

ON THE MECHANISM OF GRAIN REFINEMENT BY ULTRASONIC MELT TREATMENT IN THE PRESENCE OF TRANSITION METALS

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Abstract

Ultrasonic melt treatment is known to induce grain refining in aluminum alloys. The degree of grain refinement is strongly linked to the stage of solidification when the treatment is applied and on the alloy composition. In the latter case the presence of grain refiners is important. In this paper it is shown that strong grain refining can be achieved in aluminum and its commercial alloys when the ultrasonic treatment is combined with the introduction of Zr and Ti. Ultrasonic processing is performed in the temperature range of the primary solidification of an intermetallic phase, i.e. normal casting temperatures of aluminum alloys. Dual mechanism is discussed involving (1) the dispersion and refinement of primary intermetallic particles that act as solidification sites and (2) growth restriction by the transition metal(s) that are present in the liquid phase.

Introduction

It has long been established that the formation of a fine scale, equiaxed, grain structure is desirable in castings because it improves the mechanical properties, reduces hot tearing, increases feeding to eliminate shrinkage porosity, and gives a more uniform finer distribution of secondary phases¹. The ultimate case of grain refinement is the formation of a so-called “non-dendritic” grain structure². A distinctive feature of such a structure is the formation of globular grains without segmentation into dendrite arms. In such case the grain size will be equivalent to the size of a dendrite cell at the same cooling rate. This is the minimum grain size which one can obtain under given cooling conditions².

There are many techniques of grain refinement available in casting practice, e.g. (1) deliberate addition of master alloys containing melt inoculants, the most common of which are based on the Al–Ti–B and Al–Ti–C systems³; (2) rapid solidification with high undercooling⁴; and (3) forced action upon melt which include mechanical⁵ or magneto-hydrodynamic stirring⁶, and ultrasonic vibrations^{2,7}.

The basic principle of ultrasonic melt treatment (UST) is inducing the waves of compression and expansion passing through liquid metal with an ultrasonic frequency, namely above 18 kHz. If the acoustic pressure exceeds a certain value, which is characteristic for a particular liquid, the liquid can rupture during the expansion (tensile or negative pressure) stage of the sound wave; weak sites within the liquid (e.g., preexisting gas pockets or interfaces with fine particles, called “cavitation nuclei”) are caused to rapidly grow, thereby producing vapor

and gas-filled cavities (bubbles)⁸. The formation, growth, and implosive collapse of bubbles in liquids irradiated with sound is called cavitation⁸. The implosion of the bubbles can be extremely violent, leading to intense yet short pulses of heating and high pressures⁸. Near extended liquid–solid interfaces cavitation produces microjets and shockwaves^{2,8}.

Cavitation and its secondary effects lead to liquid agitation and homogenization, raise the rate of convective diffusion processes, and have an influence on the temperature distribution in the medium⁹.

As early as in the 1930–1960s there were successful attempts by H.J. Seemann et al. in Germany to use ultrasonic processing for affecting the structure and composition of aluminum alloys¹⁰. These efforts were further developed in USSR and already in 1965 G.I. Eskin published a book on ultrasonic processing of molten aluminum¹¹. Since that time numerous works has been published across the globe that clearly demonstrated that ultrasonic vibrations coupled with the solidifying metal result in structural changes, including grain refinement, suppression of columnar grain structure, increased homogeneity and reduced segregation^{2,7}. However, the upscaling of the technological application of ultrasonic processing to direct-chill casting processing was always a problem. The lack of understanding of the mechanisms of the cavitation-aided grain refinement led to the failures in its practical application. The selection of reported mechanisms range from affecting nucleation through local undercooling and wetting (activation) of substrates to fragmentation and transport of dendrites.

It is quite obvious that the fragmentation of the growing dendrites can be a powerful means for grain refinement, which was confirmed by our earlier studies¹². This way of grain refinement is, however, the least practical as it assumes that the processing should be performed during solidification proper, in the mushy zone. The upscaling of the technology can be done only if the processing occurs outside the solidification region, when the alloy is still liquid.

In this paper we discuss the criteria of cavitation-aided grain refinement based on the experimental results of ultrasonic melt treatment of aluminum alloys with transition metals at different stages of solidification.

Experimental procedure

Eight ternary Al–Zr–Ti alloys were analyzed in this study with the concentration of Zr ranging from 0.11 to 0.23 mass% and concentration of Ti ranging from 0.016 to 0.065 mass%.

