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INFLUENCE OF SOLUTION HEAT TREATMENT ON PHASE COMPOSITION AND STRUCTURE OF ZnAl40Cu(1-2)Ti(1-2) ALLOYS

Zn-Al-Cu alloys are characterised by very good tribological properties: high resistances to abrasive wear and adhesive wear, resistance to dry friction, low friction coefficient. Important disadvantages of Zn-Al alloys include, among others low structural and dimensional instability in as-cast stage and during long-period after pouring into moulds. Studies carried out in recent years confirm the problem of dimensional instability of Zn-Al-Cu alloys may be reduced by replace copper partially with titanium. The goal of the studies carried out was to define the influence of heat treatment on the microstructure and phase composition of ZnAl40Cu(1-2)Ti(1-2) alloys. The scope of the investigations included analysis of the phase composition, tests using a scanning electron microscope and a scanning transmission electron microscope, and X-ray microanalysis. The studies carried out indicate a presence of the e-$CuZn_5$ and Ti_2ZnAl_5, $Al_xCu_yTi_z$ phases in the ZnAl40Cu(1-2)Ti(1-2) alloys.

Keywords: Zn-Al alloys, microstructure, phase compositions

1. Introduction

Zn-Al alloys found application as an alternative material for bronzes, cast iron and aluminium alloys in bearings, and as a construction material [1-2]. Zn-Al-Cu alloys are characterised by very good tribological properties: high resistances to abrasive wear and adhesive wear, resistance to dry friction, low friction coefficient [3]. Important disadvantages of Zn-Al alloys include, among others: low creep strength and low dimensional stability during heat treatment [4].

One currently used method for reduction of changes in linear dimensions of casts made of Zn-Al-Cu alloys consists in partial or complete replacement of copper with silicon. Studies carried out in recent years confirm the possibility to replace copper partially with titanium. Works by Krajewski [5] indicate that the problem of dimensional instability of Zn-Al-Cu alloys may be reduced significantly in this way. Introduction of titanium to Zn-Al alloys affects a decrease or total elimination of dimensional instability. In paper [6], ZnAl25 alloy was studied: initial (not containing Ti) and alloys containing 0.01 and 0.1 wt. % of Ti. The investigations proved that even a small addition of titanium exerts a considerable influence on phase transformations occurring at room temperature and may affect the dimensional changes of the cast significantly. For higher titanium contents in Zn-Al alloys, the problem of dimensional instability may be eliminated almost completely. Such studies were undertaken by Krajewski in paper [5] on alloys ZnAl26Cu2.2, ZnAl26Ti1.5Cu and ZnAl26Ti1.6. The investigations proved that as the titanium content in the alloy is increased and the copper content is decreased, dimensional changes are getting smaller. The ZnAl26Ti1.6 alloy subjected to supersaturation attains a stable structure and dimensions during a very short time after heat treatment.

The influence of titanium addition on the structure and properties of Zn-Al-Cu alloys was discussed in many papers. In most works, the titanium addition does not exceed 0.1 wt. % [6-8]. However, there are little numbers of papers concerning alloys which contain at least 1 wt. % of Ti.

2. The scope and method of examinations

The goal of the studies carried out was to define the influence of heat treatment on the microstructure, phase composition and hardness of ZnAl40Cu(1-2)Ti(1-2) alloys. The following alloys were examined: Zn – 40 wt % Al – 2 wt % Cu – 1 wt. % Ti, Zn – 40 wt % Al – 1.5 wt % Cu – 1.5 wt. % Ti and Zn – 40 wt % Al – 2 wt % Ti – 1 wt. % Cu. Alloys selected for examination were melted in a VSG-02 type induction furnace from the Balzers company in a melting crucible made of Al_2O_3. The approximate weight of the raw material was 1,2 kg. Due to the intensive evaporation of zinc, melting processes were not performed in a vacuum but in an argon atmosphere inside the furnace heating chamber, under a pressure of approximately 650 Torr. Raw material components used were technically pure zinc (99,99% Zn),

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aluminum grade-3N8 (99,98% Al), M00B grade (oxygen-free) copper, technically pure titanium (grade 1), and rare earth elements (REE). More information about the techniques of casting of Zn-Al-Cu-Ti alloys can be found in the work [14].

