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**ANALYTICAL ELECTRON MICROSCOPY OF LAMELLAR PRECIPITATES  
IN  $\text{AlZnTi}$  ALLOYS**

**ANALITYCZNA MIKROSKOPIA ELEKTRONOWA WYDZIELEŃ PŁYTKOWYCH  
W STOPACH  $\text{AlZnTi}$**

A technique of analytical electron microscopy was used in order to determine the changes of chemistry of the phases formed in the microstructure of the Zn-25 wt.% Al cast alloy modified with Ti. The presence of the  $\text{Ti}(\text{Al}, \text{Zn})_3$  compound was detected as well as two kinds of lamellar structures of the  $\alpha$  and  $\beta$ -phases having different partitioning of Al and Zn and various amount of Ti. It was suggested that the first kind of lamellar precipitates was formed during monotectoid transformation at the conditions far away from the equilibrium state while the second kind was a result of a discontinuous precipitation beginning after a longer cooling time of casting. Titanium appeared only within the  $\alpha$  and  $\beta$  lamellae of monotectoid and it came from the Ti gradient adjacent to the  $\text{Ti}(\text{Al}, \text{Zn})_3$  compound. Therefore, the amount of Ti decreased along increasing distance from the compound.

Metodą analitycznej mikroskopii elektronowej dokonano oceny zmian składu chemicznego faz występujących w mikrostrukturze stopu odlewniczego Zn-25 wag.% Al po modyfikacji tytanem. Stwierdzono występowanie wydzielen bogatych w Ti, a identyfikowanych jako  $\text{Ti}(\text{Al}, \text{Zn})_3$  oraz dwóch rodzajów struktury płytkowej faz  $\alpha$  i  $\beta$ , różniących się proporcjami Al i Zn, a także zawartością Ti. Przedstawiono hipotezę, że pierwszy typ wydzielen płytkowych powstaje podczas przemiany monotektoidalnej stopu w warunkach dalekich od stanu równowagi, podczas gdy drugi jest wynikiem wydzielenia nieciągłego, zaczynającego się po dłuższym okresie stygnięcia odlewu. Ti występuje jedynie w płytkach faz  $\alpha$  i  $\beta$  monotektoidu i pochodzi z gradientu tego pierwiastka istniejącego wokół  $\text{Ti}(\text{Al}, \text{Zn})_3$ , dlatego też ilość Ti w płytkach maleje w miarę wzrostu odległości od tych wydzielen.

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## 1. Introduction

The family of the high-aluminium zinc-based alloys, i.e. containing 25–40 wt.% Al, e.g. ZA27, Z284, ZA35 becomes a very promising group of the casting alloys having high strength properties even comparable to those of malleable and ductile iron as well as some bronzes. Moreover, zinc alloys possess relatively low melting point, which allows 25–75% energy saving in comparison with aluminium alloys and bronzes [1, 2].

It should be noted at the same time, that Zn-based alloys containing a greater amount of Al show tendency to the coarse-dendritic structure of the primary  $\alpha'$ -phase, especially in ingots after slow solidification in sand moulds. Such type of the microstructure causes a decrease of the alloy elongation and impact toughness. Additionally, the coarse dendritic structure effects in difficult feeding of the interdendritic area [3].

The presence of the coarse microstructure of the high-aluminium Zn-based alloys can be avoided by addition of a proper agent for grain-refinement of the primary  $\alpha'$  phase. Recently, small amount of Ti has been successfully used to accomplish this task [4, 5]. Titanium was introduced in a form of Zn-4 wt.% Ti master alloy which resulted in the 40–75% increase of the elongation while the tensile strength remained on the same level [5]. Such an effect was caused by the grain refinement due to the  $\text{TiZn}_3$  interaction with Zn-Al melt, which led to a formation of the ternary  $\text{Ti}(\text{Zn}, \text{Al})_3$  phase [6–8]. The  $\text{Ti}(\text{Zn}, \text{Al})_3$  phase is considered to be a very effective substrate for the heterogeneous nucleation of the  $\alpha'$ -phase due to the same type of crystal structure, very little mismatch of lattice parameter and the least interatomic distance in the  $\{111\}$  strong crystallographic planes for both phases [7]. Additionally, the  $\text{Ti}(\text{Al}, \text{Zn})_3$  phase is thermodynamically more stable in the modified Zn-Al melt in comparison with the  $\text{Al}_3\text{Ti}$  or  $\text{TiZn}_3$  binary ones [9]. Moreover, addition of Ti accelerates the decomposition of quenched Zn-Al alloys, as well as diminishing a dimensional instability during service [10, 15].

