Grain refinement of Al-3.5FeNb-1.5C master alloy on pure Al and Al-9.8Si-3.4Cu alloy

Chinna Apparao Kummari and *Anil Kumar Birru

Department of Mechanical Engineering, National Institute of Technology, Manipur 795004, India

Abstract: The refinement potential of Al-3.5FeNb-1.5C master alloy on pure aluminium and Al-9.8Si-3.4Cu alloy has been investigated. Different amounts of Al-3.5FeNb-1.5C master alloy were added to estimate the optimal addition level. It was found that the addition of Al-3.5FeNb-1.5C grain refiner can promote significantly the refinement of grains in the pure aluminium, particularly at 0.1wt.%, with the mean primary aluminium α -grain size reducing to $187 \pm 3 \mu\text{m}$ from about 1–3 mm. Similarly, the microstructural study of the Al-9.8Si-3.4Cu alloy die casting at different weight percentages (viz. 0.0wt.%, 0.1wt.% and 1.0wt.%) of Al-3.5FeNb-1.5C master alloy shows that the Al-3.5FeNb-1.5C master alloy as a grain refiner is also acceptable for Al-Si cast alloys when the silicon content is more than 4wt.%. As a result of inoculation with Al-3.5FeNb-1.5C master alloy, the average grain size of α -Al is reduced to $22 \pm 3 \mu\text{m}$ from about $71 \pm 3 \mu\text{m}$ and grain refining efficiency is not characterized by any visible poisoning effect, which is the major limitation in the grain refinement of Al-Si cast alloys by applying Al-Ti-B ternary master alloys. Mechanical properties such as ultimate tensile strength and yield strength are significantly improved by 9.6% and 9.7%, respectively.

Key words: casting; Al-Si alloy; Al-3.5FeNb-1.5C; microstructure; grain refiner; Al_3Nb ; NbC

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The automotive industry, which is the vital contributor to environmental pollution, has been forced to the usage of the light structural metallic materials instead of ferro-materials to minimize the global warming problem. Compared to other materials, aluminium alloys are currently the most widely used in the automotive industry, particularly for structural applications, owing to their different combinations of advantages, such as low density, high fluidity, excellent resistivity in corrosion, superior castability, good strength with light weight, and low electrical expansion coefficient. Due to light weight, good strength and high fluidity, Al-Si cast alloys are increasingly used in the fields of automotive, aeronautics, defence, and industrial engineering^[1-4].

From the previous investigations performed on the solidification process of Al-Si alloys, it was observed that the microstructures of Al-Si cast alloys prepared by conventional methods generally have coarse α -Al primary grains or twinned columnar grains caused by

the effect of Si. The microstructure and mechanical properties of the castings are strongly dependent upon the size and distribution of eutectic Si, and the primary α -Al formed in the as-cast microstructure. The enhancement of mechanical properties may be obtained by the refinement of grains which can significantly reduce the size of the primary α -Al grains (i.e. fine equiaxed grains) in the casting. Grain refinement by introducing the inoculating particles into the melts for the heterogeneous nucleation in solidification is the most efficient approach to enhance homogeneously dispersed small equiaxed grains, which causes proper melt feeding during solidification, reduced and homogeneous distribution of porosity, improved surface finish and enhanced mechanical properties^[5-8].

Usually, the most effective grain refiners for Al alloys are prepared from Al-Ti-X (Here, X= B or C) ternary system alloys^[9-11]. For example, the Al-5Ti-B ternary master alloy with a silicon content of usually less than 2wt.% was identified as a good grain refiner for continuous and semi-continuous castings of wrought aluminium alloys. However, for the aluminium cast alloys, whose Si content is generally greater than 4wt.%, the grain refining efficiency of the commercial Al-Ti-B master alloys are comparatively poor. The reason is due to the formation of titanium silicide (i.e. TiSi and TiSi_2), by the interaction of titanium with silicon, and this phenomenon is usually termed as a poisoning effect^[12-14].

