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THE EFFECT OF MODIFICATION WITH RARE EARTH ELEMENTS ON ZnAl22Cu3 ALLOY STRUCTURE AND MECHANICAL PROPERTIES

WPŁYW MODYFIKACJI PIERWIASTKAMI ZIEM RZADKICH NA STRUKTURĘ I WŁAŚCIWOŚCI MECHANICZNE STOPU ZnAl22Cu3

The influence of modification with rare earth elements (RE) on the structure and mechanical properties of alloy ZnAl22Cu3 is presented in the paper. ZnAl22Cu3, ZnAl22Cu3SiM and ZnAl22Cu3Si (modified alloy) alloys were tested. ZnAl22Cu3Si and ZnAl22Cu3 alloys were characterized with heterogeneous, fine-grained, dendritic structure. The structure of the alloy ZnAl22Cu3SiM was much more homogeneous. It was found that the addition of silicon reduces the tensile strength. Addition of rare earth elements to the alloy with silicon resulted in the re-growth of melt strength of alloy. It was also found that the modification performed by using of rare earth elements increases the hardness of the alloy.

Keywords: ZnAl22Cu3 alloy, structure, mechanical strength

W pracy przedstawiono wpływ modyfikacji pierwiastkami ziem rzadkich na strukturę i właściwości mechaniczne stopu ZnAl22Cu3. Badaniom poddano stop ZnAl22Cu3, ZnAl22Cu3Si oraz ZnAl22Cu3SiM (stop modyfikowany). Stopy ZnAl22Cu3 oraz ZnAl22Cu3Si charakteryzowały się niejednorodną, drobnoziarnistą, dendrytyczną strukturą. Struktura stopu ZnAl22Cu3SiM była natomiast w znacznie większym stopniu jednorodna. Badania wykazały, że dodatek krzemu powoduje obniżenie wytrzymałości na rozciąganie. Dodatek pierwiastków ziem rzadkich do stopu z krzemem powodował natomiast ponowny wzrost wytrzymałości stopu. Modyfikacja pierwiastkami ziem rzadkich wpływa również na zwiększenie twardości stopu.

1. Introduction

Zn-Al-Cu alloys are characterized by advantageous set of functional quality features: tribological, strength, corrosion. They are used as an alternative material for bronze, cast iron and aluminum alloys in bearings applications as well as a structural material. The use of Zn-Al alloys for bearings exposed on high loadings which operate, in mining, milling machines, rope hoisting units etc., bring some advantageous results.

ZA-8, ZA-12 and ZA-22 ZA-27 alloys with 8, 12, 22, 27% aluminum contents respectively [1-2] primarily found their application.

Zn-Al-Cu type alloys feature a number of advantageous properties such as low melting point, good castability, superplasticity properties, good strength and hardness, good fatigue strength, low density, low friction coefficient, low wear rate and low manufacturing costs. High fatigue strength of Zn-Al-Cu alloys drops in the corrosion environment [2-3]. Copper additive to Al-Zn-Cu alloys effects not only their structure but also improves some of their properties. Strength, hardness, fracture energy, creep and fatigue strength increase together with copper content, especially in small number of cycles. When copper is added the decrease of elongation and dimensional instability during heat treatment is observed [3-4]. Literature brings numerous information about other additives that contribute to the improvement of Zn-Al alloys properties. They are additives of magnesium, silicon in amount of 1-2%, and manganese [5-6], rare earth metals (RE) [7-9] and Ti [10-12]. As in case of copper, the additive is aimed at improving the fatigue strength, tensile strength and increase hardness [13-14]. However, there is little information available in literature on the effect of the rare earth elements (RE, mischmetal) on the structure and strength properties of Zn-Al-Cu based alloys.

2. Scope and methodology of examination

The purpose of the examination was to determine the effect of silicon as well as silicon and RE addition on the structure and mechanical properties of the Zn – 22%masAl-3%mas Cu (ZnAl22Cu3) alloy. ZnAl22Cu3 initial, ZnAl22Cu3 + 1,5% mas Si alloy and ZnAl22Cu3 + 1,5%mas Si alloy with the addition of rare earth elements were subjected to thorough examinations. The alloy was melted in a VSG-02 type, Balzers induction furnace in a melting crucible made of $Al_2 0_3$, in argon environment, under pressure and inside the furnace heating chamber.

