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INFLUENCE OF SOLUTION HEAT TREATMENT ON STRUCTURE AND MECHANICAL PROPERTIES OF ZnAl22Cu3 ALLOY

The influence of solution heat treatment at 385°C over 10 h with cooling in water on the structure, hardness and strength of the ZnAl22Cu3 eutectoid alloy is presented in the paper. The eutectoid ZnAl22Cu3 alloy is characterized by a dendritic structure. Dendrites are composed of a supersaturated solid solution of Al in Zn. In the interdendritic spaces a eutectoid mixture is present, with an absence of the ε ($CuZn_4$) phase. Solution heat treatment of the ZnAl22Cu3 alloy causes the occurrence of precipitates rich in Zn and Cu, possibly ε phase. Solution heat treatment at 385°C initially causes a significant decrease of the alloy hardness, although longer solution heat treatment causes a significant increase of the hardness as compared to the as-cast alloy.

Keywords: heat treatment, mechanical properties, structure, ZnAl22Cu3 alloy

1. Introduction

Zn-Al-Cu alloys are characterized by good castability, good tribological properties. They also have a lower, than bronze, level of energy needed to form a product. Compared to bronze Zn-Al-Cu alloys have a lower density. These alloys are used as an alternative material for bronze, cast iron and aluminium alloys in bearings and as a construction material [1-2].

The eutectoid ZnAl22Cu3 alloy in the as-cast condition is characterized by a dendritic structure (the composition is given in wt.% through the text). In the interdendritic spaces, eutectoid mixture and precipitates of the metastable ε phase occur. The eutectoid mixture initially forms two supersaturated solid solutions: a supersaturated solid solution rich in Al (α'_s phase) (visible as dark precipitates) and a supersaturated solid solution rich in zinc (β'_s phase - visible as a bright matrix). Moreover, during the crystallization η'_s phase and ε CuZn4 phase can be formed. Supersaturated solid solutions decompose, thus producing a structure consisting of tiles of different thickness [3-5]. The ε phase precipitates are characterized by greater hardness than that α and η phase precipitates (about 110-120 HB). During solidification, a phase rich in Al (α's phase) precipitates first forms the core of the dendrites. Then, around the α's phase growing the β'_s phase precipitates. The chemical composition between the α'_s and β'_s phases changes continuously. η'_s and ε phases are precipitated at the end of crystallization in the interdendritic areas. η'_s is a metastable phase, and can decompose at room temperatures [4].

In accordance with the phase equilibrium system, the structure of the Zn-Al-Cu alloys is affected by the following changes [4]:

$$\beta + T' = \alpha + \varepsilon \text{ at } 285°C \quad (1)$$

$$\beta + \varepsilon = \alpha + \eta \text{ at } 276°C \quad (2)$$

$$\alpha + \varepsilon = T' + \eta \text{ at } 268°C \quad (3)$$

where: β is Zn rich f.c.c. phase, α is Al rich f.c.c. phase, ε is h.c.p. phase CuZn4 and η is Zn rich h.c.p. phase, T' is a rhombohedral structure phase Zn10Al35Cu55 (in wt.%).

In the ZnAl22Cu3Si alloy subjected to solution heat treatment over 48 hours a typical dendritic structure composed of supersaturated solid solutions is observed consisting of: α'_s, β'_s η'_s, ε phase and silicon precipitates. The most important process that occurs during heat treatment of eutectoid Zn-Al-Cu alloys is the decomposition of α's and β's phases. Initially the metastable β'_s phase is decomposed in the reaction:

$$\beta'_s \rightarrow T' + \eta + \varepsilon \quad (4)$$

As a result of this reaction no continuous precipitates are visible in the grain boundaries. The ε metastable phase does not decompose and it is visible as bright precipitates. During the soaking at 350 °C the α phase is formed from the α'_T phase by creating a transitional phases rich in Zn: α''_M and α'_M and Al-rich phases α'' and α' due to spinoidal decomposition. Then occurs the transformation:

$$\alpha + \varepsilon \rightarrow T' + \eta \quad (5)$$

T' phase precipitates are created both in the interdendritic spaces and at grain boundaries. The transformations taking place during soaking at 350°C of the eutectoid Zn-Al-Cu alloy can be present as follows:

The β'_s phase decomposition leads to the formation of a thick tile structure. The α'_s phase decomposition leads to a formation of the fine tile structure [6-7]. The described transformation corresponds to the transformation of the phase

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equilibrium $\alpha + \varepsilon = T' + \eta$ occurring at 268°C. The literature also reported η phase transformation that occurs during slow cooling (with furnace). Phase η is converted into metastable phase η'_{FC}. (Index FC - slow cooling) [5, 7].