*Anil Kumar Birru

Male, born in 1981. Ph. D. supervisor, Asst. Professor and Head of the Mechanical Engineering Department in NIT Manipur, India. His research interests are mainly focused on metal casting, nano-composites, and supply chain management. He is the author and co-author of more than 40 technical papers in Journals and International conferences.

E-mail: anilbirru@gmail.com

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To date, various trails and many investigations have been done to improve the grain refinement effect in Al-Si cast alloys to enhance the fine equiaxed grain structure by the combined addition of trace elements such as Nb, V, Zr, Ta, W, and Ce, etc.^[15-17]. Elements such as Sr, P and Mg also have been employed to prevent the “poisoning effect” of silicon^[18-19], but failed to perform adequately. Presently, the investigations that have been done to address the poisoning effect are mainly Nb-B inoculation, Al-B binary master alloys^[20], Al-1Ti-3B ternary master alloys^[21], Al-Ti-C and Al-Ti-C-B master alloys^[22] or alternatives of the Al-Ti-*X* ternary master alloys^[23]. The considerable results of investigation performed by M. Nowak et al.^[24] concluded that Nb has a similarity with the behaviour of Ti, and three kinds of intermetallic compounds (niobium silicide) are formed, specifically NbSi₂, Nb₃Si and Nb₅Si₃, which have higher melting temperatures than the titanium silicide. According to Pan VM et al.^[25], Si has an extremely low solubility in both AlNb₃ and AlNb₂ intermetallics, and only approximately 2 percent in AlNb₃. So the formation of niobium silicides comparing with the formation of titanium silicide, particularly at 850 °C of Al-Si melt, is remarkably

less; consequently, the Nb-based intermetallic phases, such as niobium borides (i.e NbB₂), have greater stability than titanium borides. Hence, the inoculation of Nb-B results in the significant refinement of both primary aluminium α -grains and the eutectic silicon phase of Al-Si alloys. In the present research, an attempt has been made to investigate the grain refinement efficiency on pure aluminium (by permanent steel mould casting) and commercial Al-9.8Si-3.4Cu (by high pressure die casting) at different addition levels of the Al-3.5FeNb-1.5C grain refiner. The significant grain refinement of Al-Si cast alloy has been observed.

1 Materials and methods

1.1 Materials

The required materials employed for the current investigations are pure Al and commercial Al-9.8Si-3.4Cu. The chemical composition of the commercial Al-9.8Si-3.4Cu is shown in Table 1.

Table 1: Chemical composition of Al-9.8Si-3.4Cu alloy (mass%)

Al	Si	Cu	Fe	Ti	Pb	Mg	Sn	Ni	Zn	Mn
86.18	9.839	3.474	0.189	0.184	0.043	0.041	0.013	0.008	0.008	0.007

1.2 Master alloy preparation

Al-3.5FeNb-1.5C grain refiner was fabricated by an inoculation technique in the melting furnace. Aluminium (99.9% pure) ingot, activated carbon powder (~150 μ m) and ferroniobium (60% Nb) metal were used as raw materials. Initially, 1 kg aluminium ingot was melted in a graphite crucible at 900 °C and held for 1 hour. Then, 1.7wt.% of preheated activated carbon powder wrapped in an aluminium foil was added to the molten metal, and after holding for 4–5 min, the 7.7wt.% of ferro-niobium (FeNb) metal was added to the melt. The temperature of the melt was increased up to 1,500 °C and held for 6–7 min to promote the dissolution of Nb into Al. The molten metal was continuously stirred with a metallic rod (coated with graphite) for about 3 min at every 20 min interval. The molten metal was then poured into a preheated cylindrical permanent metallic die. The solidified Al-3.5FeNb-1.5C grain refiner was then used to conduct grain refinement investigation on pure aluminium and Al-9.8Si-3.4Cu cast alloys.

