

A new Al-Zr-Ti master alloy for ultrasonic grain refinement of wrought and foundry aluminum alloys

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Abstract

A new grain refiner master alloy based on the Al-Zr-Ti system was prepared by salt assisted synthesis. 90% of Al₃Zr particles in the master alloy were ranged between 1 and 13 μm. 80% reduction of grain size was observed with the addition of 0.2wt% Zr equivalent master alloy combined with ultrasonic treatment in an Al alloy. The new master alloy demonstrated 30% improvement in grain refinement efficiency compared to the one prepared by a conventional alloy route.

Key words: intermetallics, grain refinement, casting, ultrasound

Introduction

Grain refinement is an important practice assuring the quality of metals during casting, e.g. reducing casting defects and improving the properties for downstream processing. Among several techniques available for grain refinement such as physical methods (mechanical shearing and ultrasonic cavitation) and chemical methods (inoculation and growth restriction), most common practice is the inoculation of aluminum with TiB₂ particles introduced in the form of Al-Ti-B master alloys. Some extra Ti in the master alloys acts a growth restriction element as well as provides activation of TiB₂ substrates [1, 2]. For industrial use, Al-Ti-B master alloys are easy to add as rods or waffles to melts whether in a batch or continuous operation. One major drawback of Al-Ti-B master alloys is the agglomeration of TiB₂ particles in the melt during master alloy addition, which may affect the quality of the cast metal and create defects in the casting. Another is the limited efficiency in high-Si alloys due to the “poisoning” of TiB₂ [2]. Direct alloying of high growth restriction elements such as Ti and V provides grain refinement in Al but requires high addition rates (0.15-0.35 wt%) and maybe expensive. Several studies have identified intermetallic compounds such as Al₃Ti, Al₃Nb, Al₃Sc in aluminum alloys that may act as efficient nucleation sites during solidification [1, 3, 4].

Ultrasonic cavitation is reported as an efficient method for grain refinement [5, 6]. In particular, ultrasonication (US) of molten Al alloys was found to reduce the size and change the morphology of the intermetallics that usually form above the solidification temperature of aluminum [7]. Grain refining in Al alloys containing Zr and subjected to US has been reported in the 1960s [8] but without proper analysis of the mechanisms. Considerable grain

refinement was achieved in Zr and Ti containing pure Al, Al–Cu, and a number of commercial alloys when ultrasonic cavitation was applied in the temperature range of primary solidification of intermetallics [7, 9]. It was suggested that the refinement of large primary Al_3Zr intermetallic particles to a size of a few μm and their dispersion make them suitable for becoming the sites for heterogeneous nucleation of aluminum [7, 9]. It was also found that the Al_3Zr phase readily nucleates on alumina inclusions [10]. In this case, the ultrasonication facilitates this process by wetting and dispersion of naturally present oxides. Hence, several mechanisms of primary intermetallic refinement under US processing could operate, e.g. enhanced nucleation of dispersed oxides and fragmentation of crystals. The grain refinement of Al alloys with primary intermetallics and ultrasonic cavitation can be attractive to the industry because it (1) eliminates the necessity of AlTiB additions (some high-strength alloys actually already contain additions of Zr and Ti as a part of the alloy formula) and (2) turns potentially harmful coarse primary intermetallics into useful substrates for nucleation of aluminum.

The current paper investigates the grain refining efficiency of an Al–Zr–Ti intermetallic feedstock alloy manufactured by salt assisted synthesis. This alloy is used as a grain refining master alloy in combination with ultrasonic cavitation for two Al alloys representative of the wrought and foundry families.

Experimental

A master alloy with a nominal composition Al–5 wt% Zr–1.25 wt% Ti¹ (MA2) was prepared by reaction between Al and K_2TiF_6 – K_2ZrF_6 salt mix. The salts were taken in a ratio to assure that Zr:Ti = 4:1 in the final composition, and were mixed manually. 1 kg of commercial pure Al (CPAI) (99.7% purity Al) was melted in a clay graphite crucible at a temperature of 800 °C and the salt powder was mixed in using a graphite rod. The reaction and subsequent increase in the temperature due to the exothermic nature of the reaction was monitored using a K-type thermocouple. The metal was allowed to react for 30–60 min with intermittent stirring and then cast in a 10-mm diameter metallic mold. The cast billets were subsequently rolled to 6 mm diameter rod using a rolling machine (samples were heated to 400 °C before rolling).