The main purpose of this paper was to study the chemistry of the constituents of Zn-25 wt.% Al alloy after doping with Ti by means of an analytical electron microscopy (AEM). Especially, the different partitioning of Ti to particular phases was expected, which might be essential for a change of mechanical properties of the alloy.

## 2. Experimental

A zinc alloy containing 25 wt.% aluminium prepared from electrolytic Al(99.96%) and zinc (99.995%) was used in the investigation. Titanium was introduced in the form of pre-alloy Zn-4 wt.% Ti (ZnTi4) which resulted in 0.05 wt. % of Ti in the bulk, which is thought to be optimum amount [4, 5, 7]. More details concerning the sample preparation are presented elsewhere [6, 11].

The investigation of the as-cast alloy were carried using a transmission electron microscopy (TEM) Philips CM20 Twin equipped with an energy dispersive X-ray (EDX) spectrometer Link exL. Thin foils for TEM examinations were prepared by standard thinning and grinding technique down to 0.05 mm. Then a punching machine was used to produce the discs 3 mm in diameter. The final operation consisted in jet electropolishing using an electrolyte of 10% perchloric acid in ethanol at the temperature of  $-30^{\circ}\text{C}$ .

The EDX analysis was performed using a microscope operating at 200 kV in the nanoprobe mode with a  $\text{LaB}_6$  source of electrons. A nominal probe diameter of 10 nm at the "full width at half maximum" was used. The specimen thickness in the region of interest was determined using a contamination spot method and it was found to be between 120–230 nm. Time of analysis was sufficient to acquire a few thousand counts of major elements, and the associated relative error ( $3\sigma$ ) due to X-ray counting was 3–4%. The atomic percentage of zinc at the points analysed was obtained from the observed peak integrals using the Cliff-Lorimer "ratio technique" and internal package of elemental sensitivity factors for pure Al, Zn, Ti being integral part of the software provided by Link Analytical.

### 3. Results and discussion

Figure 1 presents the lamellar structure formed due to monotectoid reaction starting from the outer parts of dendrites. The dendrites had initially semi-globular (petal-like) shape. The EDX analysis revealed 98.63 wt.% Zn and 1.35 wt.% Al, which corresponds very well with the composition of the  $\alpha' + \beta$  eutectic close to the solid solubility relevant for the  $\beta$ -phase.

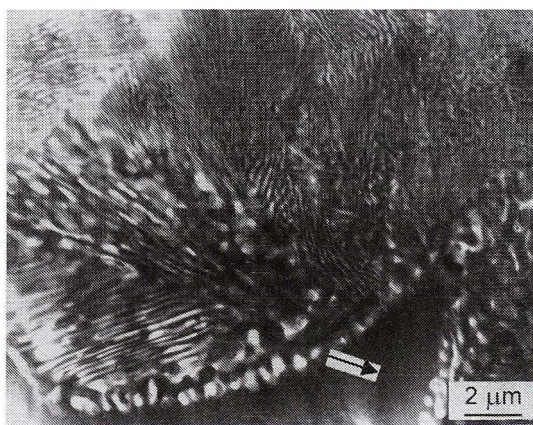


Fig. 1. TEM micrograph of the Zn-25 wt.% Al-0.05 wt.% Ti alloy. Composition in the area pointed by the arrow: 98.63 wt.% Zn and 1.35 wt.% Al