1.3 Casting fabrication

A new stir casting facility (M/s Swamequip, India) was used to fabricate castings. The facility features an electrical induction furnace attached with a bottom pouring arrangement. Initially, 1 kg of preheated pure aluminium was charged in a graphite coated crucible of the stir casting facility. The furnace temperature was raised to 800 °C to melt the aluminium ingot. The slag formed on the surface of the melt was carefully removed and a preheated graphite coated stirrer was carefully placed below the

surface of the melt at a height of 10 mm from the base to carry out the stirring process. The coating of graphite on the blades of the stirrer is essential to prevent the migration of ferrous ions from the stirrer into the molten metal. The preheated Al-3.5FeNb-1.5C master alloy pieces were added into the molten metal at 720 °C $\pm$ 8 °C and held for 15 min, with a proper stirring speed (at 450 r·min⁻¹) to enhance uniform distribution of particles in the melt. Finally, the melt was poured into a 350 °C preheated permanent steel mould of 25 $\times$ 25 $\times$ 280 mm³ in size, as shown in Fig. 1. By this method, three aluminium castings with different addition amounts of Al-3.5FeNb-1.5C master alloy (0.0wt.%, 0.1wt.% and 0.3wt.%) were cast. Also three Al-9.8Si-3.4Cu alloy die castings, with 0.0wt.%, 0.1wt.% and 1.0wt.% Al-3.5FeNb-1.5C, were prepared by high pressure die casting process under the process parameters of 720 °C melting temperature, 1.2 m·s⁻¹ plunger velocity, 260 °C die temperature and 24 MPa injection pressure.

The cast samples of 15 $\times$ 15 $\times$ 15 mm³ in size were cut from the bottom of the casting, and their surfaces for microstructural investigations were ground with 120–1200 grit SiC abrasive papers and polished with emery polishing papers (grade from 1/0 to 4/0), and finally, disc polishing was carried out with Al₂O₃ solution by means of polishing machine. The polished cross-sectional samples are etched in Tucker’s reagent (15 ml hydrofluoric acid +15 ml nitric acid +45 ml hydrochloric acid + 25 ml distilled water). Microstructural examination was carried out with a metascope metallurgical microscope. Buehler Omni Met image analysis software, in conjunction with an optical

Fig. 1: Solidified experimental casting in a permanent steel mould

microscope, was used to characterize the microstructure and measure the grain size of the specimens. Grain size calculations were performed by the linear intercept method. The sizes were measured at different locations for each specimen and the average grain size was determined. To evaluate the tensile strength properties of the experimental casting, the rectangular specimens were prepared according to ASTM: B557M-15 standard using a CNC wire cutting machine. All of the ultimate tensile strength and yield strength values were obtained directly from the resolved program of the universal testing machine. The microstructure and the intermetallic particles of the Al-3.5FeNb-1.5C master alloy were examined by XRD and FE-SEM.

2 Results and discussion

2.1 Microstructure of Al-3.5FeNb-1.5C master alloy

Figure 2 shows the X-ray diffraction (XRD) results of the Al-3.5FeNb-1.5C master alloy as a grain refiner. It was observed that the Al-3.5FeNb-1.5C grain refiner primarily contains α -Al, Al_3Nb and NbC phases. The intermetallic particles such as Al_3Nb (characterized by tetragonal structure with lattice parameters $a=3.848 \text{ \AA}$, $c=8.615 \text{ \AA}$) and NbC (characterized by face-centered cubic structure with lattice parameter $a=4.430 \text{ \AA}$) act as potential nucleation sites for improving the equiaxed structure. Also, the diffraction peak of Fe_2Nb , which is effective in strengthening grain boundaries and suppressing deformation, was detected in the XRD patterns. From Fig. 3, it can be observed that the intermetallic particles (Al_3Nb and NbC) are scattered uniformly and detached from each other; and the size of the particles are varied.

Fig. 2: XRD results of Al-3.5FeNb-1.5C master alloy

Fig. 3: SEM microstructure of dispersed intermetallic particles in Al-3.5FeNb-1.5C master alloy

2.2 Effect of Al-3.5FeNb-1.5C master alloy addition on pure aluminium

The macro and micro structures of pure Al with different additions of Al-3.5FeNb-1.5C master alloy (0.0wt.%, 0.1wt.% and 0.3wt.%) are shown in Figs. 4 and 5.