Experimental alloys were prepared using 99.97 wt. % pure aluminium, Al-5 mass% Ti, and Al-6 mass % Zr master alloys. The amount of melt, which was used for each experiment, was about 0.2 kg. The alloys firstly were molten in a stationary electric furnace until the temperature reached 780° C and then poured into graphite crucibles where they were either treated with ultrasound or cooled in the presence of the ultrasonic horn. Ultrasonic treatment was applied by means of a commercially available high-intensity ultrasonic system. The ultrasonic system comprised a 5-kW ultrasonic generator, a 5kW magnetostrictive transducer with water-cooling system, an ultrasonic wave guide made of steel, niobium ultrasonic horn, and a manipulator, which enables the movement of the system in horizontal and vertical directions. The resonant frequency of the ultrasonic system was 17.5 kHz. The input power of the generator during the current experiments was 4 kW. The amplitude of vibrations was measured on unloaded ultrasonic horn with the help of a vibrometer. The amplitude of vibrations was 40 µm.

Without ultrasonic treatment the pouring melt temperature was 730° C, while the cavitation melt treatment was performed at 700, 710 and 740° C. The chemical compositions of the alloys were verified by the optical spectrum analysis and are given in Table 1 along with corresponding temperatures of ultrasonic treatment. These temperatures represent the conditions when the treatment is performed above the liquidus of the Al₃Zr phase, close to the liquidus and below the liquidus. In all cases the temperatures were well above the formation temperature of aluminum solid solution (~660 °C)

The ultrasonic system was switched on before the horn was dipped into the liquid metal. The insertion depth of the ultrasonic radiator was chosen to be 3 mm below the surface of the liquid metal. Ultrasonic treatment was applied continuously during 10 s. Afterwards the melt was poured into a copper crucible with internal dimensions 40 by 35 mm, where it solidified.

Table 1. Alloy compositions and temperature conditions during ultrasonic treatment.

Alloy composition, mass %	Treatment temperature, ° C
Al-0.18 Zr-0.016 Ti	700
Al-0.18 Zr-0.025 Ti	
Al-0.18 Zr-0.048 Ti	
Al-0.18 Zr-0.065 Ti	
Al-0.18 Zr-0.065 Ti	710
Al-0.22 Zr-0.065 Ti	
Al-0.23 Zr-0.065 Ti	
Al-0.16 Zr-0.065 Ti	740
Al-0.22 Zr-0.065 Ti	

The observations of the solidified grain structures were made on cross sections taken at the same distance from the bottom of the sample by conventional metallography (cutting, polishing down to 1 µm diamond paste, and electrolytic oxidation at 20 VDC in a 3 % HBF₄ water solution) using a Neophot optical microscope. Grain size was measured on photographs using random linear intercept technique. Statistical analysis of the results was performed.

Morphology and composition of primary intermetallic particles were examined in a scanning electron microscope JSM 6500F using back-scattered and secondary electron images and energy dispersive X-ray spectrum analysis (EDS).

Results and Discussion

We have selected additions of Zr and Ti because there were reports that the presence of transition metals, especially Zr increases the efficiency of grain refinement by ultrasonic treatment in the direct-chill casting mold². The reason for that remained unknown. Zirconium is not known to be a good grain refiner and small additions of Ti do not produce grain refinement unless there is another substrate, e.g. TiB₂ or TiC⁵.

Figure 1 shows the effect of titanium additions on the grain size of ternary Al-Zr-Ti alloys with 0.18 mass% Zr processed by ultrasound at a temperature of 700 °C. The refinement is substantial and the grain size decreases as the concentration of Ti rises. At about 0.05–0.06% Ti the difference in grain size is 3–4 times.

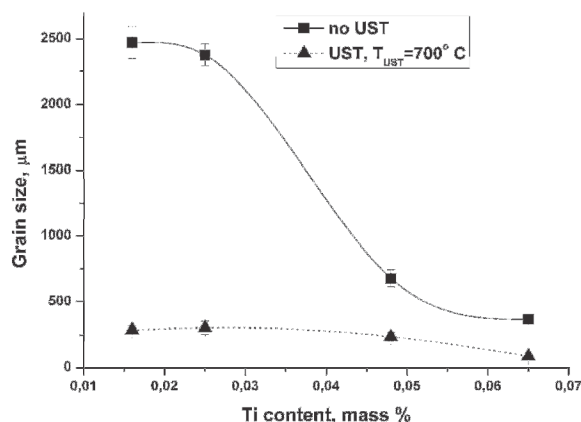


Figure 1: Effect of Ti additions on the grain size of ternary Al-0.18 mass% Zr-Ti alloys unprocessed (no UST) or treated by ultrasound at 700 °C (UST).

