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Effect of potent TiB_2 addition levels and impurities on the grain refinement of Al

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ABSTRACT

In the present work, the effect of potent TiB_2 particle addition levels and impurities on the grain refinement of two Al compositions was investigated. Results showed that no effective grain refinement was achieved in high purity Al (HP-Al) up to particle density levels as high as $2.5 \times 10^{14}/m^3$. In commercial purity Al (CP-Al) fine grain refined structures were observed with merely a particle density of $0.35 \times 10^{13}/m^3$. As more particles were added into the CP-Al melt, the number of grains formed showed an overall increase while the calculated particle efficiency showed a general decrease, consistent with the prediction of interdependence theory. Such results show that the impurities in CP-Al play a significant role in refining the grain structures.

1. Introduction

Grain refinement of aluminium alloys by Al-Ti-B grain refiners is a common industrial practice. As result of such additions, fine equiaxed grain structures usually imparts high yield strength, high toughness, uniform distribution of second phase, good surface finish, higher resistance to hot tearing, etc. [1]. In order to control and improve the effects of the Al-Ti-B grain refiners, it is of great importance to understand the grain refinement mechanism in the Al alloys. So far, several mechanisms have been proposed to account for these grain refinement mechanisms: carbide/boride theory [2], phase diagram/peritectic theory [3], peritectic hulk theory [4,5], hypernucleation theory [6], duplex nucleation theory [7], solute paradigm [8] and epitaxial nucleation theory [9]. Although there is no consensus on the exact mechanism for the grain refinement of Al alloys by Al-Ti-B grain refiners, it is generally agreed that both solute elements and TiB_2 particles play important roles in the grain refinement. Solute elements present in melt can restrict the growth of solids, and the growth restriction effect can be quantified by a growth restriction parameter $Q(Q = mC_0(k-1)$, where m is the liquidus slope, k is the partition coefficient, C_0 is the solute concentration [1]). As well TiB_2 particles can act as heterogeneous nucleation sites during nucleation of Al solids [1].

Recently, Fan et al. [10] reported observations on the Al_3Ti mono-atomic layer on the (0001) TiB_2 surface in a commercial Al-Ti-B grain refiner. It was pointed out that due to the existence of Al_3Ti mono-layer, the TiB_2 particles become very potent in nucleating Al, and these TiB_2 particles are described as potent TiB_2 particles [10]. With synthetic TiB_2 particles ($10^{13}/m^3$) added into CP-Al, mainly columnar grain structure was observed. By comparison, adding the same number density of potent TiB_2 particles into CP-Al, fine equiaxed grain structure was observed, this illustrates the importance of this mono-atomic Al_3Ti layer [10]. It was suggested that the differences can be explained by the difference in lattice misfit from −4.22 wt% for the CP-Al/TiB_2 to the very small (0.09%) misfit for the potent CP-Al/TiB_2 which has the presence of an Al_3Ti two dimensional (2DC) layer [10]. Also, it was found that the Al_3Ti layer absorbed on the TiB_2 surface is very stable during isothermal holding at 800 °C for less than 48 h [10], so using settlement experiment (refer to [10,11]) to collect potent TiB_2 particles with an Al_3Ti layer is feasible, and the successfully collected potent TiB_2 particles were used in this study and other two published work (Fan et al. [10] and Zhou and Fan [11]).

Murty considers that the addition level of particles is very

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important for achieving an effective grain refinement [1]. Insufficient inoculation may result in ineffective grain refinement; and excess addition of particles may not only cause decreased particle efficiency but also may affect the subsequent processing of the solidified ingot [1,12]. Then it is required to investigate how the potent TiB_2 additions affect the grain refinement of Al. Previous studies investigated the effect of TiB_2 addition levels on the grain refinement of Al adding synthetic TiB_2 particles [13] or commercial Al-5Ti-1B grain refiner into pure aluminium reported that divergent results in grain refining mainly because the absence of an Al_3Ti layer on the synthetic TiB_2 [13] or the extra Ti added by commercial Al-5Ti-1B grain refiner [12]. However in both studies, the columnar to equiaxed transition (CET) was not considered [10]. All the grains seem to be equiaxed grains on the cross section, however, if viewed from the vertical section, it might be actually columnar grains. Thus, the 'grain size' measured might be misleading [10]. In order to have an Al_3Ti layer on TiB_2 particles and study the effect of the potent TiB_2 as grain refiner, here it is reported the use of a self-prepared grain refiner for providing potent TiB_2 particles. The potent TiB_2 inoculants on the grain refinement of both HP-Al and CP-Al are investigated, also a comparison of the effect in refinement givens by variation of the inoculants density and the influence of impurities on the grain refinement of HP and CP Aluminium alloys.

