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# On the mechanism of grain refinement in Al–Zr–Ti alloys

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ABSTRACT

In high-strength aluminum alloys Ti and Zr are commonly present as alloying elements, mostly as anti-recrystallization agents. Grain refinement during solidification is also achieved using Ti but in the form of titanium borides. Our previous investigations showed that a combined addition of Zr and Ti enables considerable grain refinement in aluminum alloys upon cavitation treatment, much stronger than that of Zr alone. The role of titanium and ultrasonic processing remained unclear. In this paper we propose a mechanism of the grain refinement that includes structural changes in solidification sites, their refinement and initiation of heterogeneous nucleation at lower undercooling.



## 1. Introduction

There are many techniques of grain refinement available in casting practice of aluminum alloys. Currently it is commonly achieved through the addition of small amounts of Al–Ti–B master alloys [1]. This technique is easy to apply; however, it is not always suitable for all alloys due to agglomeration of borides. Besides, the grain refiners are expensive and their efficiency under typical casting conditions is very low—only some percents of titanium borides are acting as solidification sites [2]. Direct alloying with the elements that are known as efficient grain refiners, e.g. Ti and Sc, requires fairly large level of alloying, 0.15–0.35 wt%. That is why physical methods of grain refinement [3–6] are potentially attractive for the industry. Cavitation-aided grain refinement induced by ultrasonic melt treatment (UST) is one of them.

Previous investigations have clearly demonstrated that UST promotes grain refinement in different Al-based alloying systems [4–7]. Our investigations show that when applied in the solidification range of primary (Al), it results in fine grain structure in all systems studied [8]. However, it is more difficult to achieve the same result while treating in the liquid state. With the attempt to combine the efficient ultrasonic processing with the fluid state of the processed alloy, we studied the effect of UST on grain refinement of aluminum alloys containing additions of transition metals in concentrations above the peritectic point. It has been shown that additions of Zr (≥0.18 wt%) and Ti (≥0.015 wt%) enable considerable grain refinement under the influence of cavitation induced above the temperature of primary aluminum formation (Fig. 1), i.e. the grain refinement occurs when the processing is performed in the temperature range of primary solidification of $Al_3Zr$ [9]. It was shown that the achieved grain refinement was due to the increased nucleating potency of solidification sites [9]. What makes this process commercially attractive is that the grain refinement can be achieved without additional alloying of some commercial aluminum alloys that already contain Zr and Ti in their standard composition, application of Al–Ti–B being not necessary.

It was suggested that nucleation potential of $Al_3(Zr,Ti)$ particles is increased due to ultrasonic-assisted fragmentation of $Al_3Zr$ particles and their saturation with Ti [9]. Current paper is aimed to clarify the mechanism of cavitation-assisted grain refinement of aluminum alloys with Zr and Ti additions.

## 2. Experimental

To study the influence of Ti additions on the structure formation of primary intermetallics in Al–Zr–Ti alloys both in the presence and absence of ultrasonic field, X-ray measurements had to be performed, which required high concentration of intermetallics in the sample. Thus, the amount of transition metals was increased by five times as compared to the alloys investigated before [9], keeping Zr:Ti ratio the same. Two model aluminum alloys were studied: Al–1 wt% Zr and Al–1 wt% Zr–0.25 wt% Ti. The alloys were prepared using 99.95 wt% pure aluminum, Al–5 wt% Ti, and Al–6 wt% Zr master alloys. The chemical composition was verified by X-ray fluorescent analysis in a Philips X-ray spectrometer PW 2510 on the middle transversal cross section of all the samples.

