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GRAIN REFINEMENT OF COMMERCIAL PURE ALUMINIUM BY ZIRCONIUM

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ABSTRACT

The effect of Zr addition on the grain refinement of commercial pure aluminium (99.7%) has been investigated in the present study. The results showed that addition of up to 0.3wt. % Zr significantly decreases the average grain size of aluminium from 1100 µm to 162 µm at holding time of 90 seconds. The refining effect of zirconium is attributed to the presence of Al_3Zr particles in Al-Zr master alloy. These particles are acting as effective heterogeneous nucleating sites for α-Al.

Keywords: *grain refinement - aluminum-zirconium – master alloy*

1. Introduction

Aluminium is the most abundant element in the earth's crust. Pure aluminum possesses many advantages to be used extensively in industry, such as good electrical conductivity which superior to copper, better heat conductivity, lower density and higher plasticity [1-3].Metals and alloys usually solidify with coarse columnar grain structure under normal casting conditions [4]. So, the wide applications of aluminium in industry are limited because of the coarse microstructure which reduces the mechanical properties. It is of particular importance to improve the mechanical properties of aluminium by alloying or grain refining [5]. The process of grain refinement is carried out by addition of inoculants to aluminium to promote the formation of a fine and randomly oriented equiaxed grain structure upon solidification. Fine equiaxed grains impart high yield strength, high toughness, good extrudability, and uniform distribution of second phases and microporosity on a fine scale, improved machinability and cosmetic features [6-10]. The most common grain refiner used for aluminium and aluminium based alloys are the transition metals such as Ti, V, Zr, etc. Transition metals are characterized by strong interatomic bonding, low diffusivity in solid aluminium and limited solubility ofthese metals in the solid solution [11]. The 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 [12, 13]. However, use of such chemicals results in inconsistent performance and detrimental side-effects such as generation of toxic fluoride fumes, risk of

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halide inclusions and dross formation leading to high metal loss.The most common grain refiners used are Al-Ti, Al-Ti-C, and Al-Ti-B to melt before casting to promote refinement. Al-Ti-B is most widely used alloy with Ti: B ratios varying from 3:1 to 50:1. Titanium and boron are used to refine primary aluminum grains [14-16]. Addition of zirconium as a grain refiner introduces Al_3Zr trialuminide particles, which are stable, coherent to the aluminium matrix and exhibit a small lattice parameter mismatch with the α-Aland therefore act as efficient heterogeneous nucleants during solidification of aluminium [17-19]. With a Zr concentration of more than 0.1wt. %, Al_3Zr particles heterogeneously nucleate the primary aluminium. When Zr addition level is less than 0.1wt. %, no effective grain refinement can be observed [20]. The aim of this work is to investigate the factors that influence the performance of zirconium as a grain refiner for commercial pure aluminium (99.7%).

2. Experimental procedures

Commercial pure aluminium (99.7%) 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. A commercially pure Al was melted in graphite crucible using electrical resistance furnace at 740 °C. After addition of the grain refiner to molten aluminium, the melt was stirred with a graphite rod for 60 sec. to homogenize the melt. The molten aluminium was kept for a holding time ranging from 30 to 120 sec. then poured in a 75-mm diameter steel ring of 4 mm wall thickness and 25 mm height on a refractory brick. After solidifying and cooling, the specimens were prepared for macrograph by grinding and etching in solution contains 15ml. HF, 15ml. HNO_3, 45 ml. HCl and 25ml. 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.

3. Results and discussions

3.1. Effect of holding time

Fig.1 shows the macrograph of the unrefined commercial pure aluminium (99.7%). In the absence of grain refiner, it was noted that, aluminium exhibits fine columnar structure at the periphery and coarse equiaxed grains at the center of the specimen. The average grain size of unrefined aluminium is 1100 µm.

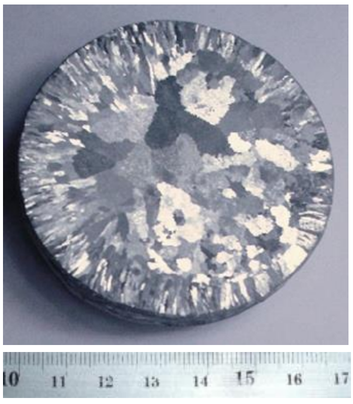


Fig. 1. Macrograph of unrefined aluminium specimen.