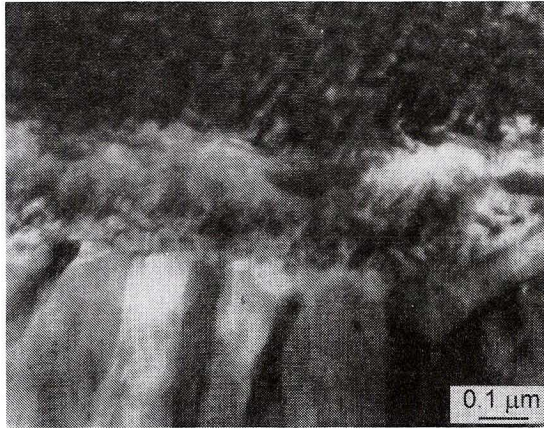


Fig. 2. TEM micrograph showing the front of the monotectoid reaction in the Zn-25 wt.% Al-0.05 wt.% Ti alloy growing into the  $\alpha'$  solid solution of primary dendrite. The dark lamellae are Zn-rich while light lamellae are rich in Al

Figure 2 presents the products of the monotectoid reaction growing into interdendritic space. They consist of alternate lamellae of the solute-rich  $\beta$ -phase (dark plates) and the solute-depleted  $\alpha$ -phase (light areas). The reaction front of the lamellar structure is separated from the dendrite interior by a distinguished zone, which in principle is precipitate free. The dendrite interior is covered by fine quasi-periodic single precipitates (Fig. 3). The systematic EDX analysis in particular areas revealed the composition presented in Table 1.

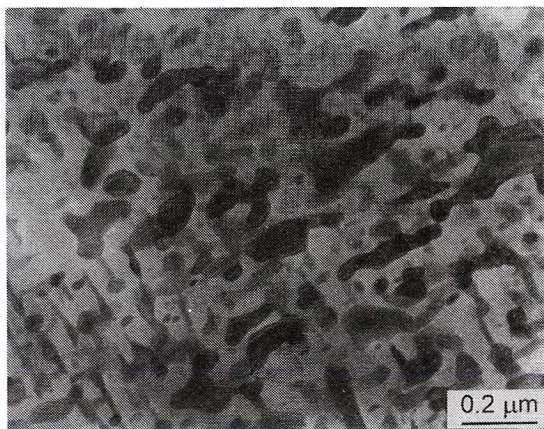


Fig. 3. TEM micrograph showing single quasi-periodic oriented Zn-rich precipitates ahead of the reaction front of lamellar colony in the Zn-25 wt.% Al-0.05 wt.% Ti alloy

TABLE 1

Chemical composition of precipitates existing in Fig. 2

Area	Element [wt.%]		
	Zn	Al	Ti
Single precipitates ahead of the reaction front	50.1	49.4	0.5
Precipitate free zone	17.3	82.1	0.57
$\beta$ lamella	59.61	40.09	0.3
$\alpha$ lamella	33.06	66.42	0.52

Figure 4 is a view of lamellar structure at large magnification taken far away from the area shown in Fig. 3. The single globular precipitates are clearly visible within the  $\alpha$  lamellae. They contain 68 wt.% Zn and 32 wt.% Al and surprisingly no titanium. Titanium was not been detected also within the  $\alpha$  and  $\beta$  lamellae. The Zn and Al contents were 17.5 wt.%, 82.5 wt.% and 91.4 wt.%, 8.6 wt.% for the  $\alpha$  and  $\beta$  lamellae, respectively.

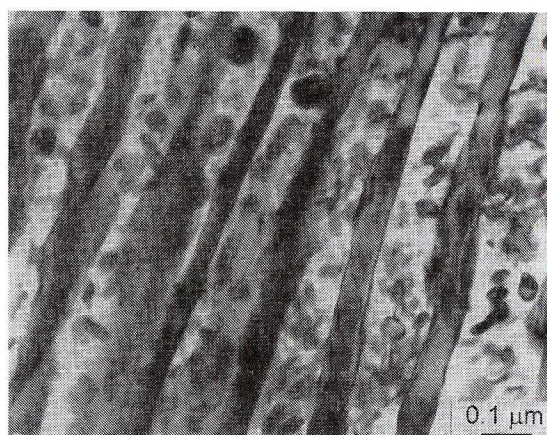


Fig. 4. TEM micrograph of the lamellar structure at high magnification. The globular Zn-rich precipitates are visible within the  $\alpha$  lamellae

