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# Shape of the in-situ (Al,Zn)-Ti reinforcing particles and their influence on structure and structural stability of selected Zn-Al and Al-Zn cast alloys

P K Krajewski<sup>1</sup>, A L Greer<sup>2</sup>, W K Krajewski<sup>1a</sup>

<sup>1</sup>AGH University of Science and Technology, Faculty of Foundry Engineering,23 Reymonta Street, 30-059 Krakow, Poland <sup>2</sup>University of Cambridge, Department of Materials Science & Metallurgy, 27 Charles

Babbage Road, Cambridge CB3 0FS, UK

Email: \*krajwit@agh.edu.pl

Abstract. The foundry engineering still needs new cast materials of improved properties. These can be achieved by elaborating completely new alloys and metal matrix composites or by elaborating the alloys/composites basing on the already very well-known matrixes. The good example of the latter solution are high-aluminium zinc (H-Al Zn) and high-zinc aluminium cast alloys (H-Zn Al). Both of these groups show good damping and strength properties but rather low ductility and insufficient structural (and dimensional) stability, caused by long term transformation of the Cu-containing bearing phases. The performed works were devoted, among others, to building composites of improved structural stability reinforced with ternary (Al,Zn)-Ti aluminides. The in-situ reinforcement was built by needle-shape ternary aluminides based on the  $DO_{22}$  TiAl<sub>3</sub> binary phase introduced with AlTi-based master alloys or by compacted semi-globular ones based on the  $L1_2$  Zn<sub>3</sub>Ti particles introduced with a ZnTi-based master alloy. The mentioned particles substitute partly or totally for Cu-based bearing phase and the influence of this substitution on the structural stability and tribological properties is also discussed in the paper.

#### 1. Introduction

Cast alloys and composites with Al and Zn based matrices show an increasing range of uses in the global economy. In the years 2007–2016, the world production of Al castings nearly increased by 50%, i.e. from 12.7 to 17.8 million metric tons Fig. 1 [1]. This trend is expected to continue in the prognosis of increased demand for Al alloys, including the Al-based cast composites. As mentioned above, among the cast alloys based on the Al-Zn system, there is a unique group, which has not been thoroughly researched, namely the high-zinc aluminium alloys containing 20% - 40% Zn, by mass. Its uniqueness lies in its wide range of potential applications, such as manufacturing alloys for castings with strength of around 300 MPa and simultaneously good tribological and damping properties. Although the high-zinc aluminium cast alloys were the subject of some early studies [2, 3], the recent literature provides little evidence of current research: what literature deals with mainly are the tribological properties of these alloys [4, 5]. Efforts to optimize the composition, structure and technology of these alloys are under way, aiming at improving their plasticity, e.g. through grain refinement [6-11]. Examinations on grain-refinement of the cast Al-Zn alloys showed that Al-Ti based and Zn-Ti based master alloys are

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very effective grain-refiners of these alloys [12, 13]. Additionally, a surplus addition of these master alloys can form in-situ reinforcing particles of the matrix.

The changes in the fineness of the refined structure can cause also changes in the damping properties, which in many applications are the key properties of an alloy [14, 15]. Thus, optimization should be aimed at forming a set of characteristics, suitable for high-technology applications, i.e. simultaneously having good strength and plasticity, as well as good tribological and damping properties.

It should be noted that recent efforts focus on energy saving and environmental protection at the same time. The readily contribution to these efforts is development of the new group of comparatively low-melting Al-Zn based composites of high damping, wear and strength properties, reinforced with insitu particles built with Al-Ti-Zn based intermetallics. It is well known that the matrix of the Al-Zn based alloys (solid solution of Zn in Al) has fcc A1 crystal structure. The in-situ Ti(Al,Zn)<sub>3</sub> reinforcing phase formed directly in molten high-zinc aluminium matrix has a similar crystal structure, i.e. L1<sub>2</sub> superstructure and very low disregistry of lattice parameter with the matrix alloy [6-8, 11]. The  $\alpha$ (Al) and L1<sub>2</sub> Ti(Al,Zn)<sub>3</sub> nearest-neighbour atomic spacing in their {111} planes are, accordingly, 0.2859 and 0.2798 nm. The percentage difference is only about 2.1%. Thus, the  $\alpha$ (Al) is nucleated with its {111} plane on {111}<sub>Ti(Al,Zn)3</sub>. This feature should be beneficial when avoiding detrimental interior stresses is considered.