2. Experimental procedure

A series of experiments were conducted by inoculating the HP-Al (99.99 wt% Al) and CP-Al (99.7 wt% Al, 0.074 wt% Fe and 0.06 wt% Si) melts with various additions of potent TiB_2 particles. The TiB_2 particle addition levels in HP-Al melts are: 0, $10^{13}/m^3$, $10^{14}/m^3$ and $2.5 \times 10^{14}/m^3$. And the particle addition levels in CP-Al are: 0, $2 \times 10^{12}/m^3$, $3.5 \times 10^{12}/m^3$, $6 \times 10^{12}/m^3$, $10^{13}/m^3$, $5 \times 10^{13}/m^3$. A-worldwide analytical systems- AG Foundry master was employed to check the compositions. A self-prepared Al-1.12Ti-0.48B grain refiner is extracted from a commercial Al-3Ti-B grain refiner and used for providing the potent TiB_2 nucleation particles (see Zhou and Fan for details of the process [11]). The resulting TiB_2 particles as grain refiner are classified as "potent" due to the existence of an Al_3Ti layer on the surface of the borides as previously analysed and reported by Fan et al. [10] and Zhou and Fan [11]. For the purpose of this study the self-prepared refiner is described as Al-1.54TiB_2 since there is only a negligible extra Ti and other impurities that were induced into melt during the inoculation. The distribution and morphology of TiB_2 in the refiner are characterized by SEM. Deep etching of 10s by 10% HCl is conducted on the refiner as preparation for SEM. SEM imaging and surface analysis were carried out on a Zeiss Supera-35 FEG microscope equipped with an energy dispersive spectroscopy (EDS) facility. The Grain structures are assessed using a standard TP-1 test [14]. In each case, Al-1.54TiB_2 grain refiners added when the liquid reaches a stable superheat of 60 K. After 2 min at this temperature the liquid is stirred before casting. During the casting process the cooling rate at the 38 mm cross-section height from the bottom of the casting is estimated to be 3.5 K/s. When solidification is completed, two types of measurements can be taken: the average columnar width is determined by the vertical section for those exhibit columnar grain structures and, for those fully equiaxed grain structures the average grain size is determined by the central of horizontal cross-section with a position of 38 mm from the cone base. The samples used for the microstructure measurement are anodized for 60 s at 20 V with a Barker's reagent (4% HBF_4 in distilled water) and then characterized under polarized light using a Zeiss optical microscope with an Axio Vision 4.3 image analysis system using the mean linear intercept technique to measure the grain size or columnar width of the sample.

3. Results and discussion

3.1. TiB_2 particles in the refiner

Fig. 1a and b shows a low and high magnification of a HP aluminium sample where, along with its characteristic microstructure the Self-prepared refiners are shown to be distribute as agglomerations (see arrows in Fig. 1a and b) where is observed that the TiB_2 particles are uniformly settled and distributed in Al matrix and exhibits a hexagonal structure as seen in Fig. 1(c). According to previous observations reported in ref.1, there are two types of particles (Al_3Ti particles and TiB_2 particles) exist in commercial Al-Ti-B grain refiners, and at high temperature, Al_3Ti particles are easily get dissolved into the Al melt and TiB_2 particles are known to be stable in aluminium melt and do not dissolve on holding. Then, EDS spectrum shown in Fig. 1(d) confirms the composition of the surviving to be the diboride particles. The size distribution of TiB_2 in the refiner is plotted in Fig. 2 as determined from an image analysis. The total number measured of TiB_2 particles for assessing the size distribution was of the order of 1000. Standard stereological methods [15] were applied to convert the length distribution measured in two dimension section into the true three dimension distribution of disc diameter. According to the free growth model [12], grain refining performance is determined by the relative larger particles (usually larger than 1.4 μm based on the calculation using free growth model with a practically measured nucleation undercooling around 0.2 K [12]), even the particles of small sizes (less than 0.2 μm) is difficult to detected, it is not a major problem.

As shown in Fig. 2, the TiB_2 particle size counts exhibits a log-normal distribution, which can be fitted by a general log-normal function given by

$$N(d) = \frac{N_0}{\sigma d\sqrt{2\pi}} \exp\left[-\left(\frac{lnd - lnd_0}{2\sigma^2}\right)^2\right] \tag{1}$$

where d is the particle diameter, d_0 is the geometric mean diameter, σ is the geometric standard deviation, N_0 is the total number of particles, $N(d)$ is the particle number with a diameter between d and $d + \Delta d$. In this fitting, d_0 is equivalent to 0.72 μm, σ is 0.56, and N_0 is 1000.

Having obtained the size distribution of TiB_2 in the refiner, the absolute numbers can be calculated from the composition of the refiner (Al-1.12Ti-0.48B [11]). For 0.48 wt% B in the refiner, the total volume fraction of TiB_2 is approximately 0.92×10^{-2} and this value was taken to be the integral of particle volume. According to previous studies, the TiB_2 particles are of hexagonal shape platelets with a rough thickness of 35% of their diameter [16–20]. The TiB_2 particles in the Al-1.54TiB_2 grain refiner must have the same shape because it was extracted from commercial Al-Ti-B grain refiner [11]. According to the shape of the size distribution, if assuming that he particles are approximated to discs of the same aspect ratio (35%), the number density of TiB_2 in Al-1.54TiB_2 grain refiner can be calculated to be $\sim 2 \times 10^{19}/m^3$. For simplification, in this work, the TiB_2 particles are assumed to be uniformly distributed in the Al matrix.

3.2. HP-Al and CP-Al with TiB_2 addition

During the solidification process the TiB_2 particles near the mould wall will be activated and initiate grains formation. The relative lower temperature of the particles (compared with the melt), causes heat dissipation through the mould wall, resulting in a thermal undercooling that promotes a heterogeneous nucleation