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AN INFLUENCE OF AGEING ON THE STRUCTURE, CORROSION RESISTANCE AND HARDNESS OF HIGH ALUMINUM ZnAl40Cu3 ALLOY

Zn-Al-Cu alloys are used primarily because of their tribological properties as an alternative material for bronze, cast iron and aluminum alloy bearings and as a construction material. Particularly interesting are high aluminum zinc alloys. Monoeutectic zinc and aluminum alloys are characterized by the highest hardness, tensile strength and wear resistance of all of the zinc alloys. A significant problem with the use of the Zn-Al-Cu alloys is their insufficient resistance to electrochemical corrosion. Properties of Zn-Al-Cu alloys can be improved by heat treatment. The purpose of examination was to determine the effect of heat treatment (aging at various temperatures) on the microstructure and corrosion resistance of the ZnAl40Cu3 alloy. The scope of the examination included: structural examinations, determination of hardness using Brinell's method and corrosion resistance examinations. Ageing at higher temperatures causes a creation of areas where is an eutectoid mixture. The study showed that ageing causes a decrease in hardness of ZnAl40Cu3 alloy. This decrease is even greater, when the temperature of ageing is lower. The studies have shown a significant influence of ageing on the corrosion resistance of the alloy ZnAl40Cu3. Maximum corrosion resistance were characterized by the sample after ageing at higher temperatures.

Keywords: Zn-Al-Cu alloys, heat treatment, corrosion resistance, hardness

1. Introduction

Zn-Al-Cu alloys are used as a material alternative of bronze, cast iron and aluminum alloys in bearings and as a structure material. Zn-Al-Cu type alloys are characterized by a number of advantageous properties that can include low fusion temperature, good castability, high strength and hardness, good fatigue strength, low density, low friction factor, low wear rate speed and low production cost. The disadvantages of these alloys could include low creep strength, low dimension durability during heat treatment and insufficient corrosion resistance [1, 2]. Monoeutectoid zinc alloys (high aluminium zinc alloys) are characterized by the highest hardness, tensile strength and wear resistance [3]. These alloys are used because of their tribological properties as an alternative material for bronze and aluminium alloys.

Properties of Zn-Al alloy can be changed among others by modifying the chemical composition, changing the terms of crystallization and heat treatment. Chemical composition of Zn-Al alloys was modified with the addition of 2-3% copper [4]. The base alloying element is aluminum [5]. The aluminum additive could increases the castability, grain size reduction, and improves the mechanical properties of these alloys [6]. Addition of the copper could improve the mechanical and tribological properties, increases the inclination to spontaneously age and increases the density [5, 6]. Exceeding a Cu content of 2% decreases the strength and wear resistance.

The structure of the ZnAl40 alloy in the cast condition forms dendrites in the Al + α phase and Zn + η phase -rich in interdendritic spaces. The addition of copper influences the formation of intermetallic ε phases (CuZn4) in the interdendritic areas. It can be also created a copper-containing T' phase ($Zn_{10}Al_{35}Cu_{55}$) which is crystallizing in the rhombohedral system. The ε phase is formed in alloys containing at least 1 (w/w)% of copper and crystallizes in the hexagonal system with a high packing density (hcp). The α phase crystallizes in a fcc structure whereas the η phase, however, crystallizes similarly like the ε phase in a hexagonal dense packing (hcp). The number and size of the ε phase precipitates increases with the copper content in the alloy [7, 8]. In the interdendritic spaces a mixture of α + η is present. Thus, the microstructure of the ZnAl40Cu3 alloy consists of dendrites rich in the Al-rich α phase, a mixture of eutectoid α + η phase and precipitates rich in copper of T' phase and ε present in the interdendritic spaces [8-10].