It should be pointed out that the structure refinement of these alloys can be also performed via inoculation process, which is widely discussed in literature, e.g. [8-11].

During the heat treatment of the eutectoid Zn-Al-Cu alloys a decrease of strength may occur. In the study by Babic et al. [12] the ZnAl27Cu2 alloy, supersaturated 370°C/5 h and 370°C/3 h, cooled in water was examined. The results (Table 1) show that the heat treatment caused a decrease in tensile strength and hardness of the alloy, and an increase in its yield strength.

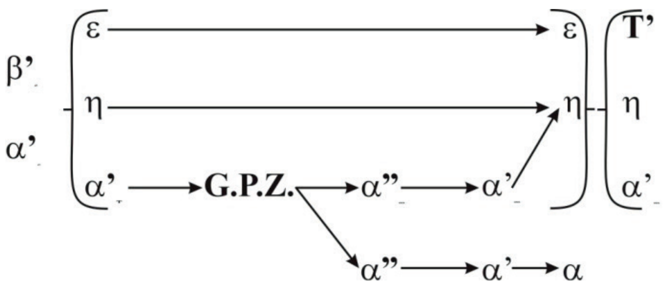

Fig. 1. Transformations occuring in ZnAl22Cu3 alloy during isothermal soaking at 350°C [4]

TABLE 1
Mechanical properties of the ZnAl27Cu2 alloy: as-cast and after supersaturation [12]

Alloy	Σ_{ult} [MPa]	A_5 [%]	Hardness [HB]
ZnAl27Cu2 as-cast	318	2.4	138
ZnAl27Cu2 370°C/3 h	301	5.2	121
ZnAl27Cu2 370°C/5 h	283	6.4	121

Strength reduction is explained here by a decrease present in the alloy's residual stress. The as-cast ZnAl27Cu2 alloy is characterized by irregular distribution of the structural components. Various mechanical and thermal properties of individual phases cause the formation of residual stresses in the alloy in micro areas. Heat treatment helps to dissolve, by diffusion, the non-equilibrium structure. In addition, the structure is fine-grained. The result is a decrease in stress. A reduction of hardness and strength, and increased elongation after heat treatment of the alloy also occurs. Reduction in the strength and hardness of the alloy by heat treatment is also suggested in other studies [13-14]. The main reason is the decomposition of the metastable T' phase. Heat treatment is one of the key ways to improve the strength properties of eutectoid ZnAl22Cu3 alloys. Literature data point to a possible loss of strength due to solution heat treatment of the alloy. Therefore, it is an important issue to determine how the strength, hardness and structure of the ZnAl22Cu3 alloy is influenced by its solution heat treatment.

2. The scope and method of examinations

The purpose of the examination was to determine the effect of solution heat treatment at a temperature of 385°C over 10 h with cooling in water on the structure, hardness and strength of the ZnAl22Cu3 eutectoid alloy. The subject of the examination was the ZnAl22Cu3 alloy. The alloy was melted in a VSG-02 type induction furnace from the Balzers company in a melting crucible made of Al_20_3 in an argon environment, under pressure inside the furnace heating chamber.

The scope of the examination included: determination of hardness using Brinell's method, and tensile strength examination. During the structural examinations an OLYMPUS GX51 optical microscope with a magnification range from x50-400 was used. During the performed examination a HITACHI S 3400N scanning electron microscope, supplied with an EDS X –ray spectrometer was also used. The tensile strength examinations were defined in terms of a static tensile test performed at room temperature. These examinations were carried out using the Zwick Z100 THW All round line strength test machine, and using round samples (dog-bone shape samples), according to PN–EN10002–1: 2004. Dimensions of the samples used for the tests are presented in Fig. 2.

