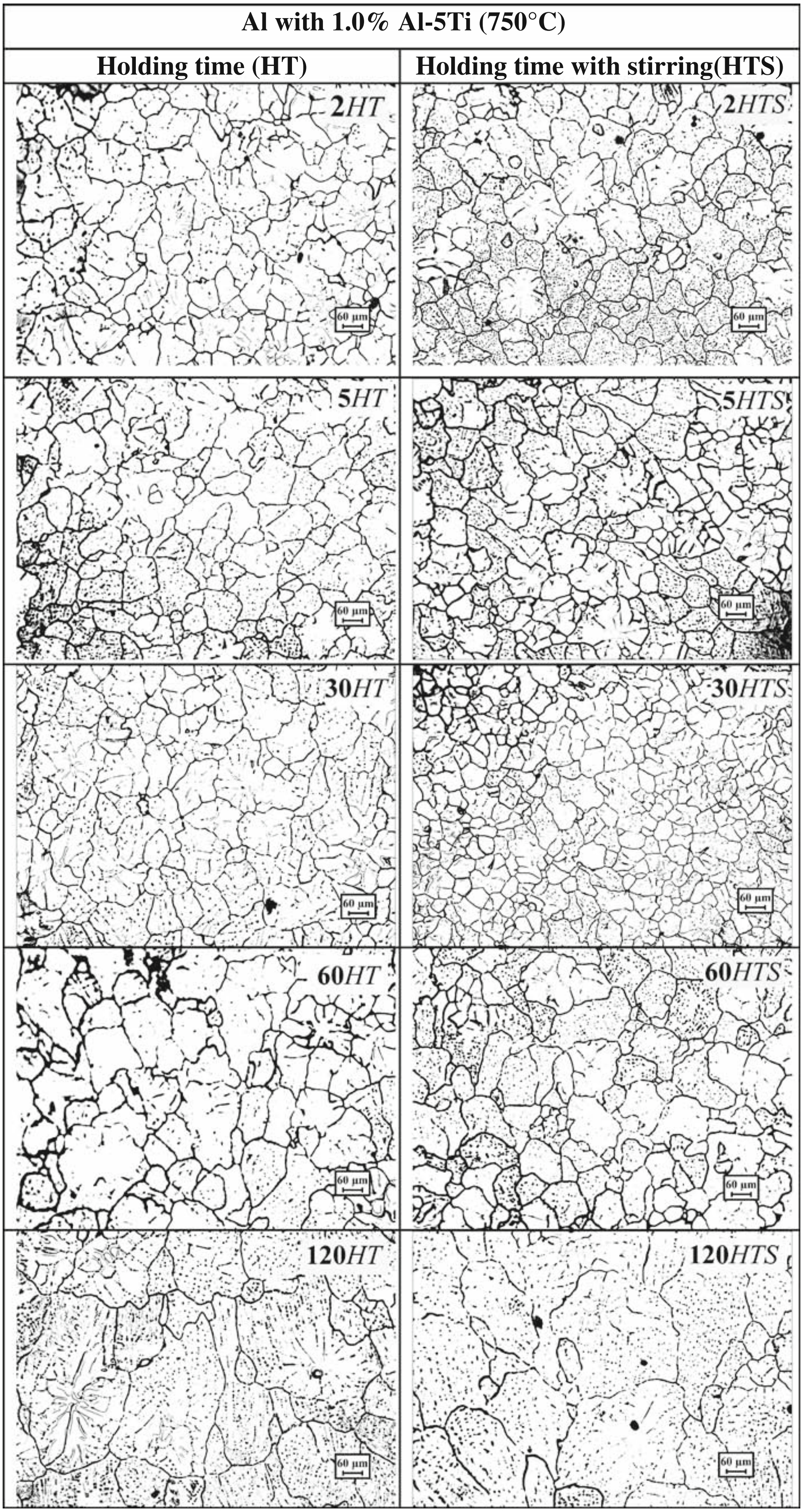


Fig. 2 Optical micrograph of Al grain refined with 1.0 wt% of Al–5Ti master alloy produced at 750 °C reaction temperature and 60 min

Fig. 3 Optical micrograph of Al grain refined with 1.0 wt% of Al–5Ti master alloy produced at 800 °C reaction temperature and 60 min

