

W.K. KRAJEWSKI\*, A.L. GREER\*\*, P.K. KRAJEWSKI\*

## TRENDS IN THE DEVELOPMENT OF HIGH-ALUMINIUM ZINC ALLOYS OF STABLE STRUCTURE AND PROPERTIES

### TRENDY ROZWOJOWE WYSOKOALUMINIOWYCH STOPÓW CYNKU O STABILNEJ STRUKTURZE I WŁAŚCIWOŚCIACH

The composition and structural modification of high-aluminium zinc alloys influence their strength, tribological properties and structural stability. In a series of studies, Zn – (25-26) wt.% Al – (1-2.5) wt.% Cu alloys have been doped with different levels of added Ti. The alloys' structure and mechanical properties have been studied using: SEM (scanning electron microscopy), LM (light microscopy), Dilatometry, Pin-on-Disc wear and Strength measurements. Grain refinement leads to significant improvement of ductility in the binary Zn-25Al alloy. 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.

*Keywords:* high-aluminium zinc alloys, grain-refinement, in-situ composite, dimensional stability, wear

Praca poświęcona jest badaniom wpływu modyfikacji składu i struktury wysokoalumiowych odlewanych stopów cynku na ich właściwości wytrzymałościowe, tribologiczne oraz stabilność struktury i wymiarów. W badaniach stopy Zn – (25-26) mas% Al – (1-2.5) mas% Cu domieszkowano zmiennym dodatkiem Ti. W badaniach stosowano techniki pomiarowe SEM (scanning electron microscopy), LM (light microscopy), badania dylatometryczne, badania ścieralności Pin-on-Disc oraz badania właściwości wytrzymałościowych. Stwierdzono, iż rozdrobnienie struktury pozwala uzyskać znaczący wzrost plastyczności stopów podwójnych typu Zn-25Al, podczas gdy zastąpienie tytanem części miedzi w stopach potrójnych Zn-26Al-Cu pozwala ograniczyć zmiany wymiarowe przy zachowaniu wysokich właściwości tribologicznych.

## 1. Introduction

Mechanization of foundry processes in modern industry requires the preparation of new or improved foundry alloys that have good, stable mechanical properties, and that are cost-saving and environmentally friendly during their melting – key priorities of European Community research programmes.

Zinc-based foundry alloys with increased Al content of 20-30 wt.% Al have high strength and good tribological properties, but their low structural stability over a long time after casting restricts their wider application in areas of modern solutions in mechanization of foundry processes. Another disadvantage is their tendency to form a coarse dendritic structure which reduces ductility. The high-aluminium zinc alloys with Cu addition have very good tribological properties due to the Cu-rich bearing phase present in the soft matrix. The Cu-rich phase, unfortunately, is unstable and its transformation causes dimensional changes, but reducing the Cu content degrades the tribological properties. This problem can be solved by partial substitution of Cu with another element, e.g. Si [6], which also leads to the formation of what is effectively a bearing phase. In the present work, Ti is used as the element replacing Cu. Titanium was added to the melted alloys with master alloys

Al-Ti or Zn-Ti, introducing the phases  $Al_3Ti$  or  $Zn_3Ti$ . These phases were intended to be substrates for heterogeneous nucleation of the matrix phase in these alloys, i.e. the  $\alpha'$  solid solution of Zn in Al [1]. Further roles of the Ti are as a solute to promote grain refinement through growth restriction and as the basis for the  $Ti(Al,Zn)_3$  bearing phase built from the binary  $Al_3Ti$  or  $Zn_3Ti$  phases [1-2]. The present work describes 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. Materials and Methodology

The alloys Zn-(25-26)%Al-(1-2.5)%Cu-(0-1.5)%Ti 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 details of melting and casting are given in Refs. [1-4]). Optical light metallography (LM) was performed using a Leica DM IRM microscope. Scanning electron microscopy (SEM) was performed on unetched samples

\* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, REYMONTA ST. 23, 30-059 KRAKÓW, POLAND

\*\* UNIVERSITY OF CAMBRIDGE, CB2 3QZ CAMBRIDGE, PEMBROKE STREET, UNITED KINGDOM

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  $\varnothing 8 \times 24$  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. The coefficient of friction and temperature of the sample were directly measured during these tests. Dilatometry was performed using samples  $\varnothing 5 \times 35$  mm, which were homogenized in air in the 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-micrometre of accuracy of 0.001 mm.

