SUMMARY

The presented paper covers works concerning grain-refinement of the high-aluminium zinc cast alloys (HAl-Zn). On the basis of the foreign works and of the research performed by the author and co-workers during the past twenty years – the results of the investigations concerning the practice of the HAl-Zn alloys grain refinement are outlined. The paper brings also results of the investigations of changes of selected properties after inoculation of the examined alloys.

Key words: zinc-aluminium alloy, grain refinement, heterogeneous nucleation, Zn-Ti master alloy

1. INTRODUCTION

Casting alloys of zinc with aluminium were introduced to industry in the 1920s. These alloys contained about 4 wt % of Al and were used mainly for pressure die casting. This group of alloys covers binary alloys Zn-4wt%Al and alloys with addition of copper, i.e. Zn-4wt%Al-1wt%Cu and Zn-4wt%Al-3 wt%Cu with addition of several hundredths of wt% of Mg. Such alloys are still being used in casting because of their very good technological and strength properties.

During the 1940s, investigations on elaboration of Zn alloys with increased Al content, to be used for shape castings and bearings, began in Germany [1, 2]. Continued investigations in 1950s [3] and 1960s [4] introduced into practice alloys ZA8, ZA12, ZA27 [5], Z284 [6] and ZA305 [7]. The sand castings of the HAI-Zn alloys solidify naturally with coarse dendritic structure, which detrimentally influences plastic properties.
Therefore, structure refinement of zinc alloys with aluminium content increased to 24-40wt% aims at breaking up of $\alpha'$ primary dendrites of solid solution of zinc in aluminium. Such dendrites make, together with non-equilibrium eutectic, basic component of structure of binary alloys Zn-(24-40)wt%Al [8, 9] - which alloys, in turn, are matrix for such industrial alloys as Z284, ZA27 or ZA35. Investigations of the process of grain refinement of HA1-Zn alloys were inspired by the fact that basic component of these alloys structure, which is solid solution of zinc in aluminium $\alpha'$, crystallizes as $\alpha$ (Al) in cubic lattice $A1$ of $Cu_{\text{cP}4}$ type with space group $Fm\overline{3}m$ and lattice parameter $a = 0.402 - 0.405$ nm, depending on the share of zinc in the solution [8]. Therefore, the HA1-Zn alloys are grain-refined using Al-Ti or Al-Ti-B master alloy (MA) which are commonly used for grain refinement of the Al and its alloys. There are also used master alloys containing rare earth elements (Al-RE), as well as the new alternatives, i.e. Zn-Ti base MA.

The present paper summarizes results of the investigations done since 1980s, which were aimed at grain refinement of the Zn (24-28)wt% Al alloys.

2. Al-Ti AND Al-RE BASE REFINERS

Usually two groups of modifying master alloys are used for structure refinement of HA1-Zn alloys. The first one contains rare earth elements (RE) and the second one contains titanium or titanium with the addition of other elements, e.g. of boron. In such master alloys aluminium is a matrix. Addition of RE to HA1-Zn alloys aims also, besides structure refinement, at improvement of casting properties and at increase of plastic properties. A detail description of the works done in this area is beyond of this paper capacity and was previously overviewed in [10, 11]. Thus, only the main conclusions are below quoted.

It was found that small addition of RE together with the addition of Mn, Ti and B results in increase of tensile strength, hardness and wear resistance of ZA27 alloy [12]. However, the dissolution of the Al-RE MA within the ZA27 melt requires it overheating to about 700°C.