The alloys were studied after supersaturation at 385°C for 24 h and aging at temperatures of 175 and 150°C for 10 and 24 h. The scope of the investigations included analysis of the phase composition, tests using a scanning electron microscope and a scanning transmission electron microscope, and X-ray microanalysis.

In the structural examinations, a HITACHI S 3400N scanning electron microscope matched with an EDS X-ray spectrometer. The hardness tests by Brinell method were carried out for a ϕ 5 sphere under a load of 2500 N. The substructure studies, including the analysis of chemical composition in microareas, we carried out using a HITACHI HD–2300A scanning transmission electron microscope (STEM), operating under an accelerating voltage of 200 kV. The samples for the STEM analyses, having a form of thin foils, were prepared by the FIB method using a HITACHI FB-2100.3 FIB device. X-ray phase analysis was performed with a JEOL JDX-7S diffraction instrument using a lamp equipped with a copper anode and a power supply under the following conditions: 40 kV voltage and a 20 mA current. The data were recorded by the step method (step 0,03°) with a counting time of 3 s in the angle range for 2θ from 30 to 80°.

3. Results of examination

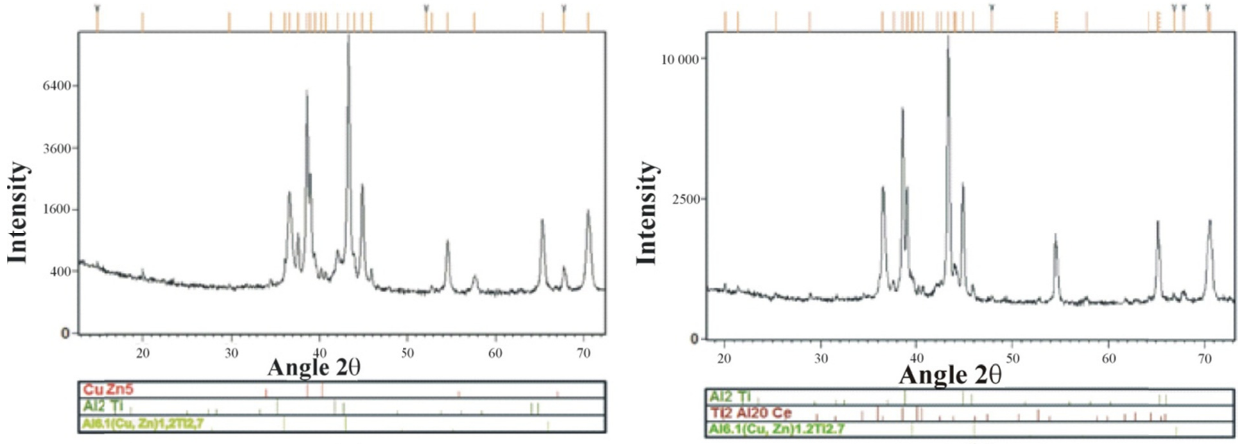
Phase composition of ZnAl40Cu(1-2)Ti(1-2) alloys after heat treatment is shown in Table 1 and Fig. 1.