Figure 2 shows the influence of zirconium additions on the grain size of ternary Al-Zr-Ti alloys with 0.065 mass% Ti processed by ultrasound at different temperatures. Corresponding grain structures are given in Fig. 3.

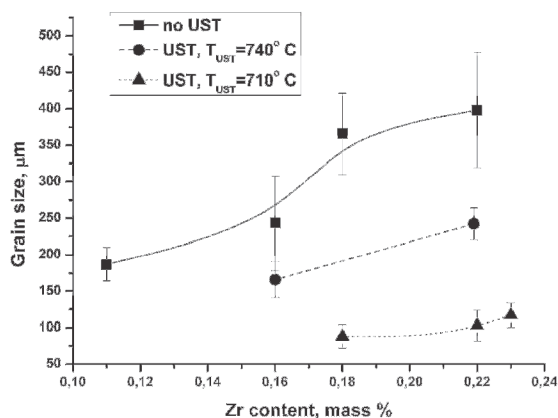


Figure 2: Effect of Zr additions on the grain size of ternary Al-0.065 mass% Ti-Zr alloys unprocessed (no UST) and treated with ultrasound (UST) at different temperatures.

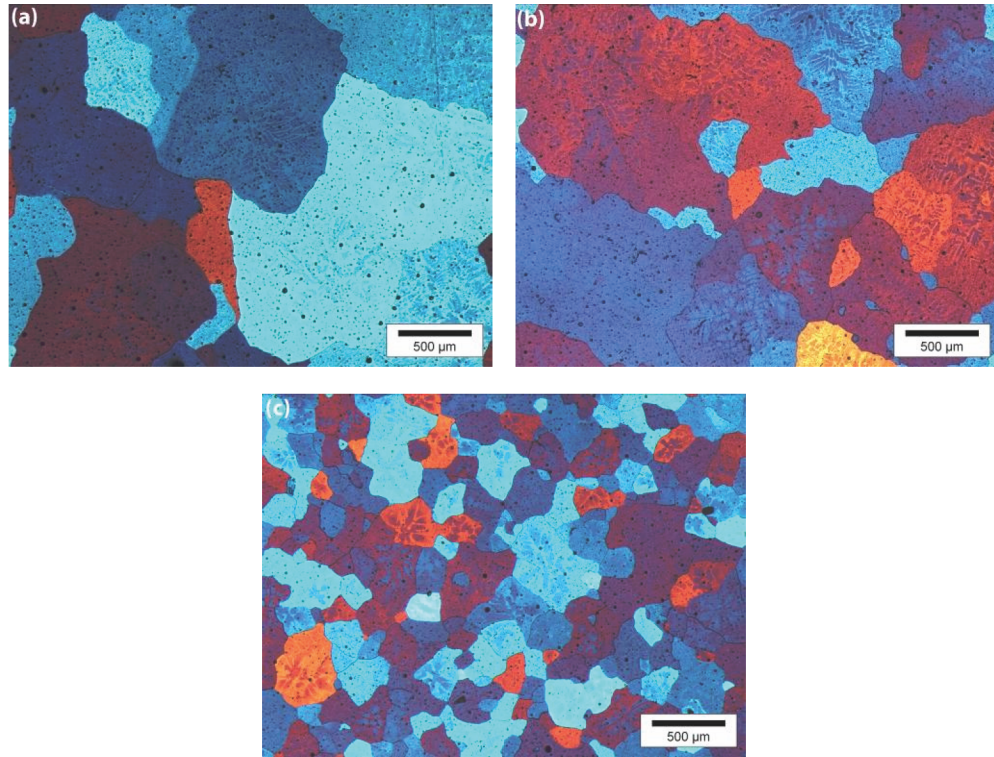


Figure 3. Effect of ultrasonic treatment on the grain size and morphology of an Al–0.22 mass% Zr–0.065 mass% Ti alloy: (a) without processing in the presence of immersed idle ultrasonic horn, casting temperature was 740° C; (b) after ultrasonic processing for 10 s at 740° C and (c) after ultrasonic processing for 10 s at 710° C.

