Property enhancement by grain refinement of zinc-aluminium foundry alloys

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Abstract. Development of cast alloys with good mechanical properties and involving less energy consumption during their melting is one of the key demands of today’s industry. Zinc foundry alloys of high and medium Al content, i.e. Zn-(15-30) wt.% Al and Zn-(8-12) wt.% Al, can satisfy these requirements. The present paper summarizes the work [1–9] on improving properties of sand-cast ZnAl10 (Zn-10 wt.% Al) and ZnAl25 (Zn-25 wt. % Al) alloys by melt inoculation. Special attention was devoted to improving ductility, whilst preserving high damping properties at the same time. The composition and structural modification of medium- and high-aluminium zinc alloys influence their strength, tribological properties and structural stability. In a series of studies, Zn – (10-12) wt. % Al and Zn – (25-26) wt.% Al - (1-2.5) wt.% Cu alloys have been doped with different levels of added Ti. The melted alloys were inoculated with ZnTi-based refiners and it was observed that the dendritic structure is significantly finer already after addition of 50 - 100 ppm Ti to the melted alloys. The alloy’s structure and mechanical properties have been studied using: SEM (scanning electron microscopy), LM (light microscopy), dilatometry, pin-on-disc wear, and tensile strength measurements. Grain refinement leads to significant improvement of ductility in the binary high-aluminium Zn-(25-27) Al alloys while in the medium-aluminium alloys the effect is rather weak. In the ternary alloys Zn-26Al-Cu, replacing a part of Cu with Ti allows dimensional changes to be reduced while preserving good tribological properties. Furthermore, the high initial damping properties were nearly entirely preserved after inoculation. The results obtained allow us to characterize grain refinement of the examined high-aluminium zinc alloys as a promising process leading to the improvement of their properties. At the same time, using low melting ZnTi-based master alloys makes it possible to avoid the excessive melt overheating needed for TiCAl or TiBAl refiners and reduces the possibility of gas pick-up and material loss.

1. Introduction

Grain refinement of non-ferrous cast alloys - mainly those based on Al, is a common practice, which allows fine microstructures to be obtained with increased ductility.

Grain-refinement can be also used for zinc-aluminium alloys with increased Al content of 20-30 wt.% Al [1 – 4]. It should be noted that AlZn-based cast alloys are numbered among the structural materials of improved damping capacity. It is well known that high-aluminium zinc alloys, for example ZA-27 alloy, fall in the category of HiDAlloys (high-damping alloys). It has also been noted that high-zinc aluminium alloys show increased damping. Both groups, i.e. high-aluminium zinc and
high-zinc aluminium alloys solidify naturally with a coarse structure and using the refinement process allows highly refined structures to be obtained [5–7]. On the other hand, many structural materials are required to have improved damping properties. However, damping capacity and a fine grain structure are believed to be contradictory factors [6]. The high-aluminium zinc alloys also display naturally low friction, which allows for their use in bushings and bearings. The bearing characteristics of ZA27 alloy are comparable with those of standard industrial bearing alloys, such as tin-lead bronze. This is due to the presence of the bearing ε-CuZn$_4$ phase in a soft α(Al) matrix. The ε-CuZn$_4$ metastable phase takes part in the so-called four-phase reaction to form the stable T'-Al$_5$Cu$_4$Zn phase. The ε-CuZn$_4$ phase is present in the structure of high-aluminium zinc for a long time after casting, while the four-phase reaction can lead to an increase of volume of the Zn-Al-Cu alloys, by as much as 4.5% [8]. A partial or total replacement of Cu with Ti, introduced with the Al-12Ti master alloy, leads to the in-situ formation of Ti(Al,Zn)$_3$ particles in the microstructure of Zn-26Al-Cu alloys [5]. It should be also noted that the Zn-Al alloys with increased Al content show structural instability of the solid solution of zinc in aluminium α', which is the main component of their microstructure. The α' solid solution also undergoes phase transformations, which are accompanied by, among other effects, changes in dimension. However, the latter transformation is usually completed in a relatively short time after casting, i.e. in ~1 month [8-9]. The present paper summarizes work on the development of high-aluminium zinc cast alloys on the basis of joint investigations performed over the last ten years at AGH University of Science and Technology – Faculty of Foundry Engineering and at University of Cambridge, UK – Department of Materials Science and Metallurgy.