Solid solutions of Zn in Al and Al in Zn (phases α, β') occur in the structure of ZnAl40Cu(1-2)Ti(1-2) alloys in their as-cast conditions, phase ε-($CuZn_5$) is also present. Titanium, together with other alloying elements, forms phases Ti(Al, Zn)$_3$, $Al_{2.7}Cu_{0.3}Ti$. Additionally, for the ZnAl40Cu2Ti and ZnAl40Cu1.5Ti1.5 alloys, the results of the X-ray phase analysis

TABLE 1

Phase composition of ZnAl40Cu(1-2)Ti(1-2) alloys after heat treatment

Alloy	Heat treatment	Phases
ZnAl40Cu2Ti	as-cast	α, β', $CuZn_5$, Ti(Al, Zn)$_3$, $Al_{2.7}Cu_{0.3}Ti$, $CuAl_2$
ZnAl40Cu1,5Ti1,5		α, β', $CuZn_5$, Ti(Al, Zn)$_3$, $Al_{2.7}Cu_{0.3}Ti$
ZnAl40Ti2Cu		
ZnAl40Cu2Ti	385°C/24h + 150°C/10h	α, β', $CuZn_5$, (Al, Zn)$_2$Ti, $Al_{6.1}$(Cu, Zn)$_{1.2}Ti_{2.7}$, $Ti_2Al_{20}Ce$
	385°C/24h + 150°C/24h	
	385°C/24h + 175°C/10h	α, β', $CuZn_5$, (Al, Zn)$_2$Ti, $Al_{6.1}$(Cu, Zn)$_{1.2}Ti_{2.7}$, $Ti_2Al_{20}Ce$
	385°C/24h + 175°C/24h	
ZnAl40Cu1,5Ti1,5	385°C/24h + 150°C/10h	α, β', $CuZn_5$, (Al, Zn)$_2$Ti, $Al_{6.1}$(Cu, Zn)$_{1.2}Ti_{2.7}$, $Ti_2Al_{20}Ce$
	385°C/24h + 150°C/24h	
	385°C/24h + 175°C/10h	α, β', $CuZn_5$, (Al, Zn)$_2$Ti, $Al_{6.1}$(Cu, Zn)$_{1.2}Ti_{2.7}$, $Ti_2Al_{20}Ce$
	385°C/24h + 175°C/24h	
ZnAl40Ti2Cu	385°C/24h + 150°C/10h	α, β', (Al, Zn)$_2$Ti, $Al_{6.1}$(Cu, Zn)$_{1.2}Ti_{2.7}$, $Ti_2Al_{20}Ce$
	385°C/24h + 150°C/24h	
	385°C/24h + 175°C/10h	
	385°C/24h + 175°C/24h	



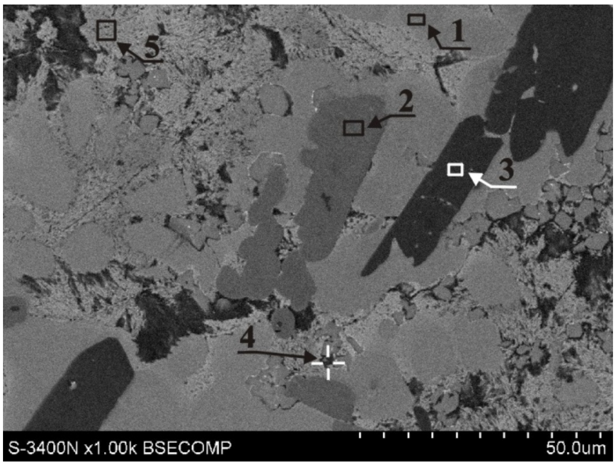
(a) (b)

Fig. 1. The XRD pattern of X-ray phase analysis of ZnAl40Cu1,5Ti1,5 alloy after supersaturation 385°C/24h and aging: (a) 150°C/10 h, (b) 175°C/10 h

indicate presence of precipitations of phase $CuAl_2$ (Table 1). Heat treatment causes significant changes in the phase composition of ZnAl40Cu(1-2)Ti(1-2) alloys. A binary Al_2Ti phase and ternary $Al_{6.1}(Cu,Zn)_{1.2}Ti_{2.7}$ and $Ti_2Al_{20}Ce$ phases form in the structure. On the other hand, presence of the $Al_xCu_yTi_z$ phase is not observed after supersaturation and aging.