Fig.2 (a-d) shows the macrographs of commercially pure Al grain refined with 0.2 wt. % Zr addition level at different holding times (30, 60, 90, and 120 seconds). It is quite clear that the grain morphologies of all the specimens exhibit an equiaxed grain structure. There was a significant degradation in the grain refining performance of zirconium when molten aluminium was held at 740 °C for various holding times. Holding times longer than 90 seconds had an undesirable effect on the grain refining performance.

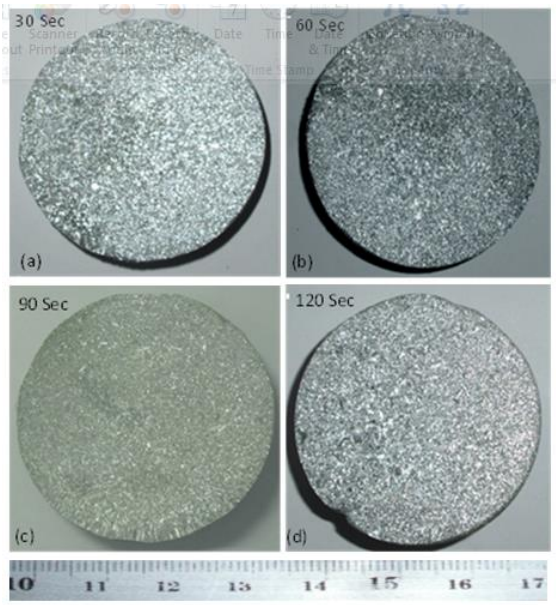


Fig. 2. Macrographs of commercially pure Al grain refined with 0. 2 wt. % Zr addition level at different holding time: (a) 30 sec., (b) 60 sec., (c) 90 sec., and (d) 120 sec.

Fig.3 (a-d) shows the effect of holding time on the microstructure of aluminium grain refined with 0.2% Zr. It can be noted that, the microstructure of the refined specimens demonstrates typical equiaxed grains and the efficiency of the grain refiner increases with increasing holding time till 90 seconds as shown in Fig.3 (c), then decreases. The fast action of zirconium in grain refinement of aluminium is an evident that the intermetallic phase Al_3Zr is fine crystals which increase their dissolution rate [21].

Fig. (4) shows the average grain sizes of aluminium as a function of holding time at zirconium addition level of 0.2 wt. %. It can be noted that the grain size progressively decreased with longer contact time till the grain size of aluminium reaches 186μm at holding time of 90 seconds, and then it increased to 220 μm at holding time of 120 seconds. The refinement is attributed to the trialuminides crystals (Al_3Zr) which gradually start to dissolve and lead to the reduction in their size and to the fragmentation of larger particles into smaller ones, providing more quantity of finer nuclei which would develop fine grain structure. If the melt is held for a long time after addition of zirconium as a grain refiner in the form of master alloy as in case of holding time of 120 seconds, the grain size of aluminium will increase. This means that the number of potent nucleating sites decreases. This is usually due to either dissolution or settling of Al_3Zr during long holding. The time of dissolution should be a function of the temperature, size, morphology, number of particles, and the nature and concentration of alloying elements present in the melt.