Figure 1. World production of Al and Zn based castings, 2007 to 2016 [1].

The present paper summarizes work on the development of high-aluminium zinc cast alloys and high-zinc aluminium 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 [14-17].

### 2. Experimental

The alloys Zn–(25-26)%Al-(1-2.5)%Cu-(0-1.5)%Ti, Al-27%Zn-2%Cu-0.8%Mn 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 electrical furnace with an argon protective atmosphere, in a clay-graphite crucible of 2-litre capacity. The melted charges were flushed with pure argon for 10 min. Then, 10 min after finishing the flushing, the dross was removed from the melt surface and the (Al,Zn)-Ti master alloy was added to the melted alloys. Five minutes after the master alloy addition, the bath

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was stirred for 2 minutes with an alumina rod, and the alloys were cast into a green sand mold (90% silica matrix, 7% bentonite, 3% water) with vertical cylindrical cavity  $\emptyset$ 30/32 x 80 mm. The mean cooling rate of the samples was about 1K/s, which is typical for green sand casting. From these castings samples  $\emptyset$ 30 x 25 mm were cut for LM and SEM examinations. 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  $\emptyset$ 8 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  $\emptyset$ 5 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.

# 3. Results and Discussion

Grain refinement of the high-aluminium molten alloys by the Zn-4Ti master alloy is very effective, as can be clearly seen in Fig. 2 (a) to (f). At the same time elongation increases while tensile strength remains basically preserved [16]. 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 2.** 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 (Leica DM IRM LM) [16].



**Figure 3.** Examples of the master alloys with ternary aluminides  $Ti(Al, Zn)_3$ : (a) coming from  $D0_{22}$  Al<sub>3</sub>Ti phase; (b) coming from  $L1_2$  TiZn<sub>3</sub> phase. (c) and (d): Pin-on-disc examined samples of Zn-25Al-(1.5-2) Ti composites with visible  $Ti(Al, Zn)_3$  reinforcing particles.

Fig. 3 shows the in-situ composites with matrix of high-aluminium zinc based alloy. Recently we demonstrated that the binary phases  $D0_{22}$  TiAl<sub>3</sub> and L1<sub>2</sub> phase Zn<sub>3</sub>Ti undergo transformation into the L1<sub>2</sub> ternary Ti(Al,Zn)<sub>3</sub> phase in the binary Al-Zn alloys [6-8, 11, 15]. The mentioned particles play role of the bearing phases which positively influence tribological properties of the examined alloys increasing their wear resistance while preserving coefficient of friction [18]. Fig. 4 shows significant structure refinement of the high-zinc aluminium alloy doped with small addition of the traditional Al-Ti based master alloy. The observed refinement positively influences plastic properties of these alloys [18].



**Figure 4.** Example of the refined Al-Zn (Al - 20 wt.% Zn) matrix after addition AlTi-based master alloy. (a) initial alloy; (b) alloy doped with the master alloy.



Figure 5. Reducing dimensional changes after partial replacing of Cu with Ti or Mn [15, 17].

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. Fig. 5 shows that a partial replacement of Cu with Ti and/or Mn significantly decreases the structural instability while preserving the good tribological properties [18].

# 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 TiCAl 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 high-zinc aluminium binary alloys with a traditional Al-Ti based master alloy causes significant refinement of the primary  $\alpha$ (Al) dendrites, which should be beneficial considering increase of ductility measured by elongation changes.

Partial replacement of Cu with Ti and/or Mn in the examined alloys leads to obtaining practically stable structure during long term natural ageing after homogenization and quenching.

Taking the mentioned conclusions into account, it is also concluded that further studies of other property changes, e.g. creep, damping, tribological and casting properties, would be desirable.

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