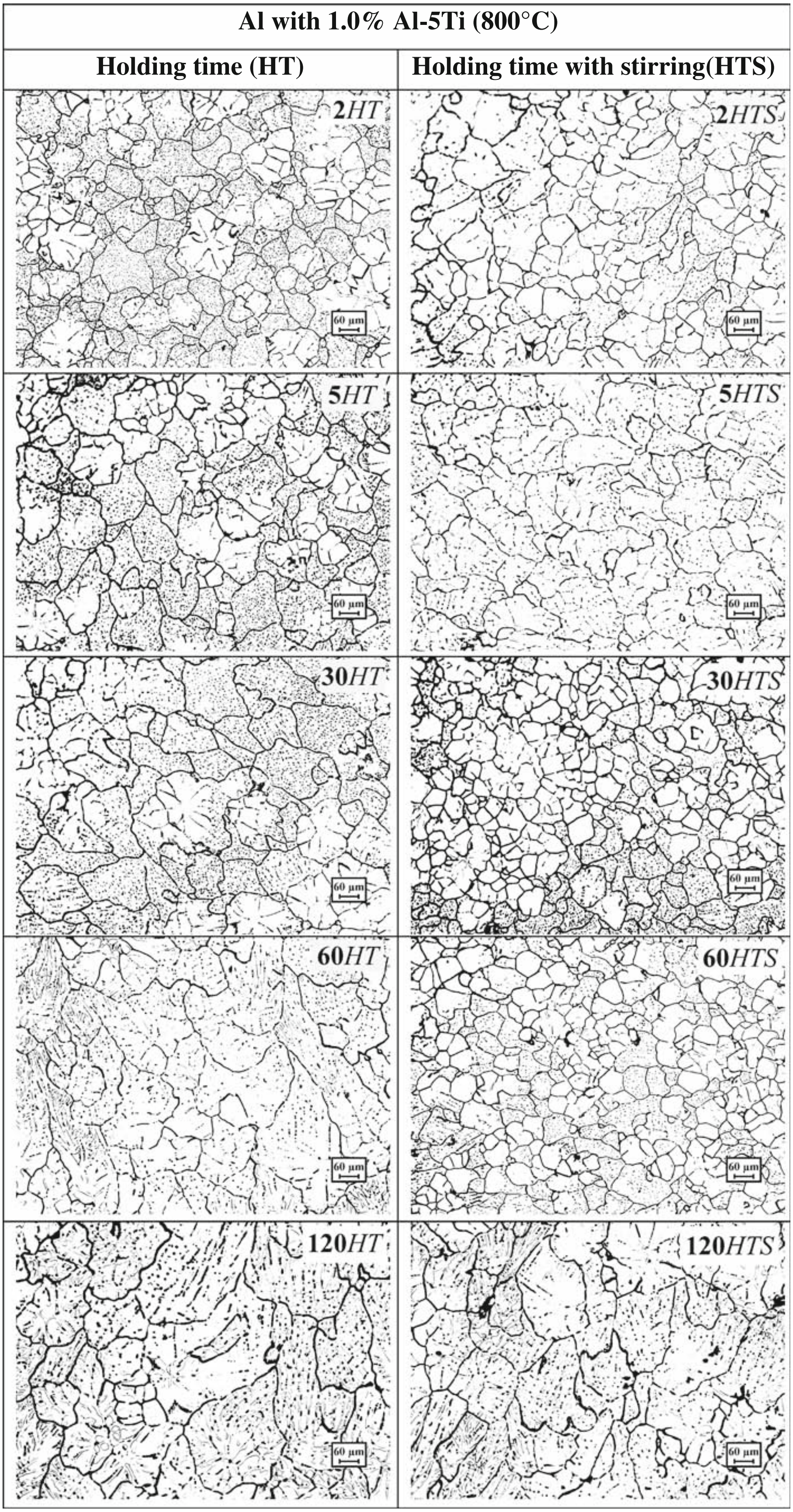
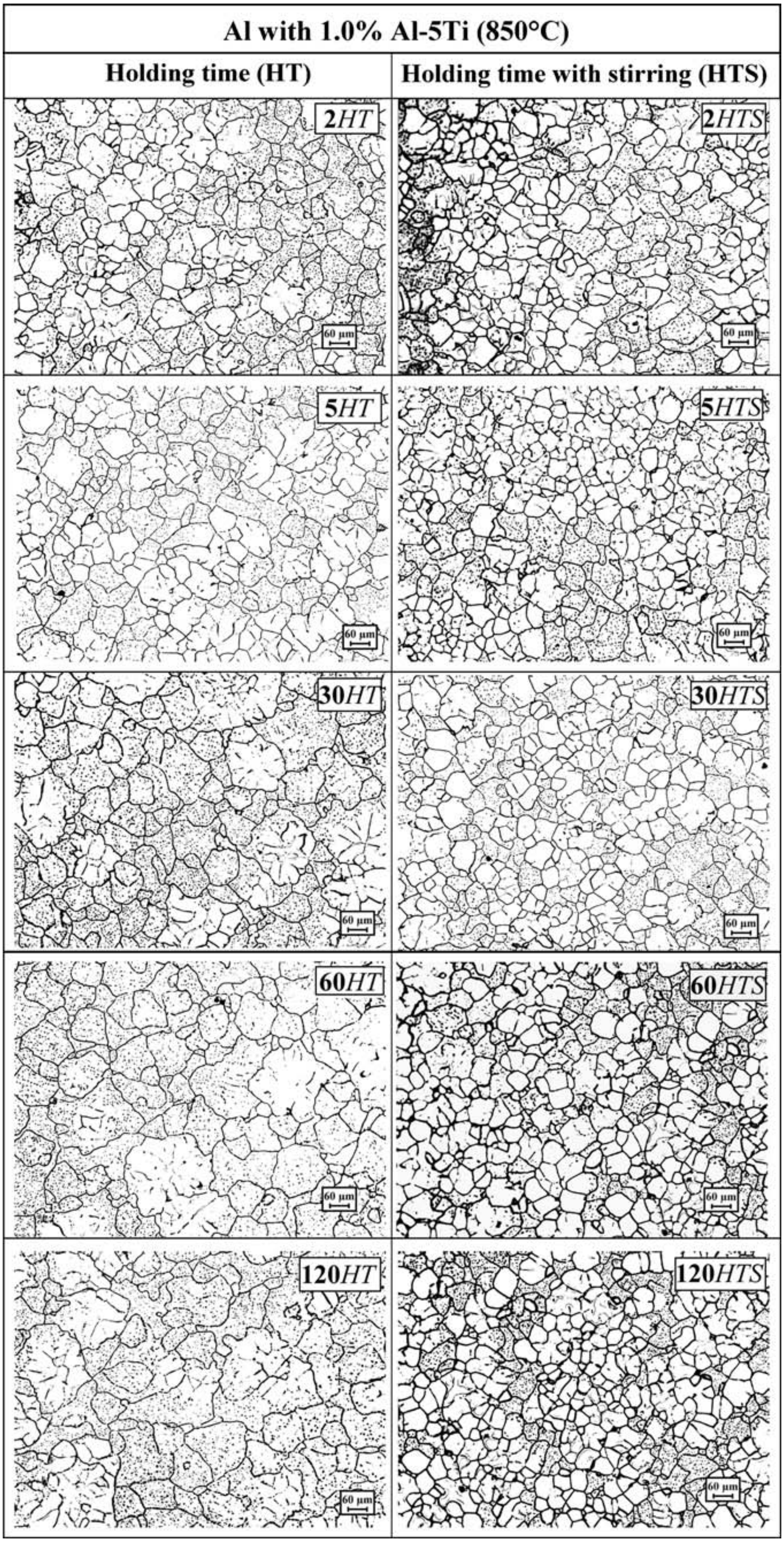