The monoeutectoid structure Zn-Al-Cu alloys largely depends on the crystallization conditions, particularly the cooling rate. The increase in cooling rate reduces the size of dendrites. Reducing the size of dendrites in turn affects the increase in hardness of the alloy [9]. The grain size can also be reduced by the addition of rare earth elements (REE). This addition results in the formation of additional nucleuses, which has an impact on the grain refinement of the alloy in cast condition. Rare earth elements has a beneficial effect on the corrosion resistance of Zn-Al-Cu alloy. The forming part of the rare earth elements, cerium is a very effective inhibitor of corrosion in seawater [11, 12]. In contact with H_2O, cerium forms hydroxide $Ce(OH)_3$. In an environment containing Cl^- ions on the surface of an alloy of Zn–Al–Cu with the addition of Ce, a layer is formed which consists of $Ce(OH)_3$, Ce_2O_3, and small quantities of $Zn(OH)_2$ and ZnO. The resulting

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film effectively inhibits any further corrosion processes. This addition also causes the formation of additional nucleation, which has an impact on grain refinement of the alloy in cast condition. Modification of chemical composition of the monoeutectoid ZnAl40Cu3 alloy should therefore have a positive impact on the hardness and strength of the alloy.

Another important factor influencing on the properties of the Zn-Al-Cu alloys is heat treatment. The literature data concerning on the effect of heat treatment on the strength of the Zn-Al-Cu alloys are different. The results from the [9] study indicate, that the solutionizing and aging the ZnAl40Cu2Si2 alloy improve the tensile strength. Different results were obtained in the study [13]. The study showed that the solutionizing and the aging of the ZnAl28Cu2 alloy cause a decrease in tensile strength. There is little information available in literature on the changes occurring during heat treatment on structure and corrosion resistance of the Zn-Al-Cu alloys with 40% mass. of aluminium.

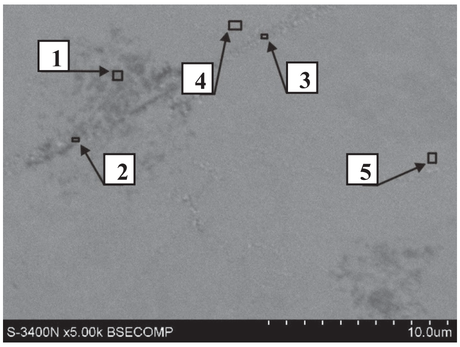
2. Experimental methods

The purpose of examination was to determine the effect of heat treatment (aging at various temperatures) on the microstructure and corrosion resistance of the ZnAl40Cu3 alloy. Alloy was melted in a VSG-02 type, induction furnace from the Balzers company in a melting crucible made of Al_2O_3 in argon environment, under pressure inside the furnace heating chamber. The following samples have been studied: after solutionizing at 385°C/24h and after solutionizing (385°C/24h) and aging: 125°C/24h, 150°C/10 and 24h, 175°C/10 and 24h.

The scope of the examination included: structural examinations, determination of hardness using Brinell's method and corrosion resistance examinations. During the structural examinations HITACHI S 3400N scanning electron microscope supplied with a EDS X-ray spectrometer was used. Corrosion tests were carried out in a solution of "acid rain", pH = 3.5 (molar ratio H_2SO_4 : HNO_3 : HCl as 1:0.3:0.17). Potentiodynamic curve polarization measurements of samples were carried out in the range including cathode and anode potentials, starting from the potential of the cathodic polarization. Rate of change of potential was 10 mV/min. Corrosion potential was determined based on the time - Open Circuid Potential (OCP) curves (the minimum test time was 60 minutes). Corrosion current density was determined from the value of the polarization resistance. The potentiostatic measurements recorded changes in current at potentials samples of 100mV more anodic (less negative) than the corrosion potential E_{corr}. The tests time was 48 hours.

