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Influence of Zirconium on the Grain Refinement of Al 6063 alloy

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Abstract
The influence of zirconium on the grain refinement of Al 6063 alloy has been experimentally investigated. The microstructure and macrostructure of the refined alloy were investigated. The experimental results reveal that, the coarse dendrites in the microstructure of the alloy are effectively refined with the addition of zirconium to the melt prior to solidification. Grains of Al 6063 alloy can be refined from 256 μm to 95 μm via addition of 0.2 wt. % Zr at holding time 90 seconds. The grain refinement effect of zirconium is found to be due to addition of zirconium to the melt in the form of master alloy introduces Al_3Zr particles which are effective nucleating sites for the primary aluminium phase.

I. Introduction

Aluminium alloys (6000 series) are good candidate materials for structural components in automotive and aerospace applications, because of excellent formability, weldability, excellent corrosion resistance and light weight with good mechanical properties [1-5]. The most widely used aluminium alloy from 6000 series is the Al 6063 alloy, due to its attractive combination of mechanical properties, processability and stress corrosion resistance [6]. Grain refinement is the most widely used technique to achieve fine and uniform distributed equiaxed grains [7-10]. Fine equiaxed grain structure plays a crucial role in improving mechanical properties, improved feeding to eliminate shrinkage porosity, distribution microporosity and intermetallics throughout the casting and improved surface finish [11, 12]. Grain refinement is achieved via introducing grain refiners in the form of master alloys to the melt prior to solidification. The most common grain refiner used for aluminium and aluminium based alloys are the transition metals such as Ti, V, Zr, etc. These transition metals are used in the form of master alloys and can be used also as fluoride salts such as K_2TiF_6 and K_2ZrF_6 [13-15]. Additions of transition metals forming trialuminides with low solubilities and diffusion coefficients in this way control the evolution of the grain and subgrain structure during subsequent processing operations [16, 17]. Addition of Zr leads to formation of L12-orderd Al_3Zr phase from the melt. These particles are coherent and thermally stable because of their high melting points compared with that of Al matrix. In addition, Al_3Zr trialuminide particles are very stable against coarsening and redissolution cause a more uniform distribution of dislocations and pin grain boundaries. If the concentration of Zr is more than 0.1%, Al_3Zr particles form from the melt as a primary phase during rapid solidification, acts as nuclei for the solidification of Al, and Zr can thus operate as grain refiner of Al [18-20].

II. Experimental procedures

Al 6063 alloy was the starting material for all grain refinement experiments. Al-Zr master alloy was used as the grain refiner. This master alloy was prepared by in-situ reduction of zirconium oxide (ZrO_2) with excess aluminum in the presence of cryolite flux. Al 6063 alloy was melted in a graphite crucible using electrical resistance furnace at 800 °C. After addition of the grain refiner to molten alloy, the melt was stirred with a graphite rod for 60 sec. to homogenize the melt. The molten alloy was kept for a holding time ranging from 30 to 120 sec. then poured in a 75mm diameter steel ring of 4mm thickness and 25mm height on a refractory brick. After solidifying and cooling, specimens were prepared for macrograph by grinding and etching in solution contains 15mm HF, 15mm HNO_3, 45 mm HCl and 25mm distilled water. For measuring the grain size of the grain refined specimens, specimens were ground and polished then the micrograph was revealed using Keller's reagent to reveal their grain boundaries. At least, 40 pictures were taken for each sample, which were used in measuring the grain size with the linear intercept method.

III. Results and Discussions

3-1 Effect of holding time

The grain refining efficiencies of the master alloys are affected by many factors which include size, morphology of the grain refiner, melt holding time, melt temperature and others. One of the most important problems in grain refinement is to find the optimum holding time (critical contact time), which gives the highest performance for the grain refiner. If the holding time is very short, fine particles may not be achieved. On the other hand, if the holding time is extended for long periods, the grain refiner may be loss its effective performance [21]. Fig.1 shows the macrostructure of the unrefined Al 6063 alloy with average grain size of approximately 256 µm. Fig. 2 (a-d) shows the macrostructure of Al 6063 alloy refined with 0.2 wt. % Zr additions at various holding times. It can be noted that all cast specimens of Al 6063 alloy performed equiaxed grains within the contact time range. The microstructure gets more refined as the holding time decreases up to 90 seconds then slightly increases.