Alternatively, a master alloy with a nominal composition Al–2 wt% Zr–0.5 wt% Ti (MA1) was prepared from commercial binary master alloys (Al–6% Zr and Al–5% Ti), note that the same 4:1 ratio between Zr and Ti concentrations was maintained. The alloy was also cast and rolled as described above.

In order to check the master alloy compositions, the master alloys were diluted by CPAI to approximately 0.2 wt% Zr (within the detectable limits of optical spectroscopy) and the resultant composition was measured using optical emission spectroscopy (Foundry Master). The experiments were repeated several times to approximate the composition of the alloys, which proved to be quite close to the nominal formulation.

¹ The 4:1 ratio between Zr and Ti follows the previously published work [9].

Grain refinement experiments were conducted on Al-3 wt% Cu and A357 (7.4 wt% Si, 0.5 wt% Mg, 0.1 wt% Fe, 0.1 wt% Ti, remaining Al) alloys. 500 g of the alloy was melted at 760 °C in a clay graphite crucible. A master alloy was added manually between 760 and 700 °C in the amount equivalent to 0.2 wt% Zr and was allowed to dissolve for 10 min with subsequent stirring of the melt. Ultrasonication (water-cooled magnetostrictive system (Reltec), 17.5 kHz, 3.5 kW, 40 µm peak to peak amplitude, Nb sonotrode) was performed after the addition of a master alloy in the temperature range 760 to 700 °C. The processing time was about 30 s. All alloys were cast at 700 °C in a metallic mold preheated at 250 °C. Sound billets without obvious casting defects were produced in all cases.

The cast samples were ground using SiC paper (400-2500 grit size) and polished using OPS. For identification of grain size, polished samples were anodised using 4% HBF₄ solution for approximately 1 min at 20 VDC and analysed in polarized light in an optical microscope (Zeiss Axioscope).

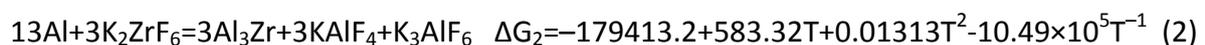
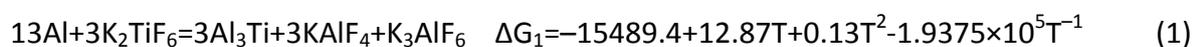
Results

Figure 1 shows the cast (a), machined (b) and rolled (c) billets of MA2. Optical microstructure of MA1 (Figure 2 (a, b)) contains large elongated Al₃Zr particles whereas MA2 (Figure 2(c, d)) shows fine Al₃Zr particles evenly distributed in the matrix. Rolling results in breaking large particles in MA1 but does not affect significantly the size and distribution of intermetallics in MA2. Figure 3 shows that Al₃Zr particles in MA2 range in size from 1 to 30 µm and 90% of the particle sizes are between 1 and 13 µm. Note that only Al₃Zr (with dissolved Ti) were found in the structure of master alloys.

The grain refinement efficiency of MA2 and MA1 was tested on Al-3 wt% Cu and A357 alloys (Figure 4). With the addition of 0.2 wt% Zr equivalent master alloy to the Al-Cu alloy, the initial grain size (390±53 µm) was reduced to 320±30 µm by US, to 170±24 µm by addition of MA2, and to 120±15 µm after both the addition of MA2 and US (Figure 5). There was no difference observed in the grain size of the alloys inoculated with cast and rolled master alloys (MA2) while ultrasonication was present. Fine Al₃Zr particles of 7-12 µm in size were found inside the grains after US processing (Figure 6). The grain refinement efficiency between MA1 and MA2 was compared for an A357 alloy (Figures 4 and 7). In the A357 alloy, the initial grain size (603±120 µm) was reduced to 460±32 µm after an addition of 0.2 wt% Zr introduced by MA1 (Figure 7(a)). With the subsequent application of US, the grain size was further reduced to 190±20 µm (Figure 7(b)). At the same time, when 0.2 wt% Zr were added by MA2, the grain size was 260±35 µm, and ultrasonication reduced it further to 140±15 µm (Figure 7(c)). Large dendrites are still present in the A357 alloy inoculated with MA1 and treated with US (Figure 7 (b)) as compared to the alloy inoculated with MA2 and treated with US where more rosette-shaped grains are formed (Figure 7 (c)).