It was observed from Figs. 4(a) and 5(a) that the grain structure of the unrefined pure Al is coarse with an average grain size of approximately 1–3 mm. These coarse α -Al grains evidently became refined equiaxed grains by the addition of Al-3.5FeNb-

Fig. 4: Macrostructures of as-cast pure aluminium: (a) without grain refinement; (b) 0.1wt.% of Al-3.5FeNb-1.5C; (c) 0.3wt.% of Al-3.5FeNb-1.5C

Fig. 5: Optical microphotographs of as-cast pure aluminium with different additions of Al-3.5FeNb-1.5C: (a) 0 wt.%, (b) 0.1 wt.%, (c) 0.3 wt.%

1.5C grain refiner at different levels, as shown in Figs. 4 and 5. As shown in Fig. 5(b), with addition of 0.1wt.% Al-3.5FeNb-1.5C, the significant refined equiaxed α -Al grains are observed, due to the heterogeneous nucleation of α -Al grains on Al_3Nb ; the average α -Al grain size is decreased to $187 \pm 7 \mu\text{m}$. While, as the addition of Al-3.5FeNb-1.5C master alloy increases to 0.3wt.%, the grain size of α -Al increases slightly again to $272 \pm 7 \mu\text{m}$. From these experimental results, it can be revealed that the grain refinement effect is significantly improved by the addition of Al-3.5FeNb-1.5C master alloy particularly at the level of 0.1wt.%.

2.3 Effect of Al-3.5FeNb-1.5C master alloy addition on Al-9.8Si-3.4Cu alloy

The microstructures of Al-9.8Si-3.4Cu alloy die castings with and without grain refiner additions are shown in Fig. 6. From these micrographs, it can be seen that the Al-9.8Si-3.4Cu cast alloy without the addition of the grain refiner has coarse primary α -Al grains (Fig. 6a). After addition of the Al-3.5FeNb-1.5C master alloy, the size of the α -Al grain size is reduced, as shown in Figs. 6(b) and 6(c), and it can be observed that the grain size of commercial Al-9.8Si-3.4Cu cast alloy with the addition of 0.1wt.% of Al-3.5FeNb-1.5C master alloy, as shown in Fig. 6(b), is significantly finer in comparison to the alloy with the

addition of 1.0wt.% Al-3.5FeNb-1.5C master alloy (Fig. 6c). The average grain size of the α -Al in the Al-9.8Si-3.4Cu alloy with addition of 0.1 wt.% Al-3.5FeNb-1.5C master alloy is reduced to $22 \pm 3 \mu\text{m}$ from $71 \pm 3 \mu\text{m}$, as shown in Fig. 6(b). But, the average grain size of the α -Al is again increased from $22 \pm 3 \mu\text{m}$ to $48 \pm 3 \mu\text{m}$ (Fig. 6c) with the increasing of Al-3.5FeNb-1.5C master alloy additions from 0.1wt.% to 1.0wt.%, which may be due to the formation of β - Al_3FeSi platelets. According to the conclusions given by Zedan et al.^[26], these β platelets often result in the formation of large shrinkage cavities, because the liquid metal cannot fill the space between the branched platelets. By the comparison of the grain size of the alloy with and without grain refinement, as shown in Fig. 6, it was observed that the Al-3.5FeNb-1.5C master alloy has a much better grain refining performance particularly at 0.1wt.% addition on Al-9.8Si-3.4Cu alloy. According to these results, it can be concluded that the developed Al-3.5FeNb-1.5C grain refiner can efficiently refine binary Al-Si alloys due to the formation of niobium silicides which are more stable than titanium silicides, therefore, significantly limiting the so-called poisoning effect. Figure 7 shows the average grain size variation in pure Al and Al-9.8Si-3.4Cu alloy at different weight percentages of Al-3.5FeNb-1.5C master alloy.