The experimental setup for ultrasonic processing is described in detail in Ref. [10]. A 17.5 kHz magnetorestrictive transducer was used. The input power at the

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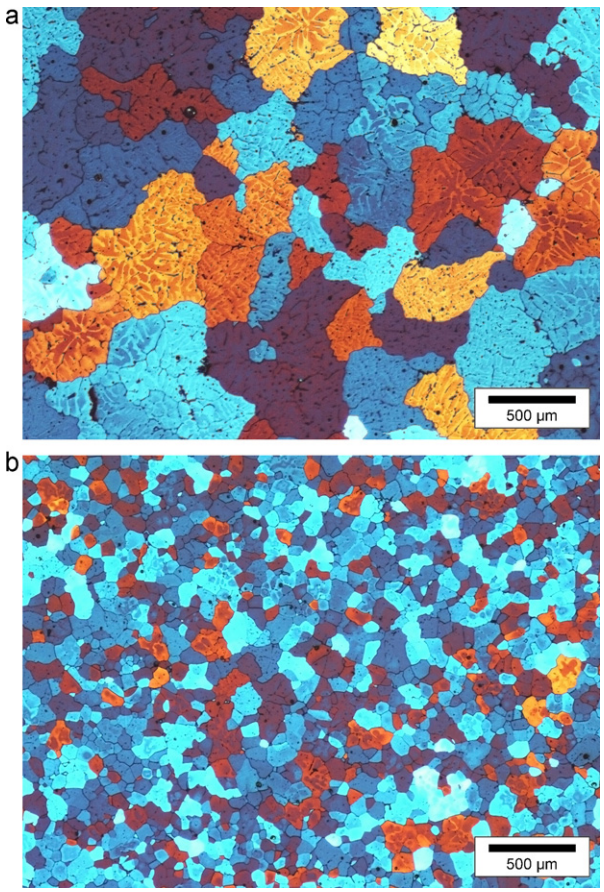


**Fig. 1.** Grain structures observed in ingot samples of an Al–0.18 Zr–0.06 mass% Ti alloy, (a) without and (b) with ultrasonic melt treatment.

generator was 4 kW. The amplitude of vibrations was measured in air on an ultrasonic horn with the help of a non-contact vibrometer. The amplitude of vibrations was 40 μm. The horn was made of niobium.

In each experiment, 350 g/180 $cm^3$ charge was melted in a stationary electric furnace at 930 °C and then poured into smaller pre-heated graphite cup-shaped crucibles (180 g/90 $cm^3$) where they were either treated with ultrasound or cooled in the presence of the idle ultrasonic horn down to 853 °C. The liquidus of an Al–1 wt% Zr alloy is 894 °C. The ultrasonic system was switched on before the horn was dipped into the liquid metal. The insertion depth of the ultrasonic horn was 3 mm below the surface of the liquid metal. Treatment time was about 10 s. After the treatment samples solidified in the graphite crucible. The cooling rate during solidification was 0.9 K/s.

All samples were sectioned transversally 10 mm above the bottom of the sample. The observations of the as-cast grain structures were made by conventional metallography (cutting, polishing down to 1 μm diamond paste, and electrolytic oxidation at 20 VDC in a 3% $HBF_4$ water solution) using a Neophot-31 optical microscope. The particle size was measured in the center of cast samples 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 electron images and energy dispersive X-ray spectrum analysis (EDS). The Bruker-AXS (Siemens) D5005 wide-angle diffractometer was used to study the lattice parameters of structure constituents.

## 3. Results and discussion

There are several parameters that make the solidification site for heterogeneous nucleation efficient: low interfacial energy (realized through crystallographic match with the nucleating phase and good wetting) and the size matching the thermal undercooling. Let us look at our results with keeping in mind these parameters.

In this study we confirmed that cavitation facilitates dissolution and homogeneous distribution of Ti along the $Al_3Zr$ particle length, as it has been reported earlier for smaller concentrations of Zr and Ti [9]. After solidification without cavitation the concentration of Ti in smaller particles (50–70 μm in size) changes along their length. In the center of the particle the concentration of Ti was about 5–6 at.%, while at the periphery it ranges from 8 to 11 at.%. The central part of larger particles (100–300 μm) does not contain any Ti, while at the periphery titanium concentration is about 4 to 10 at.%. When cavitation treatment is applied, the particles are refined to 30–50 μm and Ti is homogeneously distributed along the particles length. The concentration of Ti in the particles ranges from 5 to 12 at.%. Homogeneous distribution of Ti may be a result of smaller particle size and/or ultrasonic enhanced diffusion.