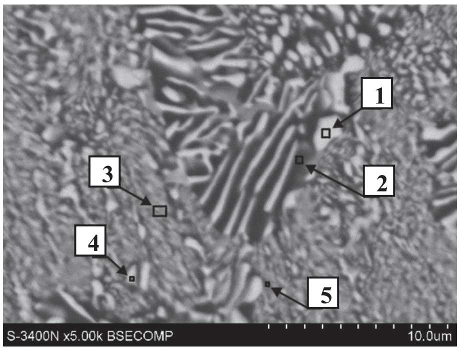
3. Results and discussion

The high zinc - aluminium alloys are characterized by a dendritic structure with CuZn5 phase precipitates visible inside the dendrites. The dendrites are rich in Zn, the interdendritic regions are rich in Al. The structure of the alloy, depending on the cooling conditions, differs depending on the morphology of the precipitated phases. Structural examination of the ZnAl40Cu3 alloy supersaturated at the temperature of 385°C during 24 hours have shown that prolonged solutionizing at the temperature of 385°C causes a complete decay of dendrites (Fig. 1). In the structure are present single areas with increased content of Al relative to the matrix content (pt 1 and 2, Fig. 1). In the matrix, regardless of test location, were 54-55% at. Al and 42 -44% at. Zn (pts 3-5, Fig. 1). In the structure of samples aged the temperature of 175°C during 24 hours was observed local occurrence of the eutectoid mixture. The mixture consisted of dark and thick, rich in Al plates (pt 2, Fig. 2) and Zn-rich matrix (pt 1, Fig. 2). Outside of these areas contents of Zn and Al was less diversified (pt 3, Fig. 2). Inside the zinc-rich matrix (pt 4, Fig. 2) occurred very small, rich in Al precipitates (pt 5, Fig. 2). A similar structure as the samples aged at 175°C characterized by the sample aged at 150°C. However areas of eutectoid mixture occurrence, were smaller. The samples aged during 10h were characterized by a significantly lower content of Zn in a matrix (pt 1, Fig. 3) and a much lower content of Al in the dark plates (pt 2, Fig. 3). Outside of areas with occurred eutectoid mixture slightly increased content of copper and zinc, decreased - aluminum (pt 3, Fig. 3). Longer ageing at 150°C/24h again caused a significant increase in the Al content in the plates (pt 2, Fig. 4) and in the matrix (pt 1, Fig. 4). However longer ageing did not cause significant change of chemical composition in the areas located outside of the eutectoid mixture (pt 3, Fig. 4). The samples after ageing at 125°C were characterized by a different structure. In the structure were present very small precipitates. The size of the precipitates was too small to determine their chemical composition using X-ray microanalysis. The average content of Al in the location of their occurrence was significantly higher than in the similar areas of the aged samples at higher temperatures (pt 4, Fig. 5). In the alloy structure were visible areas in which occurred greater precipitates. Differences in chemical composition between particular precipitates, were however very small (pts 1-3, Fig. 5).



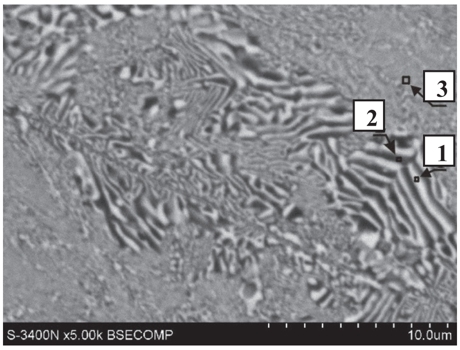
	Zn at. %	Al at. %	Cu at. %
pt. 1	37.3	60.9	1.9
pt. 2	41.2	57.1	1.8
pt. 3	42.3	55.5	2.3
pt. 4	44.1	53.6	2.2
pt. 5	44.0	54.3	1.8

Fig. 1. Structure of the ZnAl40Cu3 alloy after solutionizing 385°C/24h



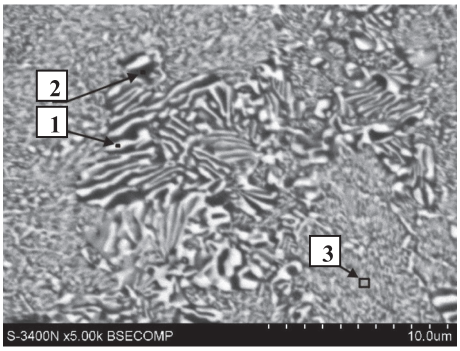
	Zn at. %	Al at. %	Cu at. %
pt. 1	75.2	24.8	–
pt. 2	21.0	74.5	4.5
pt. 3	42.3	56.2	1.5
pt. 4	55.5	43.0	1.5
pt. 5	37.3	60.2	2.5

Fig. 2. Structure of the ZnAl40Cu3 alloy after solutionizing 385°C/24h and aging 175°C/24h