Discussion

The following exothermic reactions would occur in the Al-K₂TiF₆-K₂ZrF₆ mix at 800 °C [11].



According to the Al–Zr–Ti phase diagram, Ti has large solubility in Al₃Zr phase forming DO₂₃ phase Al₃(Zr_{1-x}Ti_x) up to x=0.4 [12]. Hence, reaction (3) could be the most probable one in the later stage of the reaction.



The Al₃Zr phase is a sufficiently potent nucleant for aluminum as has been recently confirmed in a thorough study concluding that the crystallographic matching and the size distribution of Al₃Zr nucleant particles actually governs the grain refinement efficiency by this phase [13]. The reader is referred to ref. [13] for the details on the crystallography of nucleation in the Al–Zr system.

It was shown that the dissolution of Ti in Al₃Zr changes its lattice parameters, which increases the lattice mismatch with Al [14, 15]. The experimental data [9], however, showed that Ti presence is beneficial for the grain refinement with Al₃Zr particles. The effect of Ti could be two-fold. First, the changes in the lattice parameter may induce internal stresses in the solidifying intermetallic and make its cracking and fragmentation easier under ultrasonic cavitation. Second, the free Ti may act as a growth restriction element restricting the growth of Al grains and providing constitutional undercooling for nucleation of new grains, just as it does upon addition of a conventional Al–5Ti–1B grain refiner [16]. So the ultrasonication provides refining of the primary intermetallics to the sizes when they can act as seeds for Al crystals, whereas free Ti restricts the growth of Al grains and promotes (through constitutional undercooling) nucleation of new grains on Al₃Zr intermetallics. The Al₃Zr phase is apparently not susceptible to Si poisoning as this grain refining method works in high-Si alloys with the same efficiency as in wrought alloys.

As was already mentioned MA1 contained larger Al₃Zr particles and rolling fragmented some of these particles, whereas some of the large Al₃Zr particles underwent fragmentation during ultrasonic processing. At the same time the relatively low melt temperature (between 760 and 700 °C, which is below the liquidus of an Al–5% Zr alloy) and short US time limits the dissolution of the larger intermetallics rendering them useless for nucleation of Al (as they supply less solute Zr into the melt that can later-on re-precipitate as fine primary intermetallics). Therefore, the efficiency of MA1 is less than MA2. In the case of MA2, almost 90 percent of the particles range between 1 and 13 μm and either dissolve to reform during melt cooling or, if remained undissolved, act as ready substrates due to their small size. Therefore, MA2 is able to induce significant reduction in the grain size even without ultrasonication. Further grain reduction as a result of US processing is relatively small in both tested alloys. For example in A357 alloy, MA2 addition caused 57% reduction in grain size and another 20% after ultrasonication, whereas MA1 addition reduced the grain size by 24% without ultrasonication and further by 45% with ultrasonication. Similarly, the share of grain reduction with only MA2 in the Al–3 wt% Cu alloy is 54% with only further 16% attributed to ultrasonication. Previous grain refinement study on an Al–2.5 wt% Cu alloy containing 0.2 wt% Zr reported the grain size of 280 μm without ultrasonication, however, ultrasonication at 700 °C resulted in significant grain reduction to 58 μm [9]. It can be ascertained from the analysis of previous investigations [7, 9, 15] and the present study that ultrasonic treatment results in much greater reduction in grain size of the alloy

inoculated with MA1 type master alloy (or Zr and Ti added separately). But with MA2-type master alloy, where large volume of fine Al₃Zr particles are already present, a smaller share of grain refining results from ultrasonication.