Fig. 1 Macrograph of unrefined Al6063 alloy

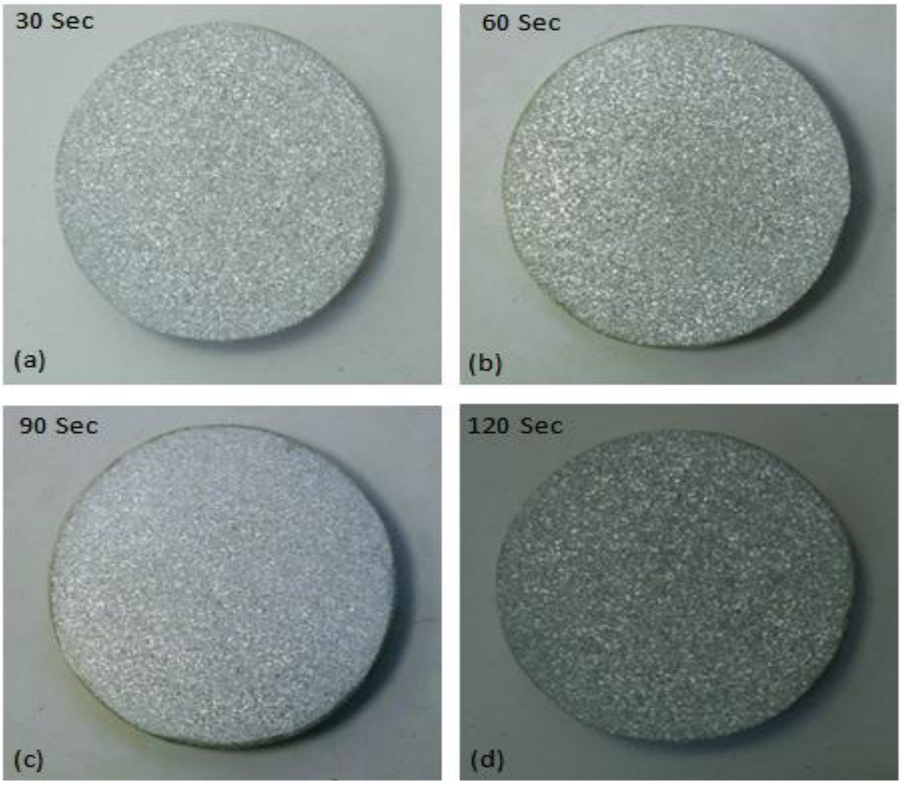

Fig. 2 Grain refining performance of 0.2 wt. % Zr on Al 6063 alloy at different holding time. (a) 30 sec., (b) 60 sec., (c) 90 sec., and (d) 120 sec.

Fig.3 (a-d) illustrates the microstructure features of the grain refined Al 6063 alloy after addition of 0.2 wt. % Zr at 30, 60, 90 and 120 sec. respectively. The grain refining performance improved with increasing holding time. The average grain size of the grain refined Al 6063 at the previous holding times are 122, 107, 95 and 110 µm respectively. It is clear that the grain refinement enhances the number of grain boundaries promoting homogeneous distribution of the second phases. As an effective surfactant, Mg was found to reduce significantly the surface tension of liquid Al which may help disperse the Al_3Zr particles in the melt. Mg has been reported to counteract the poisoning effect of Si effectively, where Mg diffuses into the grain boundary and forms Mg_2Si with Si at the grain boundaries. The precipitation of fine Mg_2Si in the aluminum matrix could strengthen the material [14, 22].