Fig. 4 Optical micrograph of Al grain refined with 1.0 wt% of Al–5Ti master alloy produced at 850 °C reaction temperature and 60 min



850 °C at both HT and HTS conditions. The master alloy shows better grain refinement at all holding time in comparison to other Al–5Ti master alloys. In addition the grain size observed from 5HTS to 120HTS is finer than that of the unstirred melt, suggesting that $TiAl_3$ particles settles early in the melt due to the presence of larger size $TiAl_3$ particles in comparison to other Al–5Ti master alloys. However, settling of $TiAl_3$ particles observed in this case does not cause any significant fading on longer holding.

The grain size analysis of HT and HTS samples are shown in Fig. 5a. The error bar represents standard deviation in the grain size. In most of the experiments the error bars are smaller in size and therefore hidden behind the symbols, indicating that the scatter is very small. A sudden decline of columnar grain size to finer grain size is evident at 2 min holding, suggesting that all Al–5Ti grain refiners used in the present study are fast acting. Considering first the HT, the grain size measured for 2HT samples in all cases are finer among all other holding time samples. Hence it can be called as the ultimate grain size (UGS) [20]. Fading on longer holding is evident for Al grain refined with all three Al–5Ti master alloys. However, Al grain refined with Al–5Ti master alloy produced at 750 °C shows significant fading. Al grain refined with Al–5Ti master alloy produced at 850 °C shows finer grain size at all holding time, and minimum fading in comparison to other Al–5Ti master alloys. The grain size analysis of HTS shows that finer grain size than UGS is obtained for 30HTS in the case of Al–5Ti at 750 °C, 30HTS and 60HTS in the case Al–5Ti at 800 °C and for 5HTS, 30HTS, 60HTS and 120HTS in the case Al–5Ti at 850 °C.