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Zinc of 99,99% purity, 3N8 (99,98%Al) aluminum, oxygen- free M00B copper, technically pure silicon and RE were used as raw materials.

The scope of examination included: X-ray, phase analysis, structural examinations, determination of hardness performed with Brinell's method and tensile strength examination. During the structural examinations OLYMPUS GX51 optical microscope with magnification range of 50 to 400× was used. The examinations were carried out on samples taken from ingots in the following way: the first one was taken from the ingot top under contraction cavity, the second one from the middle part, and the third one from the bottom part of the ingot. HITACHI S 3400N scanning electron microscope, supplied with EDS X-ray spectrometer was also used during the performed examinations. The tensile strength examinations were defined in terms of static tensile test performed at room temperature. These examinations were carried out with Zwick Z100 THW AllroundLine strength test machine upon dog-bone shape samples, according to PN–EN10002–1: 2004.

3. Analysis of the examination results

The structural examinations of ZnAl22Cu3 alloy revealed non – uniform, fine grain structure (Fig. 1). Large, bright precipitates and smaller, dark ones were visible. Moreover, brighter areas at tile structure could be seen. The examinations reported in the paper [16] showed, that crystallization of Zn22Al2Cu alloy starts at temperature of 480°C, 40 seconds after pouring,

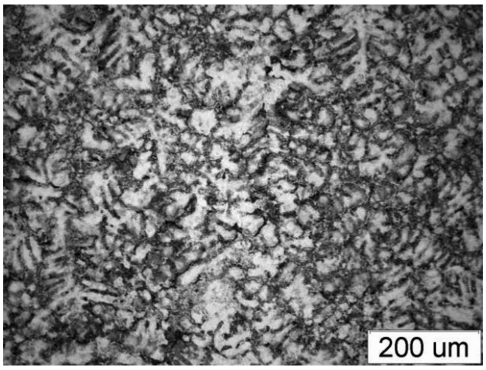

Fig. 1. Structure of ZnAl22Cu3 base alloy

Eutectic transformation at the temperature of 439°C as well as monotectoid transformation at the temperature of 257°C occur in the alloy. During eutectoid transformation, β phase (solid solution of Zn in Al, of regular lattice) undergoes decomposition into α and γ phase.

It was stated that the dendrites revealed in the structure had a random orientation and that more dendrites are observed in the middle of the ingots, while fewer – on their edges.

The mentioned above precipitates are built with zinc-rich phase containing slight amount of dissolved aluminum and copper (point 1, Fig. 2, Table. 1). Brighter areas at tile structure are richer with aluminum (points 2 and 3, Fig. 2, Table 1) when compared with the darker ones. Large, dark precipitates containing more aluminum than bright precipitates (points 4 and 1, Fig. 2, Table 1) were visible on the edges of bright precipitates. Further examinations have shown that dark and light areas are made of brighter and darker tiles, while in the dark areas the dark tiles are thicker. The darker tiles (point 1, Fig. 3, Table 2) contain more aluminum than the brighter tiles (point 2, Fig. 3, Table 2). In the structure, precipitates of α phase and eutectoid mixture are visible.

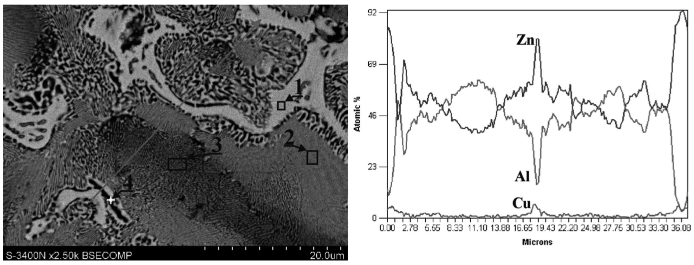

Fig. 2. Structure and linear distribution of Zn, Al and Cu of ZnAl22Cu3 alloy marked locations of carried out of local and linear X-ray analysis (Table 1)

TABLE 1
Chemical composition of the ZnAl22Cu3 alloy chosen micro-areas (Fig. 2)