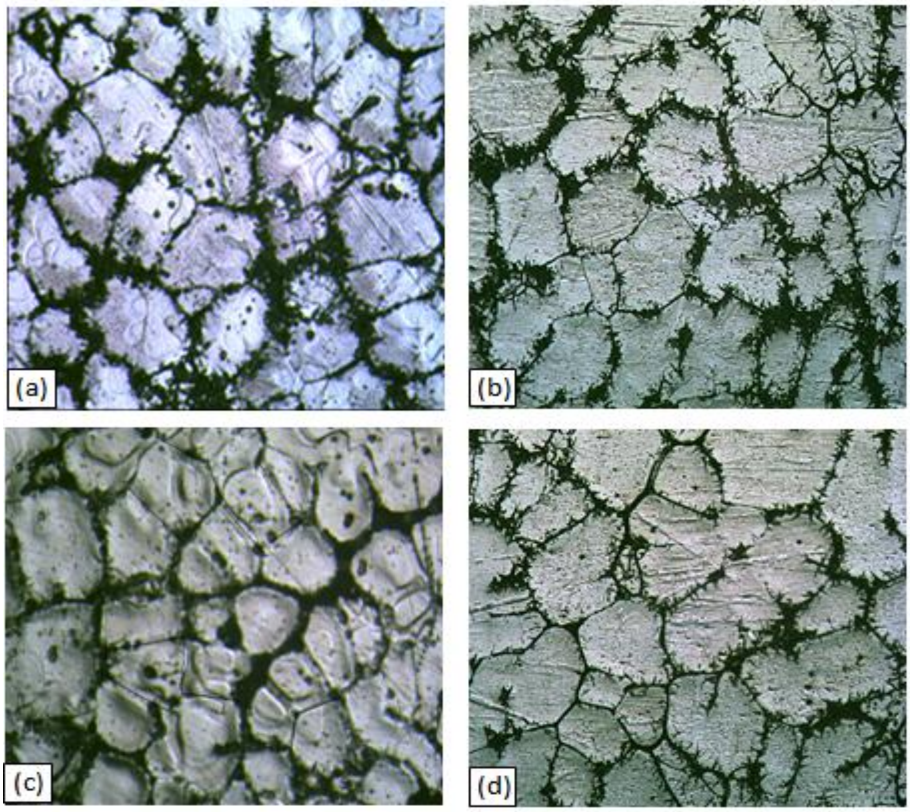

Fig.3 Micrographs of grain refined Al 6063 alloy by addition of 0.2 wt. % Zr at various holding time: (a) 30 sec., (b) 60 sec., (c) 90 sec. and (d) 120 sec.

Fig.4. shows the effect of various holding time on the grain refinement of Al 6063 alloy at 0.2 wt. % Zr addition. At the start of refining process, the grain size decreases sharply with the holding time and then increases slowly. This means that, the Al-Zr grain refiner fades with the increase of holding time. It is clear that the optimum holding time at which the nucleating sites show their full potency is 90 seconds, where the average grain size is 95 µm. At holding time of 120 seconds, the average grain size increased to 110 µm. The difference in density between Al_3Zr (which acts as heterogeneous nucleating particles) and the melt results in, these particles will sink and hence, the grain refiner losses its refining performance. In addition to settling, agglomeration also plays an important role in deteriorating the grain refinement resulting in short optimum holding time. Also, the Mg_2Si particles progressively coarsen and the average inter particle spacing between them increases with time [23, 24].

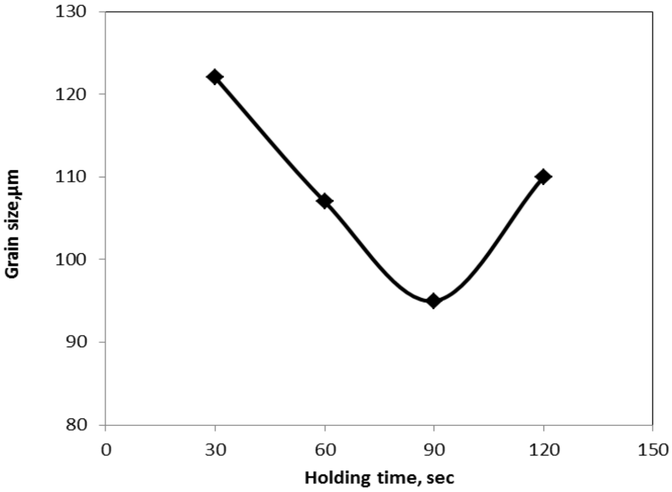

Fig.4 Grain size of Al 6063 versus holding time at Zr addition level of 0.2 wt. %. Effect of Zr addition level