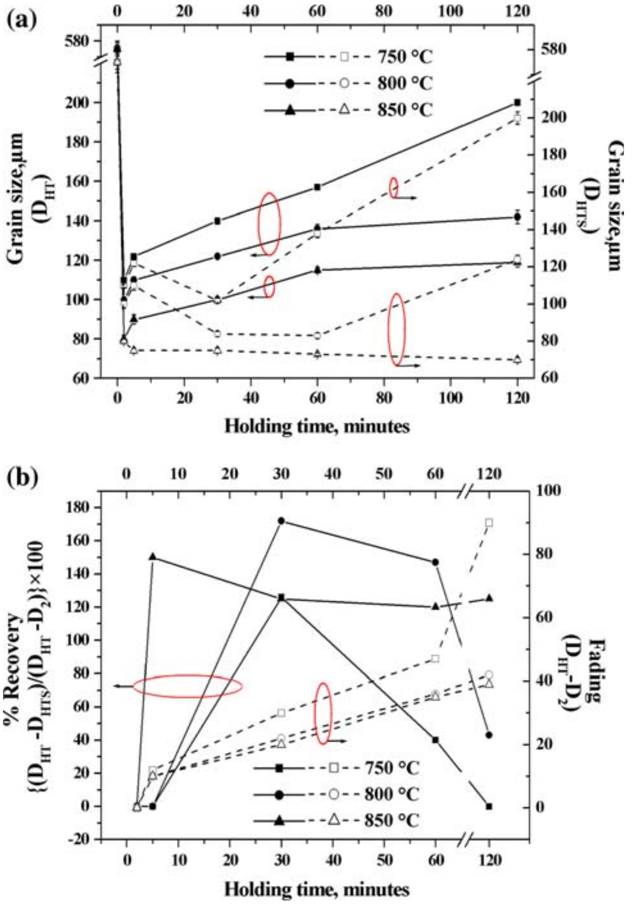


Fig. 5 **a** Comparative grain size analysis of Al grain refined with 1.0% of Al–5Ti master alloys produced at three different reaction temperatures. Error bars represent standard deviation in the grain size. In most of the experiments the error bars are smaller in size and therefore hidden behind the symbols, indicating that the scatter is very small. **b** Effect of fading in Al and the % recovery at all holding times. The *circle* in both the figures represents the *y*-axis to which the curves belong

In order to understand the phenomenon of fading the existing grain size analysis results have been used to evaluate certain key parameters. The first among these is the difference in the grain size between 'D_{HT}' and 'D_2', where D_{HT} is the grain size measured for the samples obtained at different interval and D_2 is the UGS obtained after 2 min holding. This would define the extent of fading in Al with the addition of different Al–5Ti grain refiners. The second one is % recovery on stirring the Al melt after every holding time. The % recovery is defined as $\{(D_{HT} - D_{HTS})/(D_{HT} - D_2)\} \times 100$ basically gives the contribution of particle settling and dissolution towards fading. Figure 5b clearly shows that Al–5Ti master alloy produced at 850 °C exhibits minimum fading in Al than other Al–5Ti master alloys. The fading on longer holding is found to be large in the case of Al–5Ti master alloy produced at 750 °C in comparison to that of Al–5Ti master alloy produced at 800 and 850 °C. Figure 5b also gives the % recovery of Al grain refined with different Al–5Ti master alloys at different holding time. From the calculation the following assumption can be made (1) If the recovery is $\geq$100% then all particles settle and no particle have been lost due to dissolution. All those particles settled within that particular holding time become active on stirring. In other words, the number of active nucleating sites will be higher in 120HTS sample than 2HT. (2) If the recovery is <100% some particles are lost due to dissolution and some particles are settled. (3) If the recovery is zero then all particles are dissolved in the melt and no particle is settled. However, the recovery can be also zero in the case where there is no fading or less fading observed as we could see at shorter holding time. In such a situation the zero recovery cannot be misunderstood as 100% dissolution. In all cases % recovery due to stirring can be seen only after 30 min holding except for Al grain refined with Al–5Ti master alloy produced at 850 °C, where the % recovery can be observed even after 5 min holding. Al grain refined with Al–5Ti master alloy produced at 750 °C shows recovery greater than 100% at 30 min holding.