In all the works on grain refinement of HA1-Zn alloys with the Al-Ti and Al-Ti-B MA it was stated, that the refining process results in breaking up of dendrites $\alpha'$ and in change of their morphology from the linear one through petal-like to semi-globular [7, 13, 14]. An increase by about 20% of elongation of ZA27 alloy modified with the addition of Ti+B was obtained with practically unchanged tensile strength and impact resistance [7]. Furthermore, an increase of castability of ZA27 alloy modified with the addition of Ti+B was observed [13]. Similarly as in the case of the Al-RE MA, master alloys of Al-Ti or Al-Ti-B require the melt overheated to 700-750°C in order to ensure their rapid dissolution [14].
3. Zn-Ti BASE REFINERS

3.1. Changes of the structure and strength properties

The technology of melting of HAl-Zn alloys limits temperature of the melt to about 550 - 600°C [15]. Furthermore, the Al-base MA exhibit great difference of their density in relation to the density of HAl-Zn alloys. For example, density of the Al-5wt%Ti MA is about 3 g/cm³, while density of the Zn-(25-28) wt%Al melt is about 5 g/cm³. Such great differences causes difficulties in making the refining additions with the use of traditional Al-Ti MA.

These difficulties can be avoided by replacing Al-Ti MA with ZnTi-based MA. The Zn-Ti MA, which was introduced in 1980s for grain-refinement of the HAl-Zn alloys [16], exhibit very good solubility in liquid Zn-Al alloys in temperature beginning from about 500°C and have higher density than that of modified alloys; furthermore they have similar refining effect as the Al-Ti MA. It has been stated [17, 18] that the addition of Zn-4.6 wt%Ti master alloy (ZnTi4 MA) to Zn-25wt%Al alloy (ZnAl25) causes significant refinement of the α' dendrites and changes their morphology from branched dendritic to semi-globular – Fig. 1.

Thus, the master alloy based on the Zn-Ti system allows to avoid detrimental overheating of the inoculated Zn-Al alloys, which is required when the traditional Al-Ti MA is used. Additionally, using the Zn-Ti MA allows to reduce the costs of energy and material, and to improve the plastic properties of castings – Fig. 2 (increased elongation with tensile strength preserved).

![Fig. 1. LM picture (Leica DM IRM microscope) of microstructure of the ZnAl25 alloy poured into sand mould. (a) initial, unmodified alloy; (b) the same alloy inoculated with 0.03 wt%Ti (ZnTi4 MA). Samples etched in diluted aqua regia [18] Rys. 1. Optyczny obraz (mikroskop Leica DM IRM) mikrostruktury stopu ZnAl25 odlanego do formy piaskowej. (a) stop wyjściowy, niemodyfikowany; (b) ten sam stop zmodyfikowany dodatkiem 0.03 % wag. Ti (zaprawa ZnTi4). Próbki trawione rozcieńczoną wodą królewska [18]](image-url)
3.2. Changes of Zn segregation

The dendrites of the α’ phase show high inhomogeneity of Zn distribution across the grains. Zn-microsegregation strongly influences the stability of properties of the parts of machines during their operating. Fig. 3 shows examples of the Zn concentration measurements in the primary α’ phase of the initial (a) and inoculated with Ti (b) sand-cast ZnAl25 alloy. The maximum microsegregation of Zn in the examined system, measured as a difference between Zn contents in centres and borders of the α primary phase, is collected in Table 1.
Table 1. Mean values of the calculated and measured Zn content in centres and borders of \( \alpha \) dendrites of the sand cast ZnAl25 alloy. Theoretical values calculated using Formula from [20]. Experimental values from EDS-SEM Quant measurements (ZAF quantitative method) [19]

<table>
<thead>
<tr>
<th></th>
<th>Centre</th>
<th>Border</th>
<th>Non-equilibrium eutectic</th>
<th>( \Delta \text{Zn: border-centre} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnAl25. Theoretical values</td>
<td>46.0</td>
<td>83.1</td>
<td>-----</td>
<td>37.1</td>
</tr>
<tr>
<td>ZnAl25 Experimental values</td>
<td>51.72</td>
<td>84.42</td>
<td>99.38</td>
<td>32.7</td>
</tr>
<tr>
<td>ZnAl25Ti0.05 Experimental values</td>
<td>54.40</td>
<td>85.43</td>
<td>99.46</td>
<td>31.03</td>
</tr>
</tbody>
</table>