### 3. Results

In investigations aimed at grain refinement a Zn-Ti based master alloy was used, whose  $\text{Zn}_3\text{Ti}$  phase introduced into the high-aluminium melted alloys is a very effective substrate for heterogeneous nucleation of the  $\alpha'$  matrix [1-2], Fig. 1 (a)–(b).

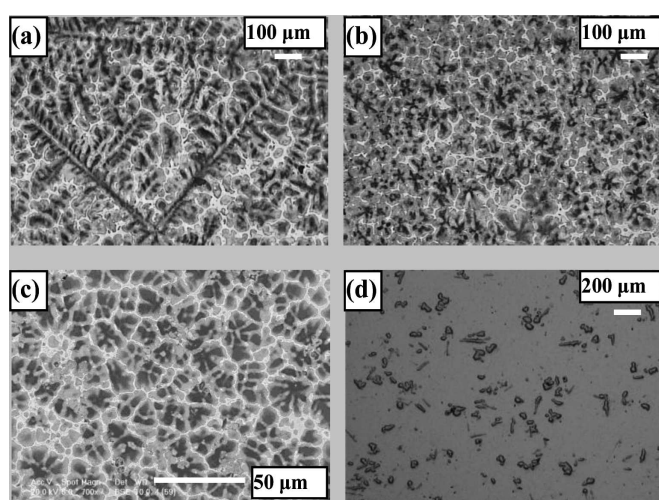


Fig. 1. Examples of Zn-25Al alloy microstructures. (a) LM picture of initial coarse dendritic alloy (b) LM picture of alloy inoculated with Zn-4Ti grain refiner (0.05 wt.% Ti); (c) alloy Zn-25Al; (c) and (d) SEM and LM pictures of alloy Zn-25Al-1Cu-2Ti (visible  $\text{Ti}(\text{Al}, \text{Zn})_3$  reinforcing particles) [1, 2]

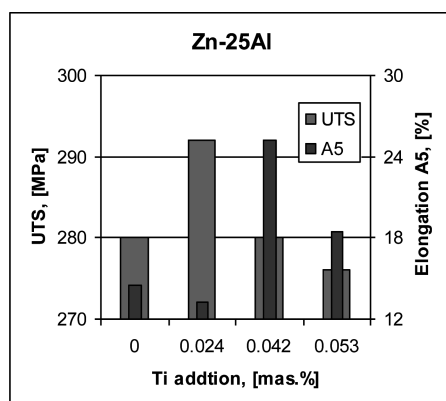


Fig. 2. Mechanical properties of the Zn-25Al alloy inoculated with Zn-4Ti master alloy [4]

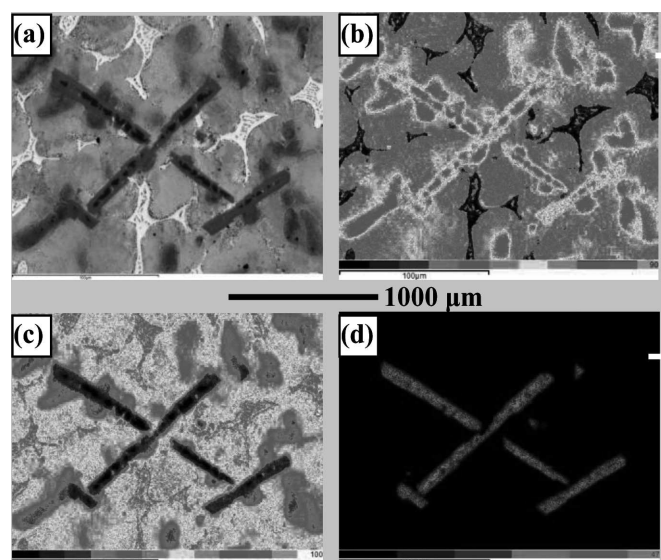


Fig. 3. SEM back-scattered electron images of the Zn-26Al-1.6Ti alloy (a) and surface distribution of Al (b), Zn (c) and Ti (d) [10]

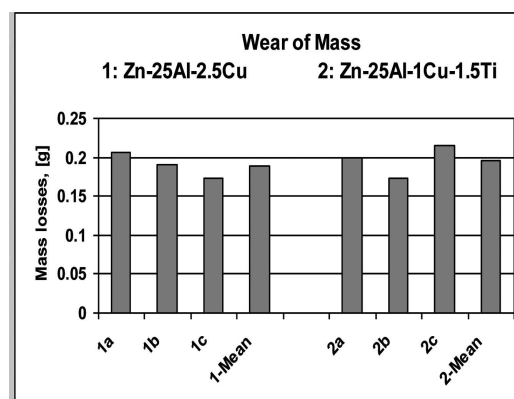


Fig. 4. Mass losses of the samples after 10 km distance of sliding wear test. The samples were aged naturally for 5 years after casting