Conclusion

A concentrated Al–Zr–Ti master alloy demonstrates good performance as a grain refiner feedstock. This master alloy can be produced by salt synthesis route and shaped as rods or billets depending on the usage. Alloys with high percentage of Zr and Ti can be produced with controlled Al₃Zr particle sizes to a few μm. The alloying elements such as Zr and Ti are regularly used in commercial Al alloys and, in addition to the grain refinement, can be useful for recrystallization control and high-temperature stability. The new master alloy produced by in-situ salt reaction showed significant grain refinement potential even without ultrasonication. It demonstrated 30% improvement in grain refinement efficiency compared to the application of a master alloy produced by smelting route. The master alloy can be used to its full potential with the assistance of ultrasonication in liquid state (down to the solidification range of primary intermetallics) typically possible in a direct-chill casting or foundry operation. Up to 80% reduction of grain size was observed with the 0.2 wt% Zr equivalent master alloy addition combined with ultrasonication of the melt.

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References

1. F. Wang, Z. Liu, D. Qiu, J.A. Taylor, M.A. Easton, and M.-X. Zhang: *Acta Mater.* 61, 360 (2013).
2. G.K. Sigworth and M.M. Guzowski: *AFS Trans.*, 93, 907 (1985).
3. F.A. Crossley and L.F. Mondolfo: *Trans. Am. Inst. Min. Metall. Eng.*, 191, 1143 (1951).
4. L.S. Toropova, D.G. Eskin, T.V. Dobatkina, and M.L. Kharakterova: *Advanced Aluminum Alloys Containing Scandium: Structure and Properties* (Amsterdam, OPA, 1998).
5. G.I. Eskin: *Ultrasonic Treatment of Molten Aluminum*, 2nd Edn. (Moscow, Metallurgiya, 1988).
6. G.I. Eskin: *Ultrasonic Treatment of Light Alloys Melts* (Amsterdam, OPA, 1998).
7. L. Zhang, D.G. Eskin and L. Katgerman: *J. Mater. Sci.* 46, 5252 (2011).
8. G.I. Eskin: *Ultrasonic Treatment of Molten Aluminum*, 1st Edn. (Moscow, Metallurgiya, 1965).

9. T.V. Atamanenko, D.G. Eskin, L. Zhang and L. Katgerman: *Metall. Mater. Trans.* 41A, 2056 (2010).
10. F. Wang, D. Eskin, T. Connolley and J. Mi: *J. Non-Ferrous Soc. China* (2016) (submitted).
11. X. Zhang, G. Li, T. Zhang, L. Cao, H. Wang, J. J. Wang, K. Gu, H. Zhang, X. J. Xu: *Appl. Mech. Mater.*, 217-219, 114 (2012)
12. L. Tretyachenko: *Ternary Alloy Systems*, Sub volume A, Part 4 (Berlin, Springer/MSI, 2006), pp. 54-67.
13. F. Wang, D. Qiu, Z.-L. Liu, J.A. Taylor, M.A. Easton, and M.-X. Zhang: *Acta Mater.* 61 5636 (2013)
14. M. Zedalis and M.E. Fine: *Scrip. Metall.* 17, 1247 (1983).
15. T.V. Atamanenko, D.G. Eskin, M. Sluiter and L. Katgerman: *J. Alloys Comp.* 509, 57 (2011).
16. M. Easton and D. StJohn: *Metall. Mater. Trans. A* 30A, 1625 (1999).