Fig. 6: Microstructures of Al-9.8Si-3.4Cu alloy die castings with different additions of Al-3.5FeNb-1.5C grain refiner: (a) 0 wt.%, (b) 0.1 wt.%, (c) 1.0 wt.%

2.4 Mechanical properties of die casting Al-9.8Si-3.4Cu alloys

The ultimate tensile strength (UTS) and yield strength (YS) of the Al-9.8Si-3.4Cu alloy die castings before and after the addition of the Al-3.5FeNb-1.5C grain refiner are shown in Fig. 8. It can be seen clearly that both UTS and YS of the Al-

9.8Si-3.4Cu alloy die castings are significantly improved by the addition of the grain refiner. The UTS of the unrefined Al-9.8Si-3.4Cu alloy is about $218 \pm 3 \text{ MPa}$. After the addition of 0.1wt.% grain refiner, it was increased to $239 \pm 3 \text{ MPa}$, increased by 9.6%. Similarly, YS of the Al-9.8Si-3.4Cu alloy is increased from 186 ± 3 to 204 ± 3 by the addition of 0.1wt.% of

Fig. 7: Comparison of average grain size of pure Al and Al-9.8Si-3.4Cu alloy with different addition of Al-3.5FeNb-1.5C grain refiner

grain refiner. With a further increase of the grain refiner from 0.1 to 1.0wt.%, both UTS and YS values are decreased, but are still higher than that the alloy without grain refiner addition. The results indicate that the grain refinement has resulted in a very evident improvement in the mechanical strength (UTS & YS) of the commercial Al-9.8Si-3.4Cu alloy. Figure 9 shows

Fig. 8: UTS and YS of Al-9.8Si-3.4Cu alloy die casting with and without grain refiner

the SEM micrograph and EDX of high pressure die casting Al-9.8Si-Cu alloy with addition of 0.1wt.% Al-3.5FeNb-1.5C master alloy. It is clear that the addition of 0.1wt.% Al-3.5FeNb-1.5C master alloy results in the formation of fine grain structure by heterogeneous nucleation due to the effect of intermetallic particles such as Al_3Nb and NbC .

Fig. 9: SEM microstructure (a) and EDX (b) of Al-9.8Si-3.4Cu alloy die casting with 0.1wt.% Al-3.5FeNb-1.5C

3 Conclusions

The Al-3.5FeNb-1.5C master alloy as a novel grain refiner with uniform microstructure has been developed and its effect on microstructure and mechanical properties of pure Al and Al-9.8Si-3.4Cu alloy were investigated. Based on the experimental results, the following conclusions can be drawn:

(1) Addition of Al-3.5FeNb-1.5C master alloy to pure aluminium leads to adequate grain refinement. The mean size of α -Al grains in the pure Al is decreased from 1–3 mm to $187 \pm 7 \mu\text{m}$ when 0.1wt.% Al-3.5FeNb-1.5C grain refiner was added.

(2) The developed Al-3.5FeNb-1.5C master alloy displays a significant grain refinement performance on the die casting Al-9.8Si-3.4Cu alloy due to the inauguration of niobium silicides (NbSi_2 , Nb_3Si and Nb_5Si_3). The average α -Al in the Al-9.8Si-3.4Cu alloy is reduced to $22 \pm 3 \mu\text{m}$ from $71 \pm 3 \mu\text{m}$ by the addition of 0.1wt.% Al-3.5FeNb-1.5C master alloy.

(3) The silicides, which are more stable than titanium silicides, effectively encounter the so-called poisoning effect. So, the mechanical properties of the Al-9.8Si-3.4Cu alloy die casting are significantly improved by the addition of the 0.1wt.% Al-3.5FeNb-1.5C master alloy; the ultimate tensile strength and yield strength of the Al-9.8Si-3.4Cu alloy are increased by 9.6% and 9.7%, respectively. Hence the effective grain refinement performance of the Al-3.5FeNb-1.5C master alloy for Al-Si cast alloys, where silicon content is more than 4wt.%, is accepted and recommended to industries.

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