It should be noted that the Zn-Ti based master alloys dissolve very quickly in the melt at temperatures below 600°C, thus avoiding the detrimental overheating of zinc-alloys that is required when using Al-Ti based refiners [2]. The implemented inoculation gave, together with significant grain refinement, improved mechanical properties, particularly the ductility of the examined binary Zn-25Al type alloys [4]. The optimal addition of Ti was in the range 200-400 ppm – Fig. 2.

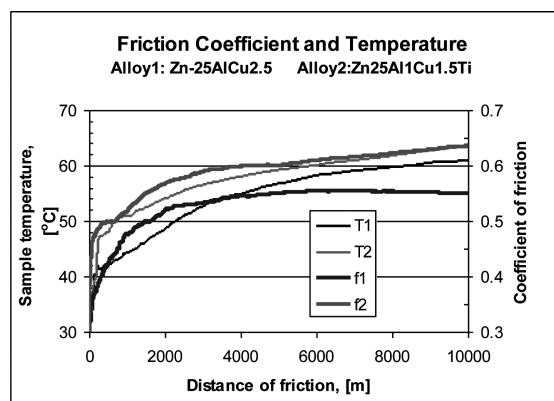


Fig. 5. Coefficient of friction and sample temperature during sliding wear tests. The samples were aged naturally for 5 years after casting

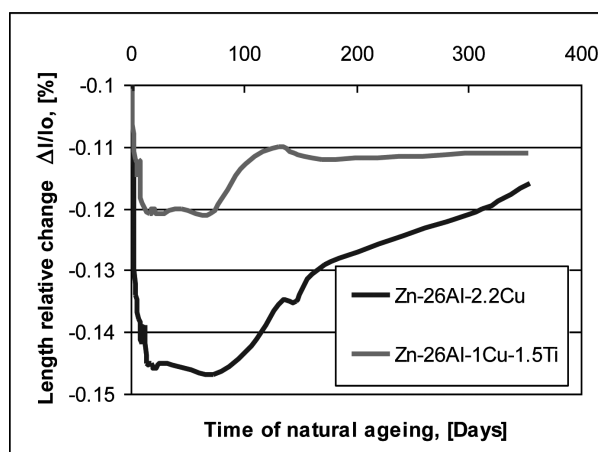


Fig. 6. Relative changes of the examined alloys length during natural ageing after solution treatment and quenching into a supersaturated state [12]

Increasing the Ti addition to 1-2 wt.% gives an in-situ composite – Fig. 1 (c) – (d), in which the reinforcement is particles of the ternary  $\text{Ti}(\text{Al},\text{Zn})_3$  phase – Fig. 3, arising in the melt from the binary  $\text{Al}_3\text{Ti}$  or  $\text{Zn}_3\text{Ti}$  phases [1, 3-5, 10]. As mentioned, the high-aluminium zinc alloys with 2-2.5 wt.% Cu possess very good tribological properties, on one hand [6-10], but on the other, a non-stable structure and long-term dimensional instability [11-12]. The instability is caused by the metastable bearing phase  $\epsilon$   $\text{CuZn}_4$ , which undergoes a transformation to the stable  $\text{T}'$  phase  $\text{Al}_5\text{Cu}_4\text{Zn}$ , accompanied by dimensional changes. A possible solution to this is to decrease the Cu content to an amount remaining in solid solution, but unfortunately tribological properties are degraded at the same time. Partial replacement of Cu with Ti appears to be a promising way to decrease or eliminate structural instability while preserving good tribological properties in the range of high-aluminium zinc alloys in this study – Figs 4-5, as confirmed in Refs. [11-12], Fig. 6.

#### 4. Final remarks

The development of high-aluminium zinc cast alloys covers the processes of grain refinement and structural stabilization and refinement. The studies performed so far show that:

1. Grain refinement using Zn-Ti based master alloys allows the ductility to be improved while preserving the strength of the binary Zn-25Al type alloys.
2. Partial replacement of Cu with Ti gives a more stable structure while preserving the good tribological properties of practical importance.
3. Future studies should focus on the mechanical properties of the alloys in which Cu is partially replaced by Ti.

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