Figures and Tables

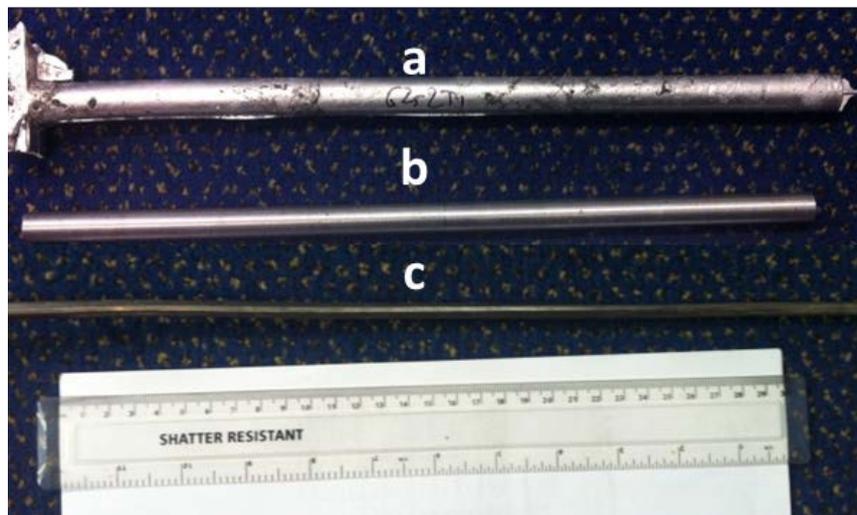


Figure 1. Cast (a), machined (b) and rolled (c) billets of MA2.