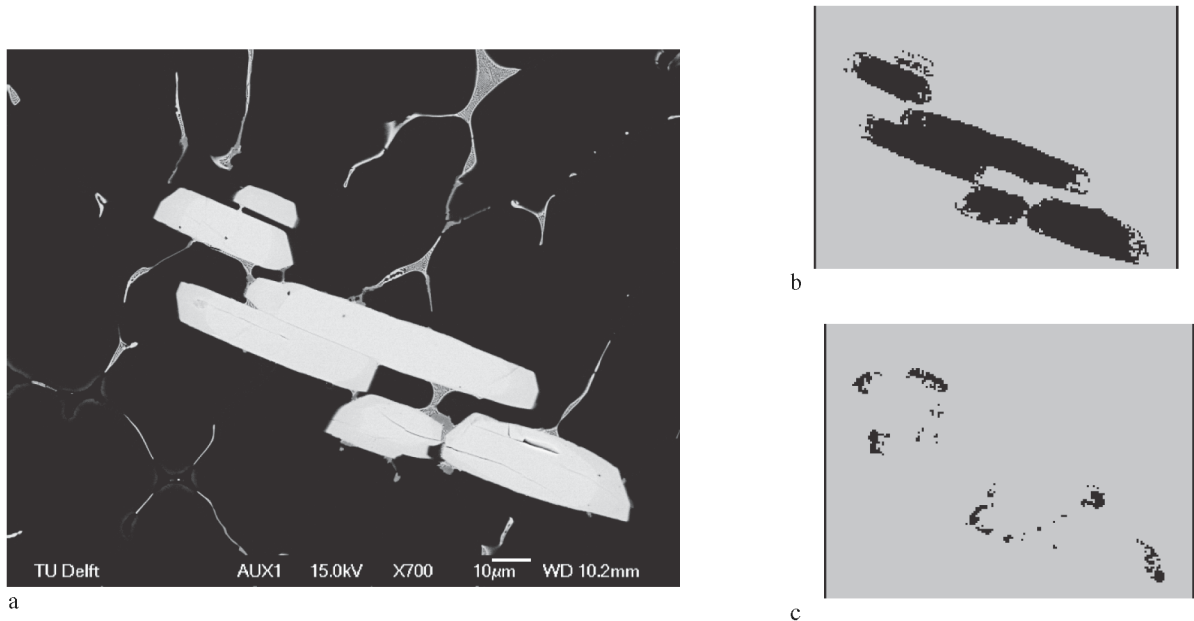


Figure 4: Intermetallics found in an aluminum alloy with 0.36 mass% Zr and 0.06 mass% Ti cast without ultrasonic treatment: (a) general view, note slightly different contrast at the edges of the plates; (b) mapping of Zr concentration; and (c) mapping of Ti concentration.

It is clear that the ultrasonic processing of aluminum containing 0.16–0.22 mass% Zr and small amounts of 0.04–0.06 mass% Ti produces significant grain refining, especially when the temperature of processing is close or the formation temperature of the Al_3Zr phase, 705–730 °C, respectively. At this temperature the aluminum alloy is still very much liquid and can be poured into the mould without feeding problems. Hence, this processing is potentially attractive for upscaling.

We need to understand what happens during ultrasonic processing that makes the combination of Zr and Ti work efficiently. There might be several reasons for that. First, Al_3Zr particles provide substrates for the formation of metastable Al_3Ti layer as it happens in the Al–Ti–B system¹³. Second, Al_3Zr particles are refined by ultrasonic treatment, e.g. by fragmentation, and become active solidification sites. Third, aluminum grains formed at the active Al_3Zr particles are restricted in growth by Ti present on the melt¹⁴. To check these hypotheses we studied the morphology and composition of the primary Al_3Zr intermetallics. Unfortunately, we were not able to find the primary intermetallic particles in the alloys shown in Table 1. Therefore we increased the amount of Zr to 0.36 mass%. With this concentration the formation of intermetallics became obvious.

Figure 4 gives a typical image of plate-like particles that, according to the EDS contain 45–55 mass% (19–27 at.%) Zr and represent therefore Al_3Zr . There is no Ti in the bulk of the particles. The edges of the plates are, however, enriched in Ti with the concentration varying from 2 to 5 mass% (1.8 to 4.0 at. %). The size of these particles is 30 to 80 μm and they hardly can be considered as potent nucleants.

After ultrasonic processing, the particles become significantly smaller with the sizes less than 5 μm and are mainly found in the center of grains (Fig. 5). Now they have a homogeneous

composition with 3.6 to 6.0 at. % Ti and about 25 at. % Zr. With this size the particles may become potent nucleation sites¹⁵. This comparison of structure with and without ultrasonic processing shows that two things happened: the intermetallics became finer and more saturated with Ti.

One of the possible mechanisms of refinement of intermetallic particles is fragmentation. The fact that we observed the refinement of particles and, consequently, grain refinement of aluminum grain after ultrasonic processing in the temperature range of Al_3Zr primary solidification attests for the hypothesis of fragmentation.