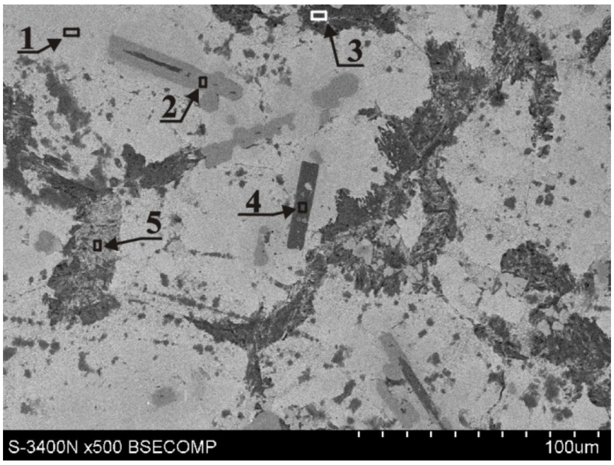
In the structure of ZnAl40Cu(1-2)Ti(1-2) alloys supersaturated and aged at a temperature of 175°C, presence of large precipitations of the (Al, Zn)$_2$Ti phase, visible as black on the scanning electron microscope, is observed (pt. 3, Fig. 2). Also, precipitations of the $Al_{6.1}(Cu,Zn)_{1.2}Ti_{2.7}$ phase, visible as gray in BSE images from the scanning electron microscope, are present in the structure (pt. 2, Fig. 2). Small precipitations containing rare earth elements are visible in the structure too (pt. 4, Fig. 2). Moreover, supersaturated solid solutions of Al in Zn and Al in Zn occur in the structure (pts. 1 and 5, Fig. 2). As the titanium concentrations in ZnAl40Cu(1-2)Ti(1-2) alloys aged at a temperature of 175°C for 10 hours increases, most of all the size of precipitations of the Al_2Ti phase decreases, the size of precipitations of the $Al_{6.1}(Cu, Zn)_{1.2}Ti_{2.7}$ phase remains similar, while the dimensions of precipitations of the $Ti_2Al_{20}Ce$ phase increase. A prolonged aging of ZnAl40Cu(1-2)Ti(1-2) alloys at a temperature of 175°C (aging time: 24 h) primarily leads to coagulation – an increase in the size of phases present in the alloy structure. Large rectangular precipitations of Al_2Ti (pt. 4, Fig. 3) and $Al_{6.1}(Cu,Zn)_{1.2}Ti_{2.7}$ phases are visible in the structure (pt. 2, Fig. 3). Areas, in which the supersaturated solid solution of Zn in Al occurs (pt. 3 Fig. 3), coagulate and are characterised by a lower zinc content than in case of shorter aging at a temperature of 175°C.

In the structure of the ZnAl40Cu2Ti alloy subjected to supersaturation and aging at a temperature of 150°C for 10h large precipitations of a zinc- and copper-rich phase (pt. 1, Fig. 4) and very small precipitations (size of the precipitations is larger than the excitation area in the X-ray microanalysis), containing rare earth elements (pt. 7, Fig. 4), may be observed. A solid solution of Zn in Al with a diversified chemical composition (pt. 2 and 3, Fig. 4) forms the matrix. Numerous precipitations of the $Al_{6.1}(Cu,Zn)_{1.2}Ti_{2.7}$ phase (pt. 4 and 5, Fig. 4), and Al- and Ti-rich precipitations, containing rare earth elements (pt. 6, Fig. 4), probably precipitations of the $Ti_2Al_{20}Ce$ phase, are visible too. Also, occurrence of very fine precipitations of the (Al, Zn)$_2$Ti phase (pt. 1, Fig. 5) may be observed in the structure. The core of some of precipitations of the $Al_{6.1}(Cu,Zn)_{1.2}Ti_{2.7}$ phase is