	Zn [% mas.]	Al [% mas.]	Cu [% mas.]
point 1	94.9	1.1	4.0
point 2	75.1	23.1	1.7
point 3	60.8	37.5	1.7
point 4	60.4	37.6	2.0

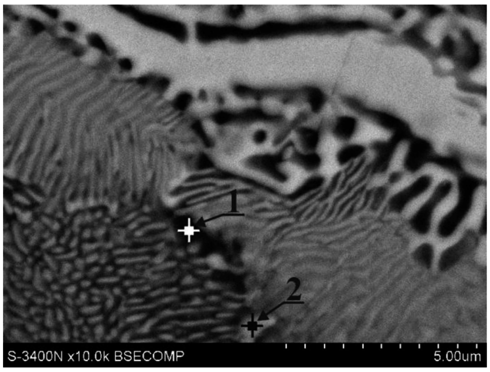

Fig. 3. Structure and linear distribution of Zn, Al and Cu of ZnAl22Cu3 alloy marked locations of carried out of local and linear X-ray analysis (Table 2)

TABLE 2
Chemical composition of the ZnAl22Cu3 alloy chosen micro-areas (Fig.3)

	Zn [% mas.]	Al [% mas.]	Cu [% mas.]
point 1	52.6	46.6	0.9
point 2	64.8	33.5	1.7

The alloy with Si addition is also characterized by a non – uniform, fine-grained structure (Fig. 4). The volume of bright precipitates was higher in the middle part of the ingot than on its edges. The presence of silicon precipitates was revealed (Fig. 5). The dark areas of tile structure occurred primarily near the dendrites. Darker areas of tile structure were higher than in case of ZnAl22Cu3 alloy. Silicon introduction accelerates crystallization (40s to 34s) and lowers the initial crystallization temperature (480°C to 469°C). Silicon addition slightly hastens eutectic transformation and lowers the transformation temperature (439°C to 432°C). During the solidification process the monotectoid transformation of the alloys with silicon addition starts later (303s → 370s) and proceeds at lower temperature (257°C → 247°C) [16]. The examinations carried out with EDS X-ray microanalyser have shown the presence of silicon precipitates in ZnAl22Cu3 alloy (point 3, Fig. 5, Table 3). These precipitates were usually visible near the bright precipitates but rarely within the bright areas of the *tile structure* (Fig. 5). Silicon precipitates were arranged unevenly. Greater amount of silicon precipitates was observed at the edges of the samples. In ZnAl22Cu3Si alloy silicon is released as the primary one at temperature of about 550°C before the real solidification of the α dendrites occur at the temperature range 460°C to 470°C [16]. Therefore, there is no possibility of subsequent improvement by means of heat treatment. On the edges of bright precipitates rich in zinc (point 1, Fig. 5, Table 3), spherical precipitates containing large amount of aluminum (point 2, Fig. 5, Table 3) were present. In case of ZnAl22Cu3Si alloy, chemical composition of the visible phase with bright precipitates and the chemical composition of the brighter areas of tile structure were similar to chemical composition of a base alloy. However, chemical composition of the darker areas of tile structure was different.

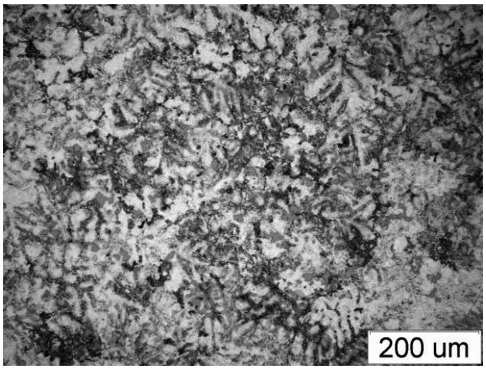

Fig. 4. Structure of ZnAl22Cu3Si alloy

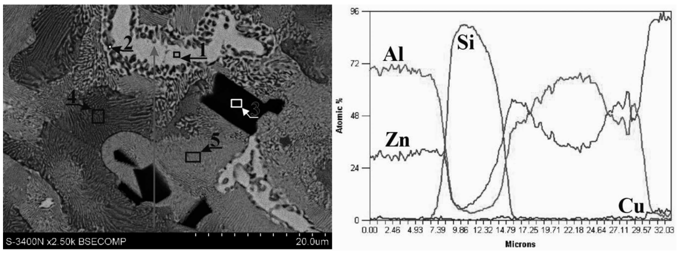

Fig. 5. Structure and linear distribution of Zn, Al and Cu of ZnAl22Cu3Si alloy marked locations of carried out of local and linear X-ray analysis Table 3)