The next important question is what Ti does when it dissolves in the Al_3Zr phase? The re-plotting of Fig. 1 in terms of reverse growth restriction factor $1/Q$ (as shown in Fig. 6) gives an indication that the nucleant potency of particles has changed, as the two lines tend to converge to a single point¹⁴.

Although there is no available ternary Al–Ti–Zr phase diagram, it is known that there are no ternary phases formed in this system, that both elements react with aluminum through peritectic reactions, that Al_3Zr phase is formed at a higher temperature than Al_3Ti , and that Ti and Zr are dissolved in the aluminides of each other. Hence, there is no surprise that Ti is dissolved in Al_3Zr . Potentially dissolution of Ti in Al_3Zr may change the lattice parameter or even the crystal structure of Al_3Zr making it a more potent nucleant¹⁶. However this requires further study.

On the other hand, Ti still being present in the liquid can hinder the growth of Al grains by growth restriction mechanism. The potential of Ti for growth restriction in this particular system will need more investigation, e.g. by taking another growth restricting element which does not have a grain refining ability by itself.

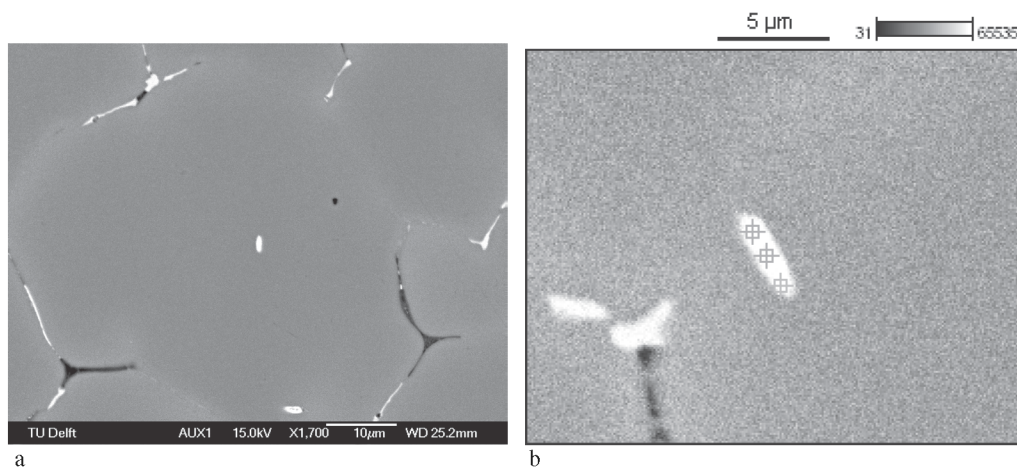


Figure 5: Intermetallics found in an aluminum alloy with 0.36 mass% Zr and 0.06 mass% Ti after ultrasonic treatment at 710 °C: (a) general view (white particle in the center) and (b) closer view at a higher magnification.

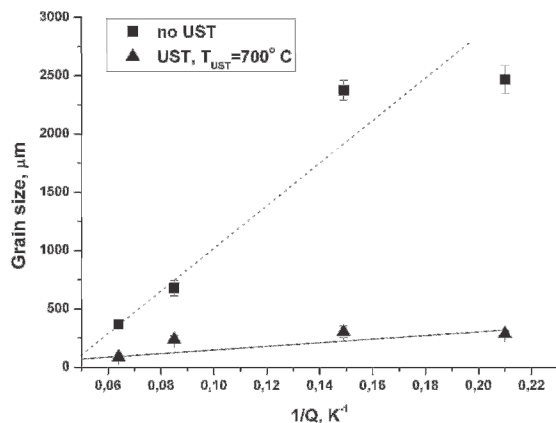


Figure 6: Relationship between the grain size and reverse growth restriction factor in Al-Zr-Ti alloys (from Fig. 1).

Conclusions

Ultrasonic processing during solidification of aluminum alloys becomes especially efficient when transition metals like Zr and Ti are present in certain ratios. In this case the grain refinement occurs when the processing is performed in the temperature range of primary solidification of Al₃Zr. As a result, the primary intermetallics become smaller and contain more dissolved Ti. It is suggested that the refinement of primary Al₃Zr particles can be a result of cavitation-assisted fragmentation. The resultant dimensions make the particles more suitable for acting as substrates for nucleation of aluminum. Dissolution of Ti in Al₃Zr further increases their nucleation potential. The nature of this as well as the growth restriction effect of titanium on aluminum requires further investigation.

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