Further it decreases to 40% at 60 min and becomes zero at 120 min holding. Aluminium grain refined with Al–5Ti master alloy produced at 800 °C shows recovery greater than 100% at both 30 and 60 min holding and becomes 42% at 120 min holding. In the case of 850 °C the recovery calculated is more than 100% at 5 min holding and it remains the same up to 120 min holding.

The aforementioned results quite clearly show that $TiAl_3$ particles have significant dissolution and settling tendency in molten Al when added at hypoperitectic concentration. $TiAl_3$ particle is known to be a powerful nucleant for α-Al [2]. However, when added in the hypoperitectic composition during grain refinement, they dissolve in molten Al and cause significant fading. This is due to the fact that $TiAl_3$ cannot be in equilibrium with pure Al liquid and hence it dissolves in the melt, thus raising the composition of the melt from 0 to 0.15 wt% Ti (equilibrium concentration of Ti in Al melt at 720 °C). Literatures have shown that the time required for complete dissolution depends on dissolution kinetics, which depends on the diffusivity of Ti into Al, particle size and temperature [2]. In our present study we showed the dissolution and settling behaviour of $TiAl_3$ particles of different size and distribution in molten Al held at constant temperature and different holding time. The results obtained are summarised as follows:

(1) Al–5Ti master alloy produced at 750 °C possess narrow particle size distribution and 95% of particles are <20 μm and the particle sizes ranges from 2 to 25 μm. Significant fading is observed on longer holding. The 0% recovery due to stirring calculated at 120 min holding indicates complete dissolution of $TiAl_3$ particles. (2) Al–5Ti master alloy produced at 800 °C has relatively wider particles size distribution in comparison to 750 °C and 82% of particles are <20 μm and the particle sizes range from 2 to 35 μm. The 40% recovery due to stirring calculated after 120 min holding suggests that the added $TiAl_3$ particles are not completely dissolved within the holding time studied. (3) Al–5Ti master alloy produced at 850 °C has wider particle size distribution among other two Al–5Ti master alloy and only 73% of particles are <20 μm and the particles sizes ranges from 2 to 50 μm. Fading is minimum and the % recovery due to stirring calculated for all holding times are more than 100% suggesting very less particle dissolution in comparison to other Al–5Ti master alloys.

These results clearly show that $TiAl_3$ particle size plays an important role on their dissolution tendency in molten Al. In our experiments the amount of Ti added through the addition of $TiAl_3$ particles is 0.05 wt%, which is less than the solubility limit. In principle all the particles should completely dissolve into the liquid Al within the holding time studied. However, due to presence of larger particles and wider particles size distribution as in the case of Al–5Ti master alloy produced at 850 °C the added $TiAl_3$ particles exist in the non-equilibrium condition for longer time in molten Al and acts as nucleation sites for α-Al. The results also show that $TiAl_3$ particles has significant settling tendency in liquid Al. The Al–5Ti master alloy produced at 850 °C containing larger size $TiAl_3$ particles shows early settling within 5 min holding. The increase in the fineness of the aluminium grains of HTS samples on holding indicates increase in the particle settling with increase in time. However, settling contribution to fading is insignificant in comparison to dissolution contribution to fading as we could observe from the results of Al grain refined with Al–5Ti master alloy produced at 850 °C.

Conclusion

1. Blocky $TiAl_3$ particles of various size and distribution in Al–5Ti master alloys are produced at various reaction temperatures for 60 min. Increasing the reaction temperature increases the size and widens the size distribution of $TiAl_3$ in their respective master alloy.
2. $TiAl_3$ particles have significant dissolution and settling tendency in molten Al when added at hypoperitectic concentration (0.05 wt% Ti). The size and distribution of the particles in Al–5Ti master alloy has significant effect on their settling and dissolution behaviour.
3. $TiAl_3$ particles produced at 750 °C posses narrow particles size distribution and 95% of particles are <20 μm, hence dissolve completely in the melt within the holding time studied and cause significant fading on long holding.
4. $TiAl_3$ particles produced at 850 °C has extensive particles size distribution and only 73% of particles are <20 μm. Here the particles can exist for longer time in molten Al and act as nucleating site due to reduced dissolution tendency even when present at hypoperitectic concentration. However, these particles shows significant settling tendency even at shorter holding time.

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