TABLE 3

Chemical composition of the ZnAl22Cu3Si alloy chosen micro-areas (Fig.5)

	Zn [% mas.]	Al [% mas.]	Cu [% mas.]	Si [% mas.]
point 1	94.7	1.1	4.2	–
point 2	60.4	38.0	1.6	–
point 3	4.2	0.9	0.0	94.9
point 4	49.8	49.2	1.0	–
point 5	73.1	25.2	1.7	–

The addition of the RE does not bring considerable change of liquidus temperature. However, it causes a slight temperature increase of eutectic transformation (3°C), a start-delay of monotectoid transformation (370s → 537s) as well as significant temperature drop of this transformation (247°C →229°C) [16].

The addition of rare earth elements exerted a strong influence on the morphology of ZnAl22Cu3SiM alloy structure. In the structure of ZnAl22Cu3SiM alloy, silicon precipitates (point 4, Fig. 7, Table 4) were visible, both near bright precipitates and within bright and dark areas at tile structure, which was not observed in case of alloys without RE additive. The addition of RE did not effect the size of silicon precipitates. However, Si releases were more evenly arranged. Therefore, the presence of rare earth elements advantageously influences homogeneity of Zn22Al2CuSiM alloy. Similarly, as in the cases discussed above, the bright precipitates were rich in zinc and contained copper (point 1, Fig. 7, Table 4). In ZnAl22Cu3SiM alloy structure, bright and dark areas with tile structure richer in aluminum, and with more bright areas were visible (points 2 and 3 respectively), (Fig. 7, Table 4).

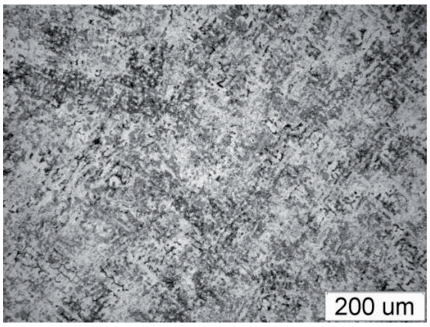

Fig. 6. Structure of ZnAl22Cu3SiM alloy

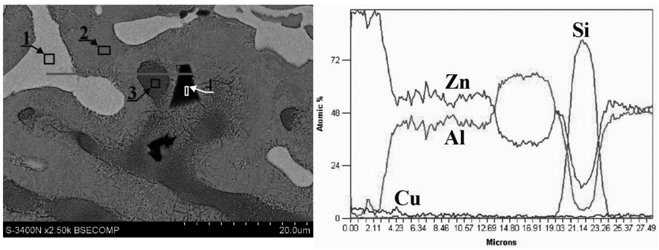

Fig. 7. Structure and linear distribution of Zn, Al and Cu of ZnAl22Cu3SiM alloy marked locations of carried out of local and linear X-ray analysis (Table 4)

TABLE 4

Chemical composition of the ZnAl22Cu3SiM alloy chosen micro-areas (Fig. 7)

	Zn [%mas.]	Al [%mas.]	Cu [%mas.]	Si [%mas.]
point 1	95.3	1.1	3.6	–
point 2	74.1	23.7	2.3	–
point 3	54.2	44.6	1.3	–
point 4	19.9	5.9	0.8	73.5