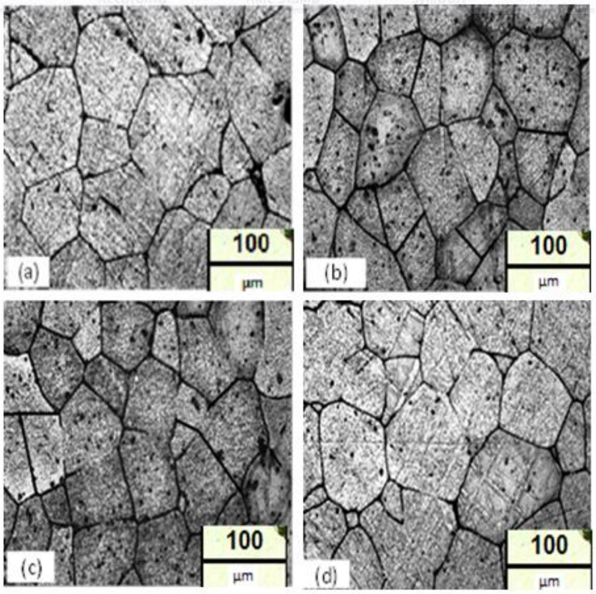


Fig. 3. Micrographs of grain refined aluminium by addition of 0.2wt. % Zr at various holding time: (a) 30 sec., (b) 60 sec., (c) 90 sec., and (d) 120 sec.

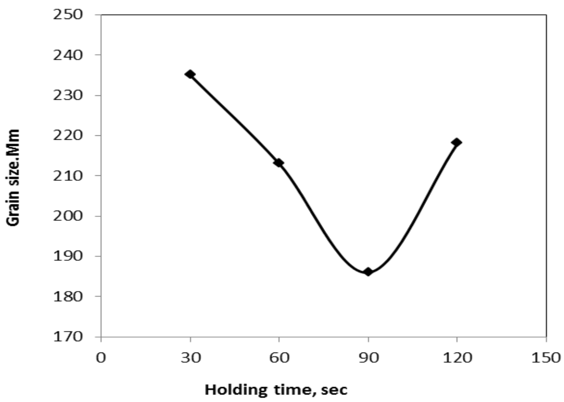


Fig. 4. Shows grain size of aluminium versus holding time at Zr addition level of 0.2 wt. %.

In the present work, 0.2wt%Zr was added to find the optimum holding time. At Zr addition higher than 0.2 wt% Al_3Zr particles act as nuclei for solidification of Al, hence Zr can operate as grain refiner of Al. At Zr addition less than 0.1 wt% poor or no refining effect has been reported [20, 22].

3.2. Effect of zirconium addition level

From Fig.5 (a-f), it can be seen that the grain size of aluminium decreases greatly with increasing the addition of zirconium. All aluminium specimens are fine equiaxed grain structure but the finest equiaxed grains obtained at zirconium addition level of 0.3 wt. % as seen in Fig. (5e). This mainly due to increasing the nuclei seeds (nucleation rate), so that a large number of crystals are formed, which soon impinge on each other and prevent each other from further growth.

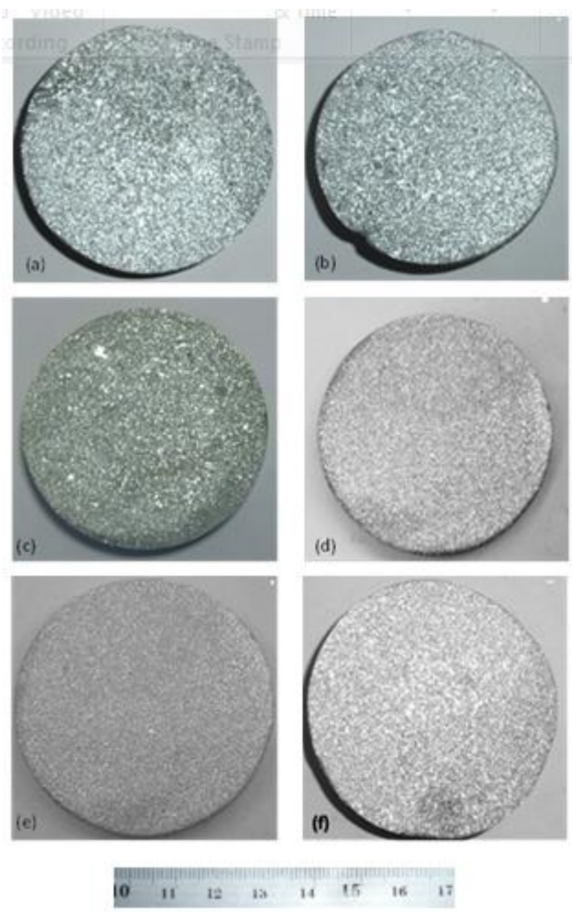


Fig. 5. Macrographs of commercially pure Al grain refined by different addition level of Zr and at holding time of 90 seconds: (a) 0.1, (b) 0.15, (c) 0.2, (d) 0.25, (e) 0.3, and (f) 0.35 wt.%