Fig.5 (a-d) illustrates the macrostructure of the refined Al 6063 alloy as a function of Zr addition level at holding time of 90 seconds. It is clear that, all cast specimens of Al 6063 alloy performed equiaxed grains within the range of Zr addition level. These fine equiaxed grains are caused by the grain refinement effect of Zr, which introduce Al_3Zr particles to the Al 6063 alloy melt when added in the form of master alloy. These metastable particles exhibit a small lattice parameter mismatch with the α-Al solid solution and therefore, act as efficient heterogeneous nucleants during solidification of α-Al phase. It can be seen that, the grains get more refined as the addition level of Zr increases from 0.1 to 0.2 wt. % as seen in Fig. 5 (a-c). Further addition of Zr results in slight increase of the alloy average grain size as in Fig.(5-d).

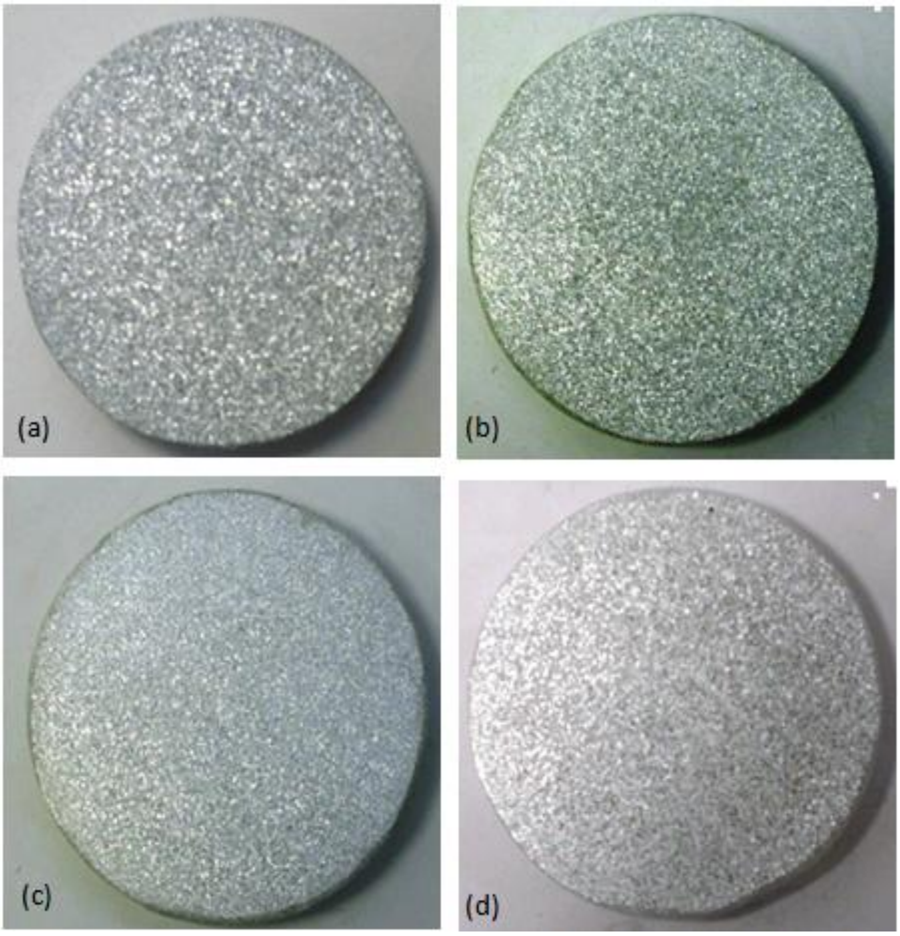

Fig.5 Macrographs of Al 6063 alloy grain refined by different addition level of Zr and at holding time of 90 sec., (a) 0.1, (b) 0.15, (c) 0.2 and (d) 0.25 wt.%.