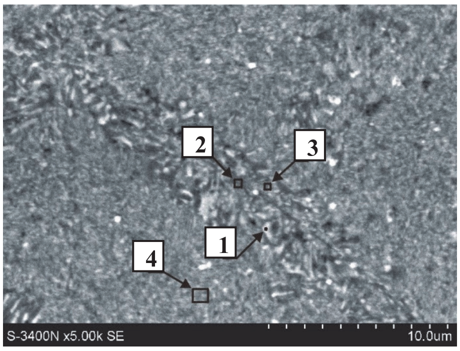
	Zn at. %	Al at. %	Cu at. %
pt. 1	52.2	47.2	–
pt. 2	38.8	59.0	2.2
pt. 3	44.3	52.9	2.7

Fig. 3. Structure of the ZnAl40Cu3 alloy after solutionizing 385°C/24h and aging 150°C/10h



	Zn at. %	Al at. %	Cu at. %
pt. 1	62.4	33.5	4.1
pt. 2	23.2	75.6	1.2
pt. 3	46.2	51.0	2.8

Fig. 4. Structure of the ZnAl40Cu3 alloy after solutionizing 385°C/24h and aging 150°C/24h



	Zn at. %	Al at. %	Cu at. %
pt. 1	35.2	62.8	2.0
pt. 2	33.5	63.8	2.7
pt. 3	27.5	67.2	5.3
pt. 4	36.8	61.2	2.0

Fig. 5. Structure of the ZnAl40Cu3 alloy after solutionizing 385°C/24h and aging 125°C/24h

As a result of hardness test, it was found that the as-cast samples have a higher hardness on the edges than in the center of the samples. The significant increase of hardness was obtained for samples after solutionizing. Ageing caused the decrease of hardness. The hardness was similar to the hardness of the "as-cast" samples only for the samples after ageing at 175°C during 24 h (Table 1).

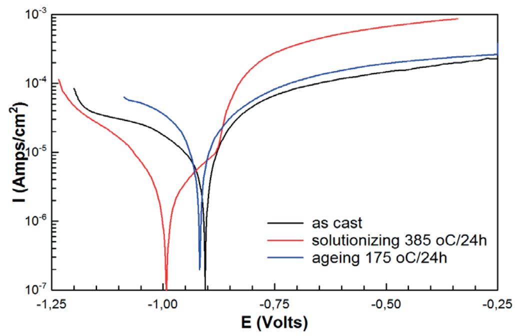
The results showed that the highest hardness are characterized by sample after solution heat treatment. Ageing

TABLE 1

Hardness of the ZnAl40Cu3 alloy

	base alloy	385°C/24h	385°C/24h +175°C/24h	385°C/24h +150°C/10h	385°C/24h +150°C/24h	385°C/24h +125°C/24h
Hardness, HB	105-114	164	110	100	96	95

caused a significant decrease in the hardness. The decrease of ageing temperature caused a decrease in the hardness. The deciding effect on the hardness is therefore strengthening of the solutions. The phases diffused due to solutionizing was very small and probably soft. Their presence in the structure does not improve hardness. However, their separation is related to the weakening of solution-strengthening effect, which reduces the hardness.



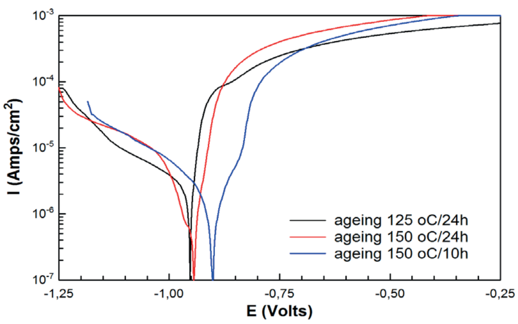


Fig. 6. Potentiodynamic curves of ZnAl40Cu3 alloy after heat treatment in „acid rain"

As a result of carried out potentiodynamic tests was found that all tested samples have a high negative value of the corrosion potential (Table 2). The samples after ageing at 150°C/24h was characterized by a lower value of corrosion current density than the base alloy. The samples after ageing at 150°C/24h was characterized by a higher value of corrosion current density. On potentiodynamic curves of tested samples, there was no occurrence of the passive range (Fig. 6). The increase in the value of the potential caused continuous increase in the current density. On the potentiodynamic curve the lowest current density values were observed for samples after solutionizing and ageing 385°C/24h +175°C/24h, the highest for alloys after solutionizing and ageing 385°C/24h +150°C/24h (Fig. 6, Table 2). Potentiostatic tests showed an initial significant decrease in the value of current density with time. Potentiostatic tests have shown that the value of current density of the tested alloys decreases and then reaches a constant value. The highest values of current density was observed for samples after solutionizing and ageing 385°C/24h + 125°C/24h. The lowest values of current density was observed for samples after solutionizing and ageing 385°C/24h + 175°C/24h (Table 3).