2. Experimental

The alloys Zn-(25-26)%Al-(1-2.5)%Cu-(0-1.5)%Ti and Zn-(10-12)% Al and master alloys Al-33%Cu, Zn-4%Ti and Al-12%Ti were melted from elements of minimum purity 99.9 % (all compositions in wt.%). Melting was performed in an electric furnace with an argon protective atmosphere, in a clay-graphite crucible of 2-litre capacity (the details of melting and casting are given in Refs [1–3]). Optical light metallography (LM) was performed using a Leica DM IRM microscope. Scanning electron microscopy (SEM) was performed on unetched samples with a Philips XL30 microscope equipped with an energy dispersive X-ray EDX spectrometer (Link-Isis). Wear-resistance pin-on-disc (T01M device, Poland) investigations were performed using sample rods Ø8 x 24 mm. Dry sliding wear tests were performed against a rotating steel disc of 50 HRC, at a load giving 0.8 MPa pressure and at a sliding speed of about 0.7 m/s, for a total sliding distance of 10 km. Dilatometry was performed using samples Ø5 x 35 mm, which were homogenized in air in an annealing furnace at 370°C for 48 h, and then quenched into water at room temperature. During the first 48 hours after quenching, measurements were made using a DI-105 dilatometer; thereafter the length changes of the samples were manually measured using a screw-micrometer of accuracy of 0.001 mm. Damping coefficient tests were carried out using the ultrasonic Krautkramer measurement set, model USLT 2000. The entire study was conducted for 1 MHz longitudinal waves, using the MK1S mini-transducer with head diameter of 10 mm. To determine the attenuation intensity, the echo method (pulse-echo method) was adopted, using the internal software of the Krautkramer USLT 2000 device. Prior to testing, the device was calibrated with a pure-zinc cast sample.

3. Results and discussion

3.1. High-Al zinc alloys

Grain refinement of the high-aluminium molten alloys by the Zn-4Ti master alloy is very effective, as can be clearly seen in figure 1 (a) to (f). At the same time elongation increases while tensile strength remains basically preserved (figure 2). It should be noted that the Zn-Ti based master alloys have a mass density very close to the inoculated Zn-Al alloys and that they dissolve very quickly already at temperatures of 500°C. This allows zinc alloys to be treated without the detrimental overheating that is required when using Al-Ti based refiners.
Figure 1. LM pictures of macrostructures and microstructures of the Zn-25Al alloy. (a), (c) and (e) initial alloy; (b), (d) and (f) alloy inoculated with Zn-Ti MA – 0.04 wt.% Ti; (a) and (b) surfaces of the samples; (c) and (d) crystalline fractures; (e) and (f) ground, polished and etched surfaces of a section [3, 6, 10].

Figure 2. Tensile strength and elongation of the Zn-25Al alloy inoculated with Zn-4Ti master alloy [10].
As noted in [10] the addition of Ti exceeding 250 ppm caused increased elongation. On the other hand the increased Ti addition of 400 ppm caused decreasing UTS. Taking this into consideration it can be concluded that optimal Ti addition should be in a range of 200 – 300 ppm Ti. However, this should be confirmed in detailed examinations.

As mentioned above, adding copper to the high-aluminium alloys leads to good tribological properties on one hand, but also causes detrimental structural instability on the other. Figures 3 and 4 show that a partial replacement of Cu with Ti significantly decreases the structural instability while preserving the good tribological properties.

**Figure 3.** Mass losses of the samples after 10 km distance in the sliding wear test. The samples were aged naturally for 5 years after casting [10, 11].

**Figure 4.** Relative changes of the sample length for the examined alloys during natural ageing after solution treatment and quenching into a supersaturated state.

### 3.2. Medium-Al zinc alloys

Figures 5–7 show the effect of grain refinement on structure and selected properties of the medium-aluminium zinc alloys represented by Zn-(10-12) wt.% Al binary alloys. During these investigations the alloys were inoculated with the Zn-Ti based master alloys. From figure 5 it appears that the inoculation causes significant refinement of the $\alpha$(Al) dendrites. However, the structure refinement causes much lower, i.e. $\sim10\%$, increase of the ductility measured by elongation – figure 6 in comparison with the high-aluminium alloys elongation changes – figure 2. Further comparing figures 2 and 5 shows that tensile strength of the inoculated alloys is maintained in both the examined
high- and medium-aluminum alloys. Figure 7 shows the influence of the performed inoculation (and structural refinement) on the damping properties measured by ultrasonic-wave attenuation. The results collected in Figure 7 show that the attenuation coefficient decreases by about 25% in comparison to the initial, unmodified alloy. However, the inoculated alloys belong to the group of the high-damping alloys, with the attenuation coefficient still being above 100 dB/m.

Figure 5. Macrostructures and microstructures of the initial (left-hand side) and inoculated (right-hand side) Zn-12Al-0.05Ti alloy modified with Zn-Ti master alloy [2, 11].

Figure 6. Tensile properties of Zn-10Al alloy inoculated with small Ti addition introduced with Zn-3Ti master alloy.
Figure 7. Influence of small Ti addition introduced with Zn-3Ti master alloy on the damping properties of Zn-10Al alloy.

4. Conclusion
Based on the studies described above, the following conclusions can be drawn:

Grain refinement of the examined high-aluminium zinc alloys is a promising process leading to improvement of their properties. At the same time, using the low-melting-point ZnTi-based master alloys avoids the excessive melt overheating needed for the TiCA1 or TiBAL refiners and reduces the possibility of gas pick-up and material loss. In the ternary alloys Zn-26Al-Cu, partially replacing Cu with Ti allows the dimensional changes to be reduced while preserving good tribological properties.

Grain refinement of the medium-aluminium binary zinc alloys is less effective, considering increase of ductility measured by elongation changes. It was also noted that grain refinement decreased the attenuation coefficient of 1 MHz ultrasonic waves by about 25%. Taking this into account, it is concluded that further studies of other property changes, e.g. creep and tribological properties, would be desirable.

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