Fig. 3. SEM-BSE micrographs with marked EDS traces (red lines): (a) through secondary arms of \( \alpha' \) dendrites of the initial, unrefined ZnAl25 alloy; (b) through a refined, semiglobular \( \alpha' \) dendrite of the ZnAl25 alloy. The arrow points to a particle of the Ti(Al,Zn)\(_3\) intermetallic, the probable substrate of the heterogeneous nucleation [19]

Rys. 3. Obrazy SEM-BSE z zaznaczonymi śladowi tras analizy składu (linie czerwone): (a) w poprzek gałęzi drugiego rzędu dendrytów \( \alpha' \) wyjściowego, niemodyfikowanego stopu ZnAl25; (b) w przekroju zmodyfikowanego dendrytu \( \alpha' \) stopu ZnAl25. Strzałka wska- zuje cząstkę fazy międzymetalicznej Ti(Al,Zn)\(_3\), prawdopodobnego podłoża heterogenicznego zarodkowania [19]
4. HAl-Zn MATRIX COMPOSITES

Strength of the HAl - Zn alloys decreases strongly in temperatures above 100 °C [5]. Thus, apart from the structure refining, the investigations are also focused on improving strength, hardness and wear properties at elevated temperatures. The insufficient strength and hardness can be improved by addition of reinforcing fibres or particles, e.g. SiC, Al₂O₃ or TiC [22-29].

During the performed examinations [21] Al₃Ti particles were used as the reinforcement and refiner of the Zn- 25 wt % Al alloy (ZnAl25) and Zn - 25 wt % Al -1 wt % Cu (ZnAl25Cu1) alloy. Wear-resistance investigations were performed using pin-on-disc method (T01M device, made in Poland), using samples 8 mm in diameter and 24 mm in length cut from the Ø30 x 80 mm castings. The dry sliding wear test was performed against a rotating steel disc of 110 mm in diameter and 10 mm in height, and hardness of 50 HRC. The test was carried out at load giving 0.8 MPa pressure and at sliding speed of about 0.7 m/s, for a total sliding distance of 10 km. The coefficient of friction was directly measured during these tests.

The obtained changes of structure and properties of the examined alloys were compared with those of the Zn-25 wt % Al-2.5wt%Cu initial alloy (ZnAl25Cu2.5).

The light-microscopy observations (LM) of structure were performed on samples etched in a diluted aqua regia, using Leica DM IRM microscope. Scanning electron microscopy (SEM) investigations were performed on unetched samples using Philips XL30 microscope.

![Fig. 4. (a) LM picture of the ZnAl25Ti2 alloy doped with AlTi12 master alloy. Visible needles of the Al₃Ti - base reinforcing particles. (b) SEM picture of the same alloy. Visible non-uniform in composition Al₃Ti - base phase in the refined matrix [21] Rys. 4. (a) Optyczny obraz stopu ZnAl25Ti2 domieszkowanego zaprawą AlTi12. Widoczne iglaste wydzielenia zbrojenia na bazie cząstek Al₃Ti. (b) Obraz SEM tego samego stopu. Na tle rozdrobnionej struktury widoczne niejednorodne co do składu cząstki zbrojenia na bazie fazy Al₃Ti [21]
As it is seen from Fig. 4 and Fig. 5, the introduced Al$_3$Ti particles build reinforcement of the structure, which leads to the increase of hardness, while the coefficient of friction remains practically unchanged – Table 2

Table 2. Hardness HRB and coefficient of friction $\mu$ (maximal values during the test) of the examined alloys [21]