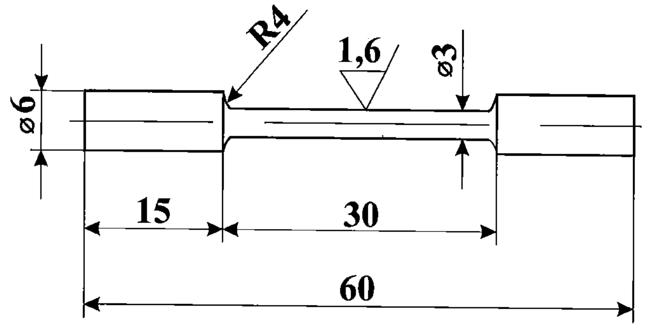

Fig. 2. Structure of ZnAl22Cu3 alloy, marked locations of carried out local X – ray analysis (Table 1)

3. Results of examination

Structural examinations carried out for the base alloy cooled in the graphite mould showed a fine-grained, dendritic structure [15]. The arrangement of dendrites was random. A greater number of dendrites was observed in the middle of the ingot, fewer on its edges regions. Dendrites were built of a zinc-rich phase containing a small amount of aluminium and copper (pt. 1, Fig. 3, Table 2). Dark precipitates rich in aluminium were also visible (pt. 4, Fig. 3, Table 2). In the interdendritic spaces bright and dark areas were visible. The brighter areas as compared to the darker are richer in zinc (pt. 2 and 3, Fig. 3, Table 2). Further examinations have shown that the dark and light areas in the interdendritic areas are constructed of brighter and darker tiles (eutectoid mixture), with thicker dark tiles in the darker areas. Darker tiles contain more aluminium than brighter ones [15].

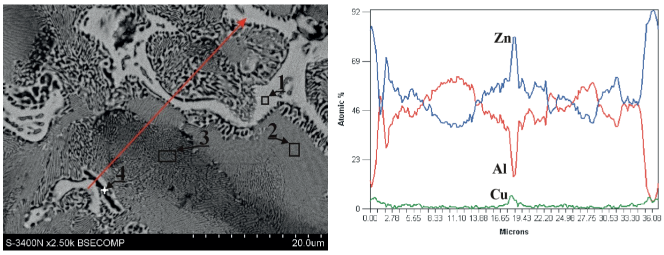

Fig. 3. Structure of ZnAl22Cu3 alloy after solution heat treatment 385°C/10 h, marked locations of carried out local X – ray analysis (Table 2)

TABLE 2

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

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

In the alloy after solution heat treatment at 385°C for 1 h the disappearance of dendrites rich in zinc was observed (pt. 1, Fig. 4, Table 3). In interdendritic spaces the bright and dark areas with diversified content of aluminium and zinc were also visible. These areas, however, were not built with tiles. The examinations revealed the disappearance of the dark areas richer in aluminium (pt. 3, Fig. 4, Table 3). In bright areas a minimal decrease in zinc content and a minimal increase in aluminium content occurred.

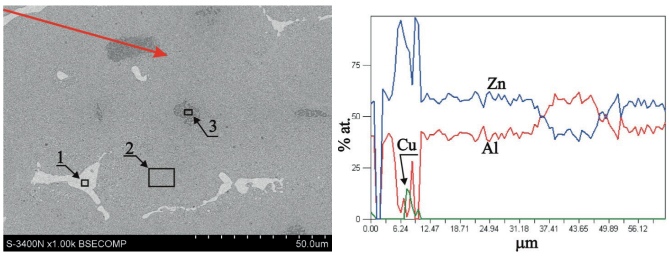

Fig. 4. Structure of ZnAl22Cu3 alloy after solution heat treatment 385°C/10 h, marked locations of carried out local X – ray analysis (Table 3)

TABLE 3

Chemical composition of the ZnAl22Cu3 alloy after solution heat treatment 385°C/10 h in chosen micro-areas (Fig. 2)

	Zn [wt. %]	Al [wt. %]	Cu [wt. %]
pt. 1	92.8	2.3	4.8
pt. 2	73.2	24.9	1.9
pt. 3	62.1	35.1	2.8

Longer solution heat treatment of the ZnAl22Cu3 alloy at 385°C over 10 h led to a further disappearance of dendrites and the complete disappearance of the dark areas in dendritic spaces. Bright precipitates remaining after dendrites were characterized by a lower content of zinc, with copper content significantly increased (pt. 1, Fig. 5, Table 4). Interdendritic space was built with a number of very fine brighter and darker precipitates. Brighter (pt. 3, Fig. 5, Table 4) were richer in zinc while the darker (pt. 4, Fig. 5, Table 4) were richer in aluminium. In interdendritic spaces larger, brighter areas richer in zinc were also visible.