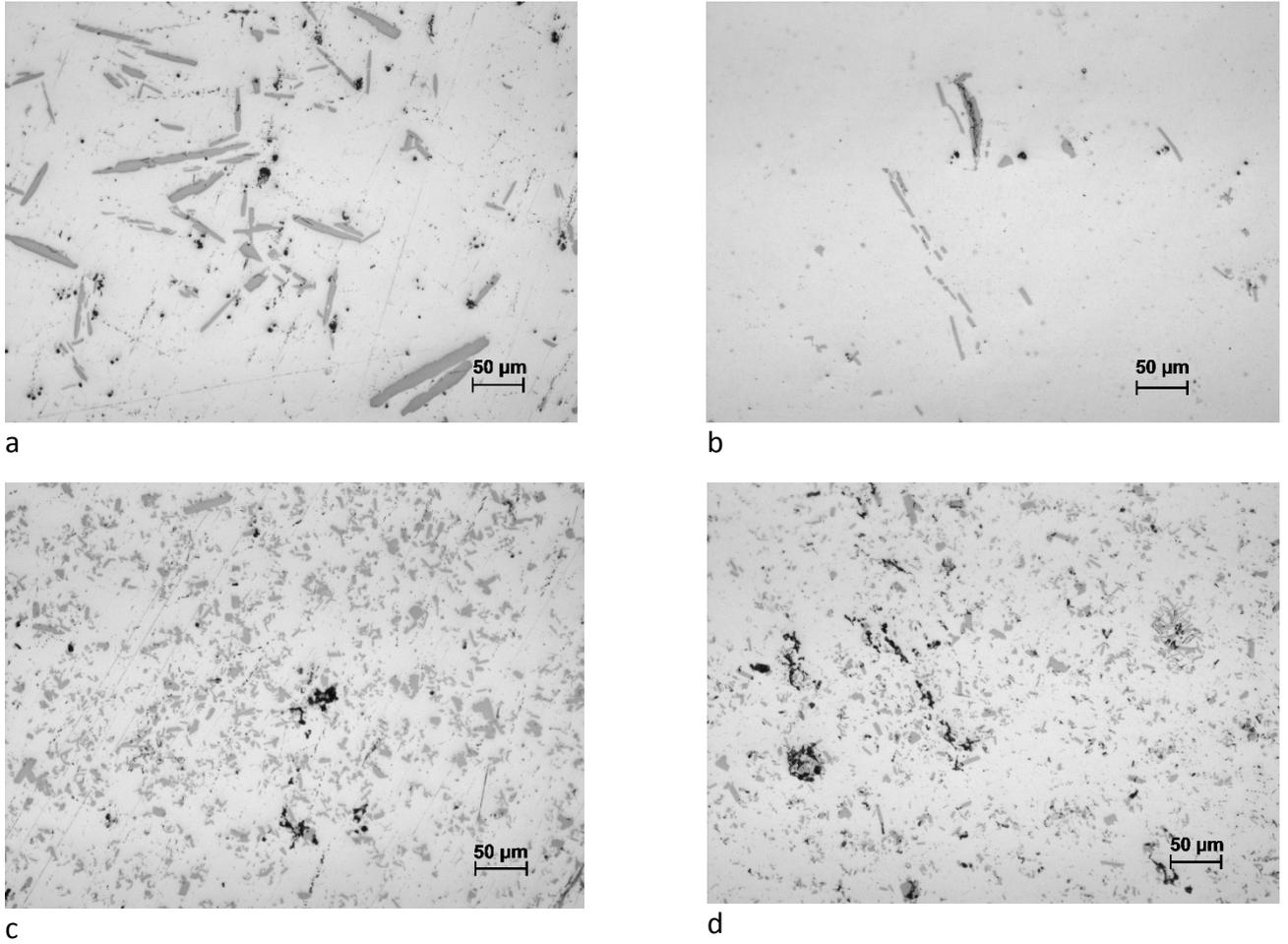


Figure 2. Microstructures of MA1 (a, b) and MA2 (c, d) after casting (a, c) and rolling (b, d).

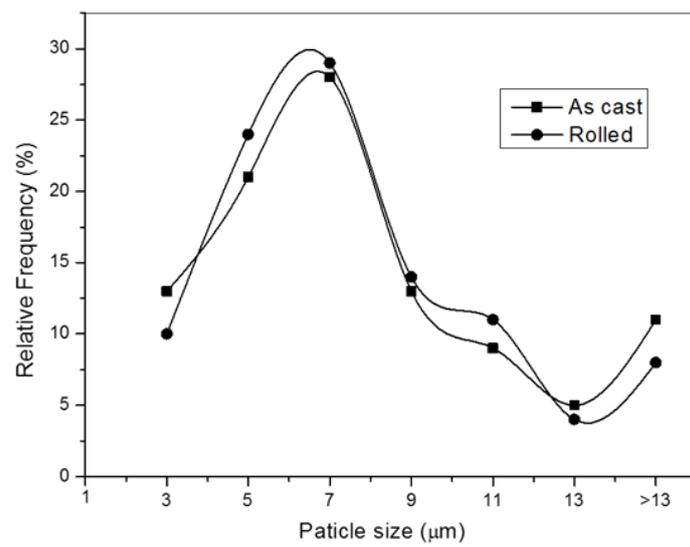


Figure 3. Al₃Zr particle size distribution in as-cast and rolled MA2 master alloys.

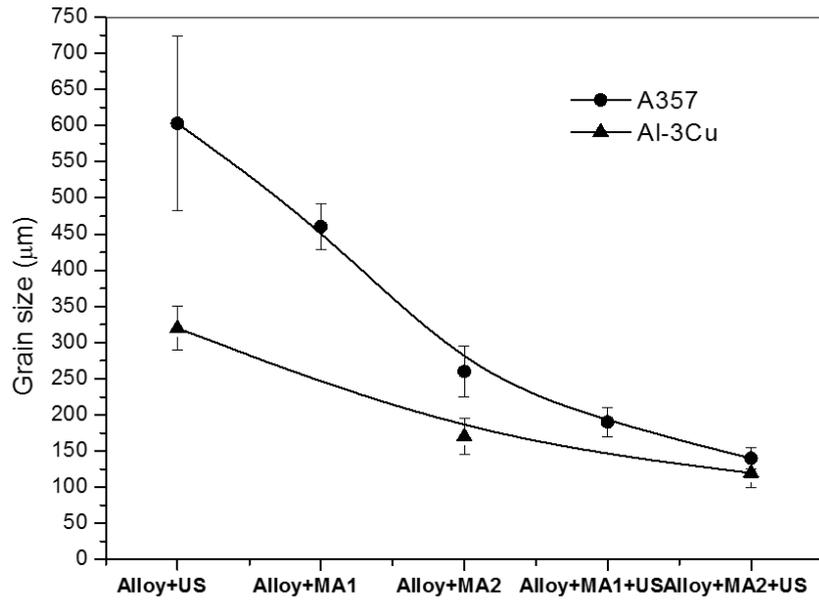


Figure 4. Grain size distribution in Al-3Cu and A357 alloys inoculated with MA1 and MA2 and treated with US.