The additions of zirconium to aluminium melt in the form of aluminium-zirconium master alloy produce numerous potent and heterogeneous nuclei in the form of Al_3Zr. 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 and refine the grain. Fig.6 (a-f) shows that, the increase of Zr content from 0.1 to 0.3 wt. % in the aluminium can result in a fine microstructure and almost significant reduction of the average grain size. However, by further addition of Zr (> 0.3 wt. %) to the aluminium, the average grain size almost slightly increased and the excess addition of Zr does not have a considerable effect on the microstructure of the aluminium.

Theoretically, the refinement mechanism of aluminum zirconium melts changes with variation of Zr content. When the Zr concentration is lower, Zr mainly interacts with atom cluster, forming steady atom clusters, then growing up and finally becoming nuclei. When the Zr concentration is higher, the formation of α-Al is dependent on the peritectic reaction [19]: L + Al_3Zr=α-Al (solid solution).

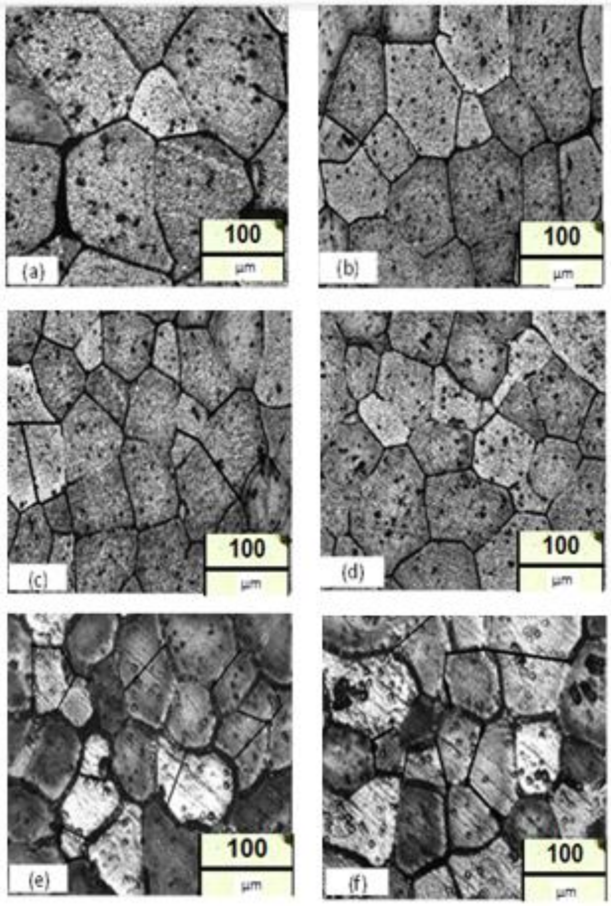
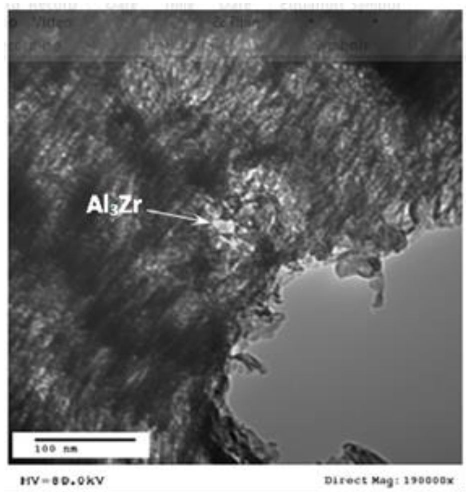
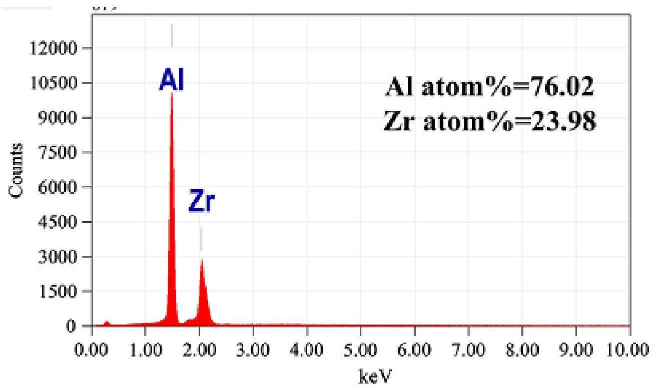