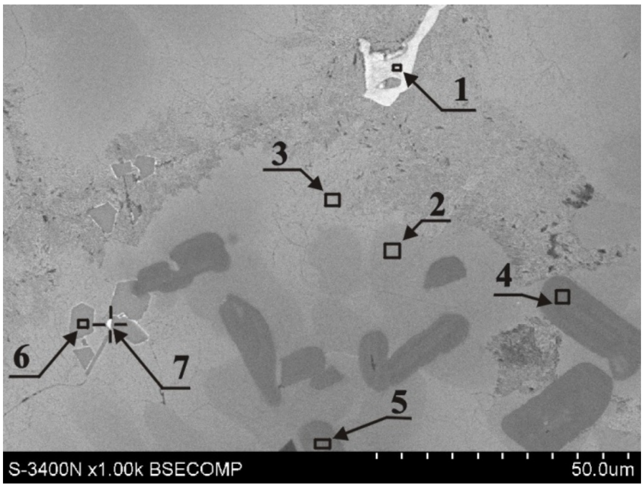
	Zn % at.	Al % at.	Cu % at.	Ti % at.	Ce+La % at.
pt 1	42,5	57,5	–	–	–
pt 2	20,4	49,4	–	30,2	–
pt 3	5,9	60,6	–	33,5	–
pt 4	29,3	61,3	3,9	4,3	1,2
pt 5	46,4	52,2	1,4	–	–

Fig. 2. Structure of ZnAl40Ti2Cu alloy after supersaturation and aging 385°C/24 h + 175°C/10 h



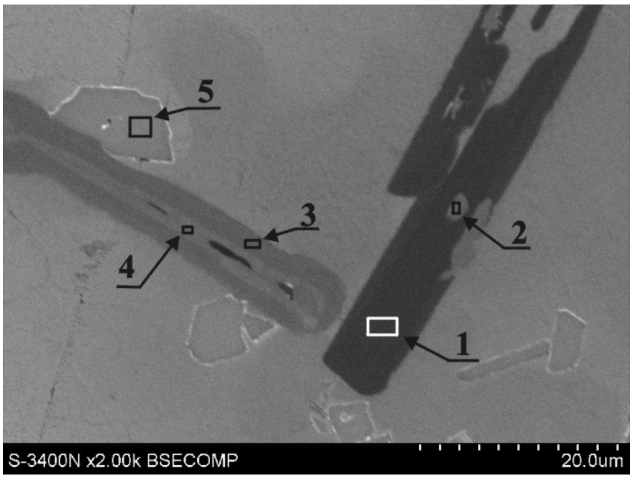
	Zn % at.	Al % at.	Cu % at.	Ti % at.
pt 1	42,7	57,3	–	–
pt 2	20,2	49,4	–	30,4
pt 3	24,7	75,3	–	–
pt 4	6,8	60,4	–	32,8
pt 5	43,5	55,0	1,5	–

Fig. 3. Microstructure of ZnAl40Ti2Cu alloy after supersaturation and aging 385°C/24h+175°C/24h



	Zn % at.	Al. % at.	Cu % at.	Ti % at.	Mg % at.	Ce+La % at.
pt 1	74,9	6,4	9,8	–	8,9	–
pt 2	38,3	59,2	2,5	–	–	–
pt 3	46,2	51,3	2,5	–	–	–
pt 4	19,9	52,5	–	27,6	–	–
pt 5	20,7	50,2	–	29,1	–	–
pt 6	12,2	72,5	–	11,9	–	3,4
pt 7	45,9	36,2	11,6	2,1	–	4,2

Fig. 4. Microstructure of ZnAl40Cu2Ti alloy after supersaturation and aging 385°C/24h+150°C/10h