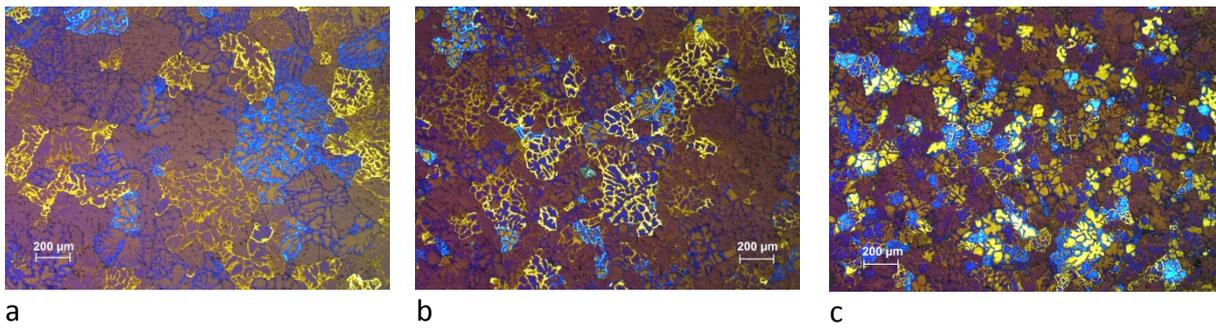


Figure 5. Anodized microstructure of an Al-3Cu alloy: (a) no MA2, US; (b) MA2, no US; (c) MA2 and US.

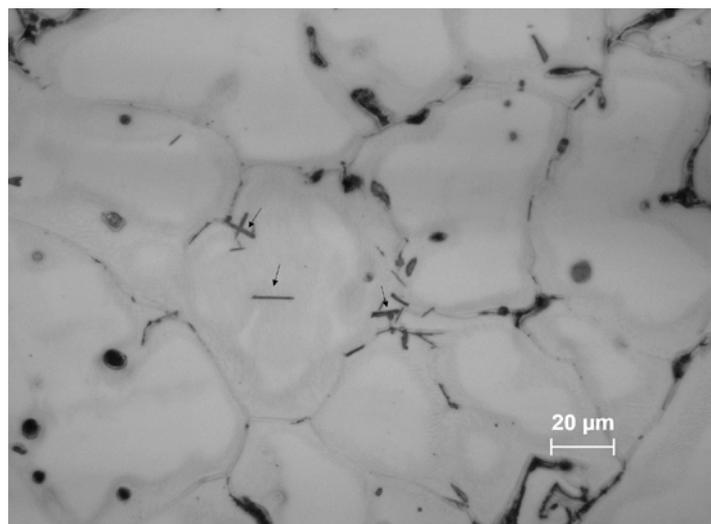
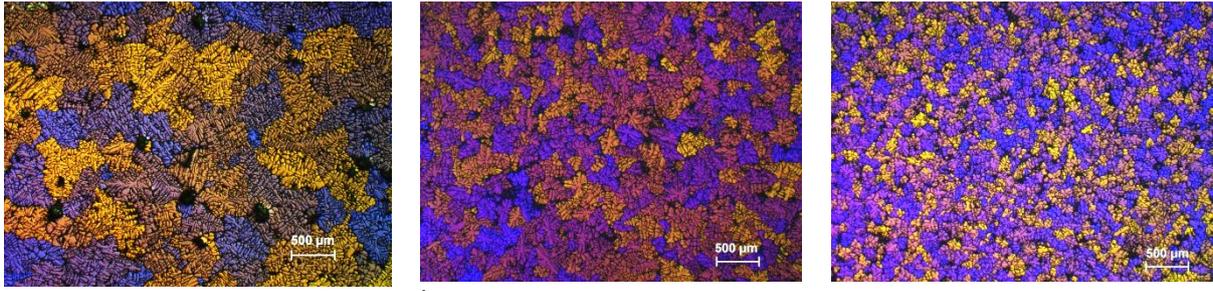


Figure 6. Microstructure of an Al-3Cu alloy inoculated with MA2 and treated with US (fine Al_3Zr particles are visible within the grain bulk).



a
b
c
Figure 7. Microstructure of an A357 alloy: (a) MA1, no US; (b) MA1, US and (c) MA2, US.