The detailed examination of the structure and composition allowed establishing that such large differences in composition are associated with the presence of single precipitates within the lamellar structure (Fig. 5). They contain 20 at.% Zn, 53 at.% Al and 27 at.% Ti. This means that the ZnTi4 master alloy interacted with the melt to form the  $\text{Ti}(\text{Al}, \text{Zn})_3$  compound. Simultaneously, some amount of Ti dissolves itself in the melt. The point to point EDX analysis revealed a characteristic solute gradient near the  $\text{Ti}(\text{Al}, \text{Zn})_3$  precipitates. Especially, a remarkable decrease of Ti amount is worth to note (see table 2). The subsequent monotectoid reaction

consumes both areas close to Ti-rich precipitates and away from them. This explains why Ti was present in lamellar structure only in the areas close to the Ti-rich precipitates. However, the level of Ti enrichment does not justify such large differences within Zn and Al in the  $\alpha$  and  $\beta$  lamellae.

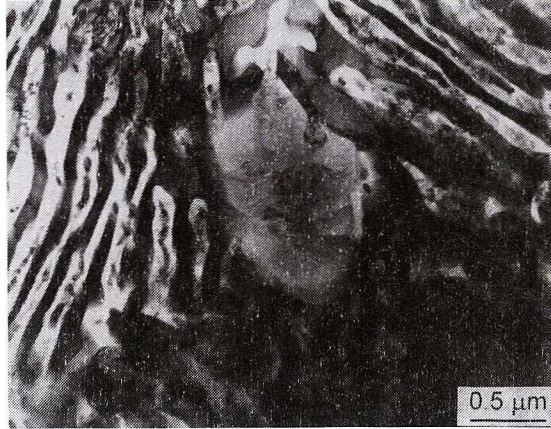


Fig. 5. TEM micrograph of the lamellar microstructure in the Zn-25 wt.% Al-0.05 wt.% Ti. Note the presence of large single particles identified as the  $\text{Ti}(\text{Al}, \text{Zn})_3$  compound

TABLE 2

Chemical composition of the  $\beta$  lamella at various distances from the  $\text{Ti}(\text{Al}, \text{Zn})_3$

Distance from $\text{Ti}(\text{Al}, \text{Zn})_3$ precipitate [ $\mu\text{m}$ ]	Composition [wt.%]		
	Zn	Al	Ti
0.1	60.0	38.8	1.2
0.5	66.8	32.8	0.4
0.8	63.2	36.6	0.3

Therefore, it is supposed that areas of the dendrite adjacent to the  $\text{Ti}(\text{Al}, \text{Zn})_3$  undergo monotectoid transformation after relatively short time of cooling. In this way, the composition of the lamellae is strongly deviated from the location of solid solubility lines in the Al-Zn equilibrium phase diagram [12]. On the other hand, the average composition of the  $\alpha$  and  $\beta$  lamellae far away from the Ti-rich precipitates are much closer to the solvus lines of the Al- and Zn-rich solid solutions. Such partitioning is close to that observed during discontinuous precipitation in Al-Zn alloys [13, 14] which begins after longer period of cooling when the temperature of ingot is 100–150 K below the monotectoid line. However, the open question still remains whether the  $\text{Ti}(\text{Al}, \text{Zn})_3$  compound could also be a favourable site for the initiation of the monotectoid reaction, and how both types of lamellar structure interact between themselves.

#### 4. Conclusions

The examination of the microstructure and chemistry of the Zn-25 wt.% Al alloys modified with Ti using the technique of analytical electron microscopy enabled to distinguish the following constituents:

- The single globular precipitates of the  $\text{Ti}(\text{Al},\text{Zn})_3$  compound within interdendritic area.
- Two kinds of cellular structure having different partitioning of Zn, Al and Ti. The first kind of lamellar precipitates forms during monotectoid transformation at the conditions far away from the equilibrium state while the second kind is a result of a discontinuous precipitation starting after a longer cooling time of casting. Titanium appears only within the  $\alpha$  and  $\beta$  lamellae of monotectoid and it comes from the Ti gradient adjacent to the  $\text{Ti}(\text{Al},\text{Zn})_3$  compound. Therefore, the amount of Ti decreases along increasing distance from the compound.

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