Fig.6 (a-d) shows the micrographs of Al 6063 alloy grain refined by different addition level of Zr and at holding time of 90 seconds: (a) 0.1, (b) 0.15, (c) 0.2 and (d) 0.25 wt.%. It can be noted that, all alloy specimens exhibit an equiaxed grains and the average grain size decreases as the addition level of Zr increases up to 0.2 % Zr. The presence of precipitations of Mg_2Si influences the size of grains, avoiding the excessive growth of grain. The presence of some alloying elements, particularly Mg is known to improve the efficiency of some grain refiners, where Mg enhances the nucleation rate of the trialuminide particles [25].

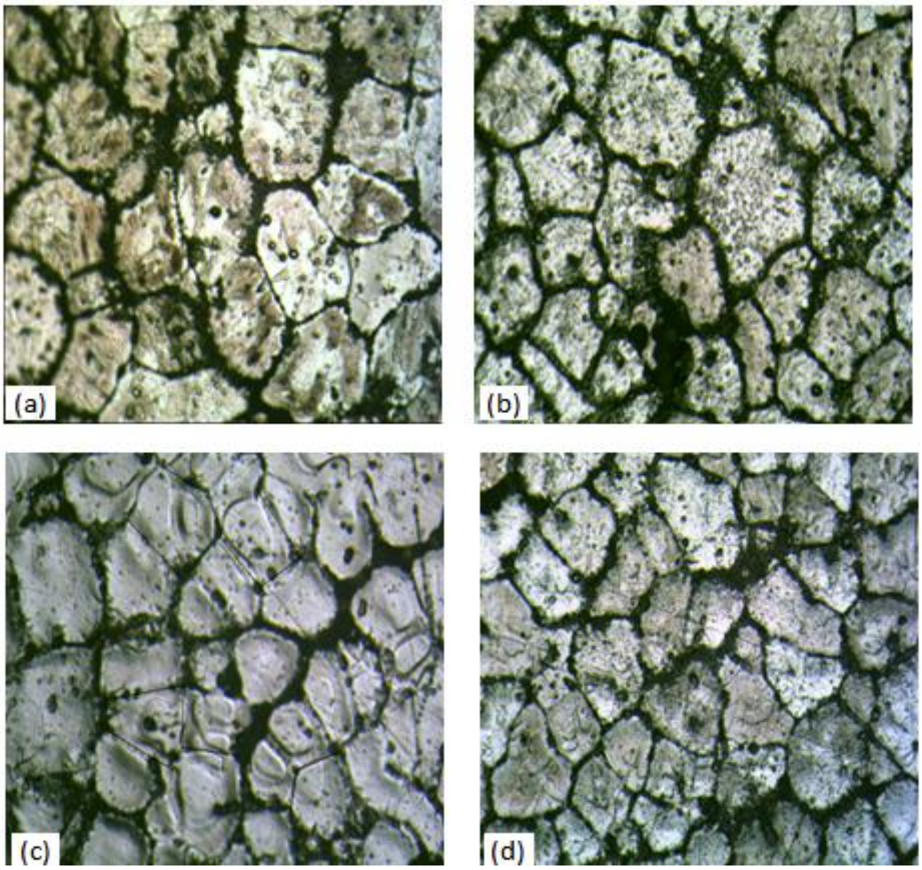

Fig.6 Micrographs of Al 6063 alloy grain refined by different addition level of Zr and at holding time of 90 sec.: (a) 0.1, (b) 0.15, (c) 0.2 and (d) 0.25 wt.%.