Fig. 6. Shows micrographs of commercially pure Al grain refined by different addition level of Zr and at holding time of 90 seconds: (a) 0.1, (b) 0.15, (c) 0.2, (d) 0.25, (e) 0.3, and (f) 0.35 wt.%.

Fig. 7a Shows TEM image of Al grain refined with Zr. Fig. 7b shows a typical EDX spectrum of the particles observed at/or near the grain centers. Al_3Zr particles which are very fine appear bright against the darker matrix. The variation of aluminium grain size due to increasing zirconium addition level is plotted in Fig.8. It can be noted that initial addition of 0.1% Zr with holding time 90 sec. decreases the average grain size of aluminium from 1100 µm to 240 µm. Further addition of zirconium 0.15, 0.2, 0.25, and 0.3 wt. % at the same holding time (90 sec.) to aluminium results in finer grain sizes 212, 186, 172, and 162 µm respectively. At Zr addition level of 0.35 wt. % the grain size of aluminium increased to 174 µm.



(a)



(b)

Fig. 7. (a) TEM image of Al grain refined with Zr (b) EDX spectrum taken from the particle at the grain centre.

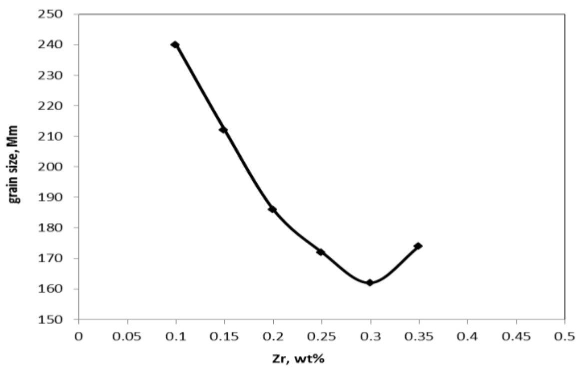


Fig. 8. Shows grain size of aluminium versus addition level of Zr at holding time of 90 seconds.

4. Conclusions

The effect of zirconium on the grain refinement of commercial pure aluminium (99.7%) is investigated by microstructure and macrostructure observation. The following conclusions can be made:

1- The optimum holding time of zirconium as a grain refiner in the melt of aluminium is 90 seconds.
2- The addition of 0.3% wt. % Zr at holding time of 90 seconds, refine the grains of aluminium from 1100μm to 162μm.
3- The efficiency of zirconium in grain refinement of aluminium is due to Al_3Zr, which heterogeneously nucleate the primary aluminium.

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تدقيق الحبيبات للألمونيوم التجارى بواسطة الزركنيوم

الملخص العربي:

تم دراسة تأثير عنصر الزكرونيوم في تدقيق حبيبات الألومنيوم تجاري النقاوة (99.7٪) في الدراسة الحالية. أظهرت النتائج أن إضافة ما يصل إلى 0.3٪ بالوزن من الزركونيوم يقلل بشكل كبير من متوسط حجم الحبيبات من الألمنيوم من 1100 ميكرون إلى 162ميكرون عند زمن 90 ثانية. ويرجع تأثير تدقيق الحبيبات للزركونيوم إلي وجود حبيبات مركب Al_3Zr في سبيكة الألومنيوم زركونيوم الرئيسية. هذه الحبيبات تعمل كمواقع تنوية غير متجانسة للطور ألفا ألومنيوم (α-Al).