In the non - stationary conditions the highest corrosion resistance was characterized by samples after solutionizing. However, this increase of corrosion resistance is unstable. Zn-Al-Cu alloys have a very high tendency for spontaneous ageing. Among samples after solutionizing and ageing highest resistance to corrosion is characterized by the samples after ageing at 175°C. Decreasing the temperature of ageing caused decrease in corrosion resistance.

Good corrosion resistance of the samples after solutionizing is likely the result of homogenization of the structure. Ageing reduces the homogeneity of the structure. When the structure of the material is more fine-grained, the number of the grain boundaries is higher. The grain boundaries are a place with high internal energy, which determines their

TABLE 2

Results of potentiodynamic examinations

	E_{corr} mV	I_{corr} $\times 10^{-6}$ A/cm²	R_p Ohm/cm²	I $\times 10^{-6}$ A/cm² E_{corr}+100mV	I $\times 10^{-6}$ A/cm² E_{corr}+300mV	I $\times 10^{-6}$ A/cm² E_{corr}+500mV
base alloy	-904	8.2	3181	43	115	175
385°C/24h	-940	2.9	8995	8.4	376	675
385°C/24h+175°C/24h	-890	12.0	2170	46	146	220
385°C/24h+150°C/10h	-890	2,0	12966	78	509	901
385°C/24h+150°C/24h	-955	2,3	11383	188	615	960
385°C/24h+125°C/24h	-945	8.6	3025	100	364	581

TABLE 3

Results of potentiostatic examinations

	Current density after time, 10^{-6} A/cm²															
	3h	6h	9h	12h	15h	18h	21h	24h	27h	30h	33h	36h	39h	42h	45h	48h
base alloy	19	27	36	42	46	49	49	49	45	42	36	30	26	22	22	23
385°C/24h	5.1	0.5	-3.1	-5.6	-8.0	-9.7	-11.7	-12.0	-10.6	-10.2	-10.9	-10.2	-9.7	-9.2	-9.3	-9.0
385°C/24h+175°C/24h	13.0	11.3	13.5	17.8	20.4	22.2	23.5	23.3	22.3	21.2	18.9	17.8	16.0	14.8	15.2	14.9
385°C/24h+150°C/10h	22.2	26.6	31.8	36.0	37.3	34.7	31.7	28.8	21.5	20.5	21.1	21.6	21.7	21.9	22.7	22.9
385°C/24h+150°C/24h	18.1	25.2	34.0	39.7	43.4	45.4	45.1	45.1	43.9	38.7	31.7	23.2	19.0	20.5	20.4	21.3
385°C/24h+125°C/24h	112	117	118	59	54	53	56	57	53	50	50	50	48	50	51	49

lower resistance to influence of corrosive environments. The energy needed to remove an atom depends on its position in the crystal lattice. It is easier to remove atoms characterized by a smaller number of adjacent atoms (the lower number of coordination), and thus situated on the edges of the crystallites and in the inter-crystalline areas. In these places the number of the grain boundaries is much smaller than behind them. Less is therefore active places for corrosive processes.

4. Conclusions

The carried out examinations allow to formulate the following conclusions:

- The ageing of the high aluminum ZnAl40Cu3 alloy leads to formation of a fine grain structure (large number of very small precipitates). In the microstructure of samples after ageing at temperatures of 175°C and 150°C are also present areas with eutectoid mixture. Plates forming a mixture are characterized by a high plate thickness.
- Solutionizing of the ZnAl40Cu3 alloy at a temperature of 385°C during 24 h causes increase the hardness of the alloy and improves corrosion resistance.
- Ageing causes a reduction in hardness and corrosion resistance of the ZnAl40Cu3 alloy (compared to samples after solutionizing).
- Among the samples after solutionizing and ageing the highest hardness and corrosion resistance reached the samples after ageing at 175°C.
- Decreasing temperature of ageing causes a decrease in hardness and corrosion resistance of the ZnAl40Cu3 alloy.

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