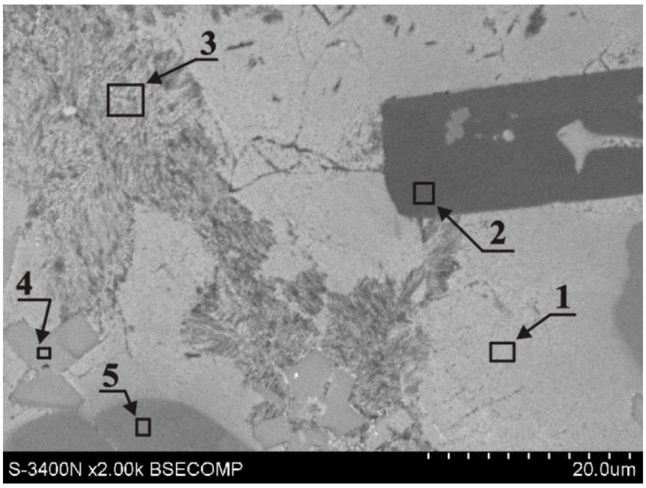
	Zn % at.	Al % at.	Ti % at.	Ce+La % at.
pt 1	4,8	63,8	31,4	–
pt 2	15,3	56,1	28,6	–
pt 3	18,5	53,4	28,1	–
pt 4	21,4	50,5	28,1	–
pt 5	13,9	71,7	11,7	2,7

Fig. 5. Microstructure of ZnAl40Cu2Ti alloy after supersaturation and aging 385°C/24h+150°C/10 h

characterised by a slightly higher zinc content than the outer part of the precipitations (pts. 3 and 4, Fig. 5).

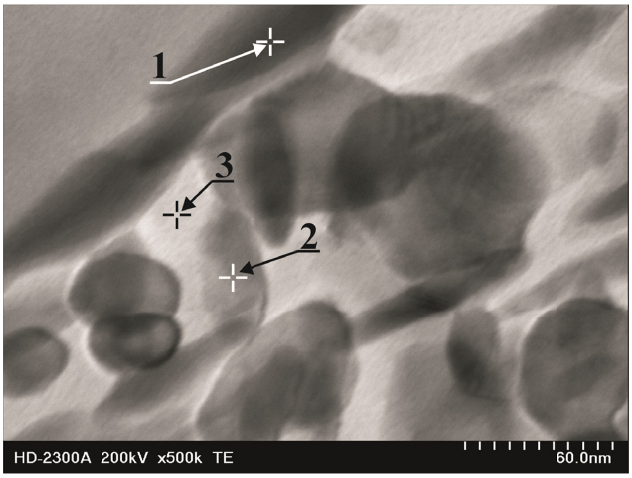
An extension of the precipitation time at a temperature of 150°C causes mainly a coagulation of titanium-rich precipitations and precipitations of the ε-($CuZn_5$) phase. A presence of large rectangular precipitations of the (Al, Zn)$_2$Ti phase (pt. 2, Fig. 6) may be observed in the structure of the ZnAl40Cu2Ti alloy. Also, precipitations of the $Al_{6.1}(Cu, Zn)_{1.2}Ti_{2.7}$ phase (pt. 5, Fig. 6) and precipitations of an Al-rich phase, containing Zn, Ti and rare earth elements (pt. 4, Fig. 6) are visible. In the matrix, formed by a solid solution of alloying elements in Al (pt. 1, Fig. 6), areas, in which numerous minute precipitations occur (pt. 3, Fig. 6), are visible. Similar areas occur in the structure of the ZnAl40Cu1.5Ti1.5 alloy aged at a temperature of 150°C for 24 h, while they do not occur in the case of the ZnAl40Ti2Cu alloy.