The carried out strength tests showed relatively high tensile strength of the tested alloys (Table 5). From the data collected in Table 5 it appears, that strength decreased together with silicon, the addition of which aimed at improving the tribological properties. The addition of RE caused further increase of the tensile strength values of the tested alloy to the level characteristic for ZnAl22Cu3 alloy. Simultaneously, the value of yield stress for the alloy with the addition of silicon and RE slightly increased in comparison with the one of ZnAl22Cu3 alloy (Table 5). The observed significant decrease of plastic properties is a disadvantageous feature of the tested alloys with addition of silicon or silicon and RE. The examined ZnAl22Cu3 alloy is characterized by good plasticity (Fig. 8, Table. 5), in contrast to the alloys with the addition of silicon or silicon and RE (Fig. 9, Table. 5). Hardness test proved that the lowest hardness was obtained for the ZnAl22Cu3 alloy, while the largest value was obtained for the alloy with silicon and RE addition. ZnAl22Cu3 and ZnAl22Cu3Si alloys featured different hardness in the middle part of the sample and on their edges. The hardness of the alloy with silicon and RE addition reached similar values regardless the measurement points location (Table 6). Large, bright precipitates and bright and dark areas with tile structure are present in the structure of the tested alloys. The tiles are visible as the brighter and darker areas due to their varied arrangement. The addition of silicon is primarily aimed at improving the tribological properties of the examined alloy, but it causes decrease of the alloy strength. The observed hardness differences between the center and the edge of the sample are the result of their heterogeneous structure. The silicon precipitates crystallize as the first during crystallization of the alloy, at much higher temperature than other phases – constituents of the alloy structure [15]. Heat treatment which would advantageously influence a more uniform arrangement of silicon precipitates is not possible. For the samples with the addition of silicon and modified with RE, hardness was uniform at cross-section of the sample. Additionally, the RE addition repels further decrease of tensile strength observed after silicon adding to the alloy. This can be the result of a more fine-grained structure. Thus, the performed modification of the alloy ZnAl22Cu3Si by RE addition is beneficial for improving its mechanical properties.

TABLE 5

Strength properties of ZnAl22Cu3 alloy

Alloy	$R_{0.2}$ [MPa]	R_m [MPa]	A_5 [%]	Z [%]
ZnAl22Cu3	345	370	16	36
ZnAl22Cu3Si	325	340	2	2.5
ZnAl22Cu3SiM	350	370	2.5	3.5

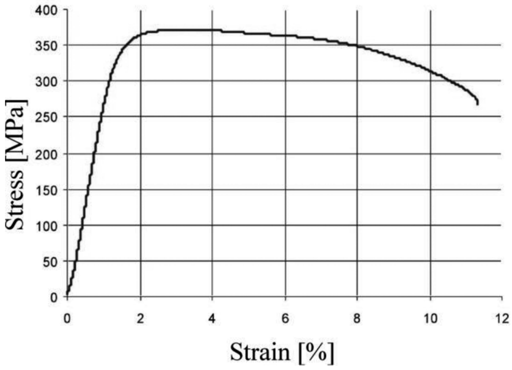

Fig. 8. ZnAl22Cu3 alloy tensile curve

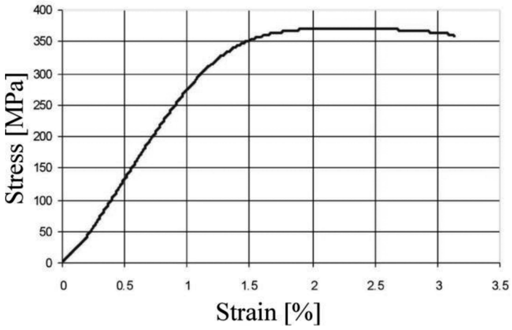

Fig. 9. ZnAl22Cu3SiM alloy tensile curve

TABLE 6

Brinell hardness of the ZnAl22Cu3 alloy

Alloy	Base		+Si		+Si+mischmetal	
	centre	boundary	centre	boundary	centre	boundary
Zn22Al2Cu	111	109	115	123	139	139

4. Conclusions

The carried out examinations allow to formulate the following conclusions:

- In the examined alloys the silicon is released in the form of pure crystals of non-uniform shape and cross section.
- Addition of RE causes structure refinement and leads to a more uniform arrangement of silicon.
- The introduction of silicon and RE causes a slight increase of tensile strength and hardness but simultaneous significant drop of plastic properties.
- The structure of ZnAl22Cu3 alloy is characterized with the tile structure in which bright precipitates of Cu and Al in Zn solid solution are present.

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