It is known that there is a good matching between the lattice parameters of aluminum and $Al_3Zr$ particles, the overall mismatch is about 2.9% [11]. Obviously, our first hypothesis was that Ti being dissolved in $Al_3Zr$ decreased the mismatch and improved the nucleation potential of $Al_3(Zr_{1-x}Ti_x)$ particles. However, according to the results of XRD investigations, the additions of Ti decrease the lattice parameters of $DO_{23}$ structure in good agreement with reported data [12]. Fig. 2 represents the XRD scans of two discs made of Al–1 wt% Zr and Al–1 wt% Zr–0.25 wt% Ti alloys. The grey pattern (Al–1 wt% Zr alloy) matches well with the reflections of $Al_3Zr$ standard data file, indicating that the sample contains $DO_{23}$ structure ($Al_3Zr$). The reflections of Al–1 wt% Zr–0.25 wt% Ti alloy sample solidified both in the presence and in the absence of cavitation (black pattern) are identical and show somewhat larger diffraction angles. Its is known that the tetragonal equilibrium $DO_{23}$ type structure ($Al_3(Zr_{1-x}Ti_x)$) exists in a wide range of compositions from pure $Al_3Zr$ to x = 0.4 [13]. Ti substitutes Zr in the $DO_{23}$ phase [13]. That is why the lattice parameters of the $DO_{23}$ phase continuously vary along the $Al_3Zr$–$Al_3Ti$ section of the phase diagram almost over the whole concentration range [12]. To match the reflections of the standard $Al_3Zr$ data and the sample made of an Al–1 wt% Zr–0.25 wt% Ti alloy, the lattice parameters had to be adjusted. As a result, it was found that the lattice parameter $a$ decreased from 0.4009 [14] to 0.3993 nm, while the $c$ parameter is reduced from 1.728 nm [14] to 1.713 nm.

The lattice mismatch between two phases is defined as

$$\delta = \frac{2(a - a_0)}{a + a_0}. \quad (1)$$

If one compares $a$ and $c/4$ interplanar distances of tetragonal $Al_3(Zr_{1-x}Ti_x)$ structure ($DO_{23}$) with the lattice parameter of FCC aluminum at room temperature, which is equal to 0.40496 nm [12], it is clear that Ti additions only increase the mismatch between $a$ parameter of $Al_3(Zr_{1-x}Ti_x)$ structure and aluminum from 1 to 1.4%. The mismatch between $c/4$ and aluminum is decreased from 6.5 to 5.6%, however it is still too high to promote nucleation along this plane. Taking into the account that aluminum expands at higher temperatures ($\alpha = 34.3 \times 10^{-6}\ K^{-1}$, $a$ = 0.4124 nm at 660 °C [15]) to

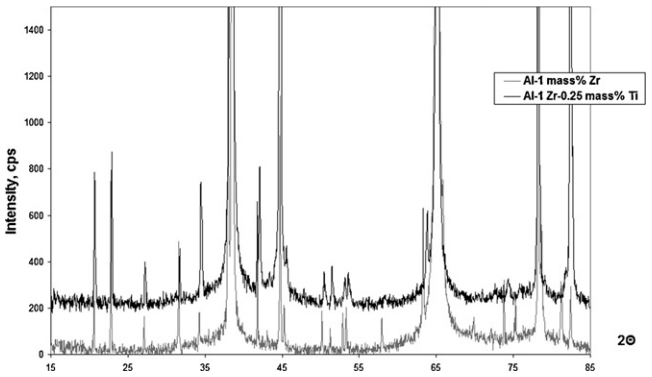


**Fig. 2.** XRD scans of Al–1 mass% Zr and Al–1 Zr–0.25 mass% Ti discs solidified without cavitation treatment.