A complete characterisation of the structure of the ZnAl40Cu3 and ZnAl40Cu(1-2)Ti(1-2) alloys requires tests using a scanning transmission electron microscope. Studies on the microstructure using STEM proved a presence of a monotectoid mixtures in interdendritic spaces of the ZnAl40Cu3 and ZnAl40Cu(1-2)Ti(1-2) alloys (Fig. 6). The mixture is formed by precipitations of the β' phase in a matrix of the α phase. In the case of the ZnAl40Cu3 alloy, the precipitations of the β' phase most often assume a form of plates. In the case of ZnAl40Cu(1-2)Ti(1-2) alloys, the precipitations of the β' are smaller and assume forms of both fine-crystalline plates, and fine-crystalline spherical precipitations (Figs. 7, 8). Quantitative analysis of chemical composition of the ZnAl40Cu1.5Ti1.5 alloy from a representative point indicates that at the phase boundary between the monotectoid mixture and large precipitations of the Al- and Ti-rich phases (probably the $TiAl_2$ phase), precipitations of the ε-($CuZn_5$) phase occur (pt. 1, Fig. 7, pt. 2, Fig. 8). In the case of ZnAl40Cu(1-2)Ti(1-2) alloys, the precipitations of the β' phase contain, apart from Al and Zn, also copper and a small amount of titanium (pt. 2, Fig. 7). A higher copper content than in the β' phase, may be observed in the α phase (pt. 2, Fig. 7). Precipitations of the ε-($CuZn_5$) phase at the boundary of precipitations of Ti- and Al-rich phases may be observed also for the ZnAl40Ti2Cu alloy, thus an alloy containing only 1 wt. % of Cu (pts. 1-3, Fig. 8).



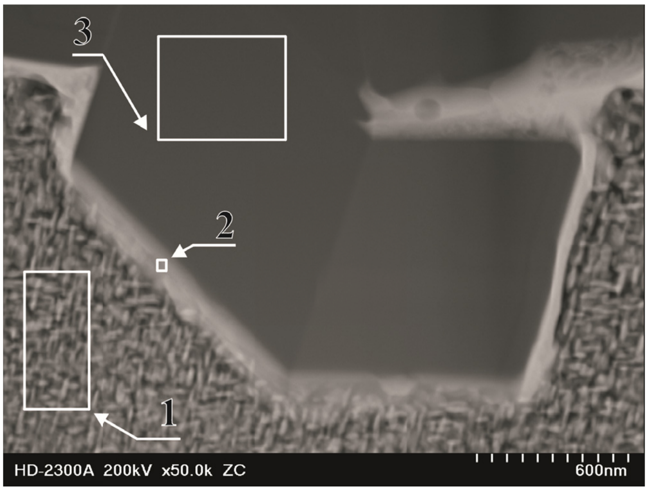
	Zn % at.	Al % at.	Cu % at.	Ti % at.	Mg % at.	Ce+La % at.
pt 1	41,9	55,7	2,4	–	–	–
pt 2	5,6	63,2	–	31,2	–	–
pt 3	42,0	55,8	2,2	–	–	–
pt 4	13,2	71,5	–	11,8	1,2	2,3
pt 5	17,6	53,5	–	28,9	–	–

Fig. 6. Microstructure of ZnAl40Cu2Ti alloy after supersaturation and aging 385°C/24 h+150°C/24 h



	Zn % at.	Al % at.	Cu % at.	Ti % at.	Si % at.
pt 1	60,9	21,8	10,3	5,1	1,9
pt 2	20,4	72,5	5,4	0,2	1,5
pt 3	41,9	49,2	7,3	0,1	1,5

Fig. 7. Microstructure of ZnAl40Cu1,5Ti1,5 alloy as-cast



	Zn % at.	Al % at.	Cu % at.	Ti % at.	Ce % at.
pt 1	29,2	64,7	6,0	0,1	–
pt 2	57,9	29,4	10,2	2,1	0,4
pt 3	3,5	81,9	5,2	8,1	1,3

Fig. 8. Microstructure of ZnAl40Ti2Cu alloy as-cast

4. Discussion of results

The studies carried out indicate a presence of the ε-$CuZn_5$ phase in the ZnAl40Cu1.5Ti1.5 and ZnAl40Cu2Ti alloys, which is inconsistent with the literature data [9-13], because the latter indicate that this phase precipitates in Zn-Al-Cu alloys only when a content of 2 wt. % is exceeded. In ZnAl40Cu(1-2) Ti(1-2) alloys, a presence of precipitations of the ε phase is observed already at the content of 1 wt. %. Therefore, the following hypothesis concerning precipitation of the ε phase in ZnAl40Cu(1-2)Ti(1-2) alloys may be proposed:

- according to the Ti-Al system, precipitation of Ti- and Al-rich phases occurs first, probably even before the beginning of crystallisation of the α phase dendrites
- it causes a depletion of aluminium in the liquid metal and formation of an excess of Zn and Cu atoms (the Zn/Al/Cu ratio in the liquid metal is close to that occurring in alloys containing at least 3 wt. % of Cu)
- after a monotectoid reaction, the “surplus” Zn and Cu atoms form precipitations of the ε phase at the phase boundary between the monotectoid mixture and precipitations of Ti- and Al-rich phases.