Fig.7 shows the effect of various addition level of Zr (0.1, 0.15, 0.2 and 0.25 wt. %), respectively at holding time of 90 seconds. It can be noted that, as the concentration of Zr increases, the average grain size of Al 6063 alloy decreases. This is due to the increase of Al_3Zr particles (which act as potent nucleating sites for α-Al phase) as the addition level of Zr increases. The optimum addition of Zr is 0.2 wt. %, where the average grain size corresponding to this addition level is 95 µm. Concentration of zirconium higher than 0.2 wt. %, result in slight increase in the average grain size of the refined Al 6063 alloy.

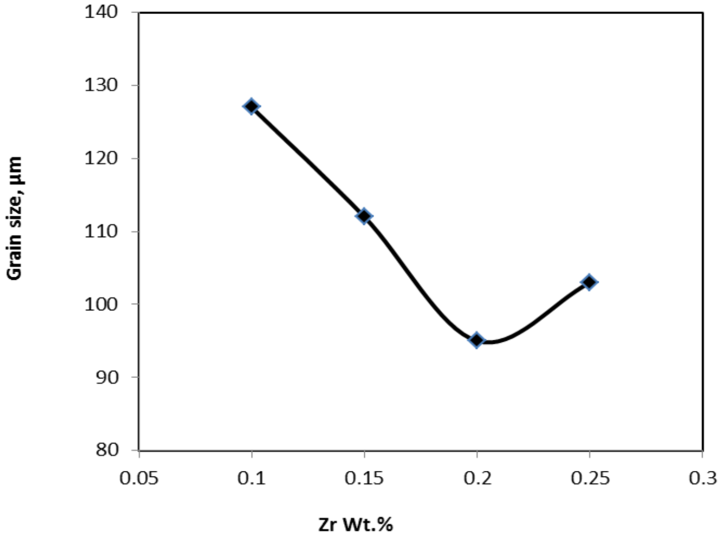

Fig.7 Al 6063 average grain size versus Zr addition level with 90 sec. holding time.

Al_3Zr particles which are embedded in α-Al grains are shown in Transmission Electron Microscope (TEM) micrograph, Fig.8. TEM examination confirmed that the Al_3Zr particles display a blocky morphology.

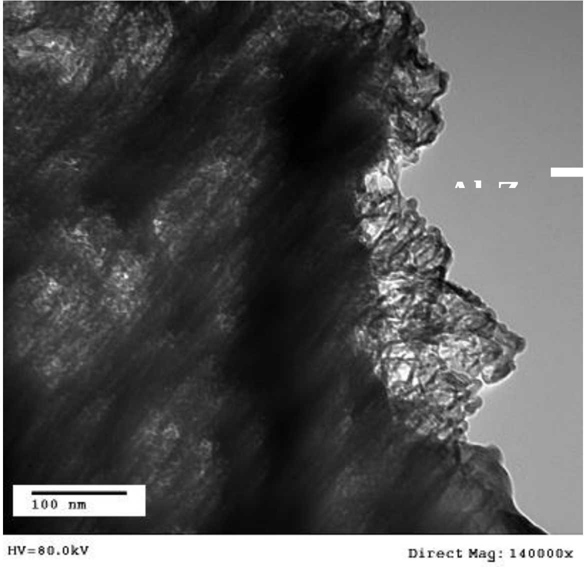

Fig. 8 TEM micrograph showing Al_3Zr particles in the grain refined Al 6063 alloy

IV. Conclusions

In the present work, the effect of minor Zr addition on the grain refinement of Al 6063 alloy was investigated. Based on the experimental results, the conclusions can be drawn as follows:

1- The optimum holding time of the grain refiner in the melt of Al 6063 alloy is 90 seconds.
2- The average grain size of the Al 6063 alloy is reduced to 95 µm from 256 µm by the addition of 0.2% wt. Zr at holding time of 90 seconds.
3- The grain refining performance of zirconium is due to, the presence of Al_3Zr which acts as an effective heterogeneous nucleating site for α-Al. In addition, these particles are effective in pinning dislocations, grain boundaries or sub-boundaries.

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