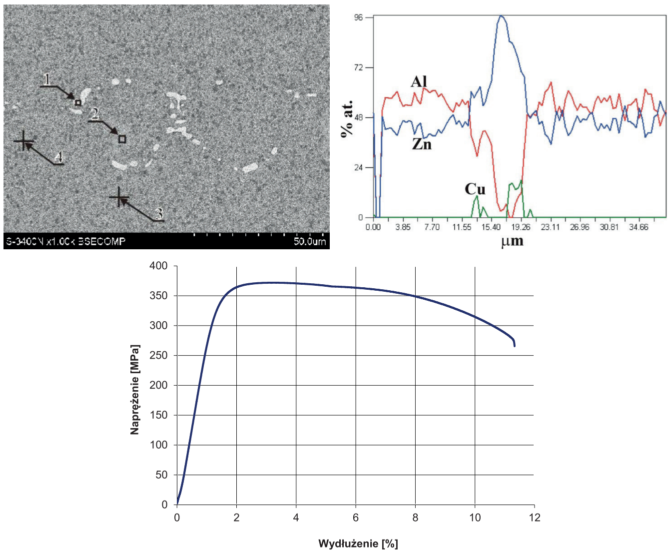

Fig. 5. ZnAl22Cu3 alloy tensile curve

TABLE 4

Chemical composition of the ZnAl22Cu3 alloy after solutioning 385°C/10 h in chosen micro-areas (Fig. 2)

	Zn [wt. %]	Al [wt. %]	Cu [wt. %]
pt. 1	81.9	3.8	14.4
pt. 2	70.0	27.0	3.0
pt. 3	57.4	40.0	2.6
pt. 4	47.4	48.3	4.3

Tensile strength tests of the alloys tested showed a relatively high strength, higher than of SAE 660 aluminium bronze with a similar range of applications as Zn-Al-Cu (Fig. 6-7, Table 5). For the SAE 660 alloy, the ultimate tensile strength reached $\sigma ult = 250$ MPa and the hardness reached 90 HB [16]. It was found that the solution heat treatment increases the strength of the tested alloy. However, it was accompanied by a significant decrease in yield and a decrease in elongation of samples (Table 5). Hardness tests showed that the tested as-cast alloy has a greater hardness than aluminium bronze (Table 6). Some differences in hardness between the centre and the edge of the samples were also found. Probably the edge of as – cast samples is softer than the core due to differences in the chemical composition between the core and the edge of the sample. The results of previous research [15] have shown than on the edge of the as - cast samples of ZnAl22Cu3 alloy occur larger number of soft phases rich in Zn. For samples after solution heat treatment over 1 h at 385°C a significant decrease in the hardness of the alloy was observed. However, longer solution heat treatment resulted in a significant increase in hardness in the solutioned samples compared to the as-cast samples (Table 6).

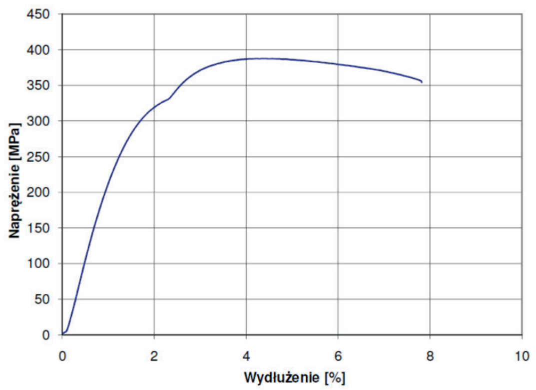

Fig. 6. ZnAl22Cu3 alloy tensile curve, solution heat treatment 385°C/10 h

TABLE 5
Mechanical properties of ZnAl22Cu3 alloy

	σ_{ult} [MPa]	σ_{YS} [MPa]	A_5 [%]
ZnAl22Cu3 as cast	370	345	11
ZnAl22Cu3 after solution heat treatment	387	274	8