A presence of intermetallic phases in the structure of ZnAl40Cu(1-2)Ti(1-2) alloys, both in their as-cast conditions, and after heat treatment, is an important observation. Because of a significantly higher bond energy than in the case of solid solutions, the presence of these phases may affect the properties of the alloys, e.g. their resistance to electrochemical corrosion. The presence of the $CuAl_2$ phase requires further investigations. This phase is an intermetallic binary phase occurring in the Al-Cu system, and crystallising in a tetragonal system. Precipitations of this phase are hard and brittle, and they play a role of a hardening component in Al-Cu alloys. Also, the presence of precipitations of the $(Al, Zn)_2Ti$ phase crystallising in a rhombohedral system, may have an important influence on the alloy properties. These precipitations may affect favourably hardness and abrasive resistance of ZnAl40Cu(1-2)Ti(1-2) alloys. The presence of copper-containing phase in the structure of the alloy should be considered unfavourable. Precipitation of these phases, similarly as in the case of the ε-$(CuZn_5)$ phase, may lead to a decrease in the copper content in the solid solution, which may result in a lower strength of the alloy.

Mg is one of the main alloying elements in Zn-Al alloys. The addition of 0.3 mass % Mg to the alloys containing 40 mass % Al allows to completely eliminate the discontinuous transformation [3]. In the Al-Zn-Mg alloys addition of Mg increases strength, which is associated with the precipitation due to supersaturation and aging very fine phases such as $MgZn_2$ and $Al_2Mg_3Zn_3$. The results indicate that in the examined alloys Mg is dissolved in the existing precipitations of $Al_{6.1}(Cu, Zn)_{1.2}Ti_{2.7}$ phase (pt 1 Fig. 4, pt. 4 Fig. 6). REE creates $Ti_2Al_{20}Ce$ phase. REE are also dissolved in the precipitations of $Al_{6.1}(Cu, Zn)_{1.2}Ti_{2.7}$ phase (pt 4 Fig. 2, pt. 5 Fig. 5, pt 4 Fig. 6).

5. Conclusions

The presented results allow for enunciating of the following conclusions:

1. The ε phase may precipitate also in ZnAl40Cu(1-2)Ti(1-2) alloys, or in Zn-Al alloys containing less than 3 wt. % of Cu
2. Intermetallic phases rich in Al and Ti are present In the structure of ZnAl40Cu(1-2)Ti(1-2) alloys in their as-cast condition: $Ti(Al, Zn)_3$, $Al_xCu_yTi_z$
3. Supersaturation and aging of ZnAl40Cu(1-2)Ti(1-2) alloys causes precipitation of new intermetallic phases, which do not occur in the case of alloys in the as-cast condition: $(Al, Zn)_2Ti$, $Al_{6.1}(Cu,Zn)_{1.2}Ti_{2.7}$, $Ti_2Al_{20}Ce$. The Al- and Ti-rich intermetallic phases present in the structure of the as-cast alloys decay
4. In ZnAl40Cu(1-2)Ti(1-2) alloys, titanium does not participate in solution hardening, but it forms precipitations of intermetallic phases
5. Heat treatment of ZnAl40Cu(1-2)Ti(1-2) alloys leads to formation of new Al- and Ti-rich intermetallic phases in the structure: ($(Al, Zn)_2Ti$, $Al_{6.1}(Cu, Zn)_{1.2}Ti_{2.7}$ and $Ti_2Al_{20}Ce$)

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