<table>
<thead>
<tr>
<th></th>
<th>ZnAl25Cu2.5</th>
<th>ZnAl25Ti2</th>
<th>ZnAl25Cu1Ti1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRB</td>
<td>$\mu$</td>
<td>HRB</td>
<td>$\mu$</td>
</tr>
<tr>
<td>75</td>
<td>0.28</td>
<td>95</td>
<td>0.33</td>
</tr>
<tr>
<td>200 $\mu$m</td>
<td></td>
<td>100 $\mu$m</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5. (a) LM picture of the ZnAl25Cu1Ti1.5 alloy doped with AlTi12 master alloy. Visible mixed needle-blocky reinforcing particles of the Al$_3$Ti - base phase. (b) SEM picture of the same alloy. Visible non-uniform in composition Al$_3$Ti - base phase in the refined matrix [21]

Rys. 5. (a) Optyczny obraz struktury stopu ZnAl25Cu1Ti1.5 domieszkanego zaprawą Al-Ti12. Widoczne mieszane, iglasto-blokowe wydzielenia zbrojenia na bazie cząstek Al$_3$Ti. (b) Obraz SEM tego samego stopu. Na tle rozdrobnionej struktury widoczne nie-jednорodne co do składu cząstki zbrojenia na bazie fazy Al$_3$Ti [21]

5. CONCLUSIONS

The works on structure refinement of the high aluminium zinc alloys showed that the traditional Al-Ti and Al-RE base master alloys cause significant refinement of the $\alpha'$ primary dendrites of solid solution of zinc in aluminum, which is beneficial for improving plastic properties. On the other hand, the Al-base master alloys require melt temper-
ature of about 700-750 °C, which can cause oxidation of the alloy and increases the costs of energy. The newly developed ZnTi – base master alloys show good solubility in ZnAl melt in much lower temperatures, of about 500 °C, they allow to avoid detrimental overheating and allow to obtain savings of the energy costs. The ZnTi MA introduce into the inoculated melt particles serving as substrates of the heterogeneous nucleation of the α' phase, which allow to obtain significantly refined structure and to improve plastic properties. The mechanism of this process is discussed in details in [10, 11, 17, 18].

The grain refinement causes decrease of the maximum Zn-segregation across the α' grains, which is practical advantage of the applied structure refinement. Partial or total replacement of Cu with Ti, introduced as the Al3Ti phase, evolves in situ Ti(Al,Zn)3 particles in microstructure of the examined high aluminium zinc alloys. These particles act as the reinforcement of the ZnAl25-based composite, which allow obtaining increased hardness with preserved value of the coefficient of friction.

ACKNOWLEDGEMENTS

The financial support by the Polish Committee for Scientific Research under the research grants No. 7 T08B 035 13, 7 T08D 027 18 and 4 T08A 040 25 is kindly acknowledged.
The author would like to thank cordially The Family Wasilewski, The Clare Hall Cambridge and The British Council for financial support in frame of the Roman Wasilewski Scholarship.
The Krupkowski Institute of Metallurgy in Krakow and The Department of Materials Science and Metallurgy – University of Cambridge are kindly acknowledged for the provision of laboratory facilities.
The author would like to express his warm gratitude to Prof. L. A. Dobrzański (Silesian Technical University in Gliwice), Prof. A. Lindsay Geer (University of Cambridge) and Prof. J.S. Suchy (AGH University of Science and Technology) for help, advice and helpful scientific discussion.

REFERENCES

STRUKTURA I WŁAŚCIWOŚCI WYSOKO-ALUMINIOWYCH STOPÓW CYNUKU ZMODYFIKOWANYCH DODATKIEM Ti

STRESZCZENIE

Praca poświęcona jest badaniom modyfikacji (rozdrabniania) struktury wysoko-aluminiowych, odlewanych stopów cynku (HAl-Zn). Na podstawie prac zagranicznych oraz prac własnych, wykonanych przez autora i współpracowników w ostatnich 20 latach, omówione zostały badania z obszaru praktyki modyfikowania wysoko-aluminiowych stopów cynku dodatkiem tytanu w zaprawach, a także badania zmian wybranych właściwości tych stopów w następstwie zastosowanej modyfikacji.

Recenzował Prof. Józef Suchy