TABLE 6
Hardness of as-cast and heat treated ZnAl22 and ZnAl22Cu3 alloy

Alloy	Hardness [HB]	
	centre	edge
ZnAl22Cu3 as - cast	111	109
ZnAl22Cu3 385°C/1 h	88	
ZnAl22Cu3 385°C/10 h	138	

4. Discussion of results

The results of the carried out examinations indicate that the dendrites contain Zn-rich phase: solutioned solid solution of Al in Zn and not as described in literature is rich in Al solutioned solid solution of Zn in Al. According to the literature data the rich in Al solutioned solid solution (Zn-Al) solidifies first, forming the core of dendrites. Obtained results point to another possible crystallization process. The Zn-rich phase forming the dendrites, due to a lower melting point than Al Zn, cannot be formed first. A detailed explanation of this problem requires further examination. Variations in the content of Al and Zn visible in the spaces have been attributed by other researchers to the presence of two phases - the supersaturated α's and β's solid solutions. The carried out examinations showed, however, that this is connected mainly, with a different thickness of aluminium tiles richer in aluminium, which are thicker in the darker areas. The tested alloy contains 3% by weight Cu. With this content, the ε phase should be created in the alloy according to literature data. However, this phase was not revealed in the as-cast alloy ZnAl22Cu3. The literature data show that the main factor influencing the strengthening of the alloy is a solid solution strengthening with copper. The obtained results showed that strong influence on the strengthening of the alloy has also the refinement of the structure. Solutioning mainly causes a loss of dendrites and the disappearance of the dark areas in the interdendritic areas richer in aluminium. The result is a significant decrease in hardness.

A significant increase in the copper content in the bright precipitates remaining after dendrites suggests the possibility to create the ε phase or T'. Since this phase is hard and brittle, its appearance in the alloy may be responsible for the increase in the hardness and brittleness of the alloy (decrease in yield point and elongation). The significant enrichment in aluminium and zinc depletion in the bright areas present in the interdendritic spaces and the presence in them of small precipitates could have an influence on the increase in hardness and strength. The obtained results of the ZnAl22Cu3 alloy strength indicate a higher strength than the tested ZnAl27Cu2 alloy (Table 1). Solution heat treatment of the alloy, otherwise than described in literature, caused an increase of the alloy strength. Connected to this, the decrease of the yield can be associated with the precipitation of a hard and brittle Zn-Cu phase, probably ε phase. The point of contraflexure visible on the stress-strain curve (Fig. 6) may be connected with the presence of bright precipitates with a considerably higher content of copper in the structure of the alloys subjected to solution heat treatment (point 1, Fig. 4, Table 4). Their presence may cause momentary blocking of the dislocations being formed during tension.

5. Conclusions

The carried out examinations allow the following conclusions:

1. Eutectoid ZnAl22Cu3 alloy is characterized by a dendritic structure. Dendrites are composed of a supersaturated solid solution of Al in the Zn. In interdendritic spaces an eutectoid mixture is present, whereas there is an absence of ε phase.
2. Solution heat treatment of ZnAl22Cu3 alloy initially causes the disappearance of dendrites and darker areas richer in aluminium. This is accompanied by the disappearance of the characteristic title structure of the interdendritic space.
3. Longer solution heat treatment of the ZnAl22Cu3 alloy causes the formation of precipitates rich in Zn and Cu in the structure, possibly ε phase. This leads to enrichment in aluminium and zinc precipitates in bright areas present in the interdendritic spaces and the formation of small precipitates.
4. Solution heat treatment of the ZnAl22Cu3 alloy causes an increase in the strength of the ZnAl22Cu3 alloy and a decrease in its plasticity.
5. ZnAl22Cu3 alloy after solution heat treatment at 385°C initially causes a significant decrease in the hardness of the alloy. However, longer solution heat treatment causes a significant increase in the hardness of the alloy as compared to the hardness of the as-cast alloy.

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