

INFLUENCE OF HEAT TREATMENT ON THE WEAR RESISTANCE OF THE ZnAl40Cu1.5Ti1.5 ALLOY

Zn-Al-Cu alloys are predominantly used due to their tribological properties. One of the crucial issues related to the use of Zn-Al alloys is their dimensional instability. Partial replacement of copper with titanium greatly contributes to the reduction of the dimensional instability issue. The study involved the ZnAl40Cu1.5Ti1.5 alloy. In this work, microstructure and wear properties of ZnAl40Cu1.5Ti1.5 alloy were studied in both as-cast and heat treated conditions. The heat treatment was performed by solution treatment at a temperature of 385°C for 24 hours, quenching in cold water and artificial aging at 125°C for 3 hours. The hardness tests enabled to specify the optimum ageing time span, which amounts to 3 hours. Wear tests indicated that the ZnAl40Cu1.5Ti1.5 alloy is characterized with high wear resistance. It was also observed that the applied heat treatment increases the wear resistance of the experimental alloy.

Keywords: Zn-Al-Cu-Ti alloys, wear resistance, hardness, structure

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 good castability, high strength and hardness, good fatigue strength, low density, low friction factor, low wear rate speed and low production cost. Monotectoid zinc alloys (high aluminium zinc alloys) are characterized by the highest hardness, tensile strength and wear resistance [1,2]. In the majority of cases, lower value of the friction coefficient is observed in Zn-Al-Cu alloys than in bronze. Zn-Al-Cu alloys are highly resistant to seizure. Seizure resistance increases along with the aluminum content in the alloy. Wear resistance increases along with the Al content in the alloy. Thus, the alloys are characterized with a significantly greater wear resistance than hyper-eutectoid or eutectoid alloys [3,4].

Properties of Zn-Al alloy can be changed among others by modifying the chemical composition, changing the terms of crystallization and heat treatment. Aluminium is the primary alloying element in Zn-Al alloys. The addition of aluminium influences on improvement of the alloy cast ability. The addition of aluminium and small amounts of copper enables to obtain an optimal set of mechanical properties. The higher content of aluminium causes that high aluminium alloys are characterized by lower density and a higher resistance to electrochemical corrosion than other Zn-Al-Cu alloy. Copper is another major alloying element used to improve the mechanical properties of Al-Zn alloys. When the Cu content of the ZnAl40Cu alloys ex-

ceeds 2%, their tensile strength and wear resistance decrease due to formation of relatively hard and brittle ϵ (CuZn₄) phase [5,6].

Crystallization of the high-aluminium Zn-Al-Cu alloys leads to the formation of dendrites rich in zinc-containing copper in an amount much higher than the average content of the other structural components. A dual phase $\alpha + \beta$ structure is formed. Copper forms a solid solution with zinc from which the dendrites are built. Copper is, however, also present in minimal quantities in the eutectoid mixture [1-10].

An important problem associated with the use of Zn-Al alloy is low creep strength and low dimensional stability during heat treatment. The problem of linear dimensional changes of castings can be reduced among others, by partial or complete substitution of copper by silicon. Publication [11] indicate that advantageous results can also be obtained by partial copper replacement with titanium.

The most basic way of increasing tribological properties in Zn-Al-Cu alloys is the addition of silicon. The size of silicon particles is of great importance. It cannot be too small or too big, as this could significantly accelerate the wear of the particles. The particles that are too small may be ripped out of the alloy's surface during the wearing process; too big particles may break into smaller pieces. The addition of silicon may positively influence other properties of the alloy, for example its corrosion resistance [4,7-10].

Another way of improving the properties of alloys may be found in partial replacement of copper with titanium. Titanium is used in smaller amounts as a modifier in order to fragment the structure. When introduced in greater amounts, titanium contrib-

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utes to reduction or complete elimination of dimensional instability. There are Precipitates of the Ti phase $(Al, Zn)_3$ present in the structure of the ZnAl26 alloy, where copper was completely or partially replaced with titanium. Precipitate of this phase have a role of the moving phase and positively influence tribological properties of the alloy. After solution treatment, there are no changes in the solid phase observed that could be the cause of dimensional instability of Zn-Al-Cu alloys [11].

Another important factor influencing tribological properties of Zn-Al-Cu alloys is heat treatment. In a previous study hyper-eutectoid ZnAl27Cu2 was tested, with solution treatment of 370°C/3h/water and 370°C/5h/water [12]. It was observed that the solution treatment of the present alloy lowers the friction coefficient. Different results were obtained in the study [13]. The monotectoid ZnAl40Cu2Si2 alloy in as-cast state was tested as well as the alloy subjected to solution treatment 375°C/24h with the subsequent artificial ageing 150°C/2h. The results of the study pointed out that both, solution treatment and ageing, cause a relatively low increase of the friction coefficient when compared with the samples in as-cast state. These results are not in full accordance with the results of the solution treatment and ageing influence over resistance and hardness of alloys. Some of the works point out that solution treatment and ageing may cause the decrease in resistance and hardness of monotectoidal Zn-Al-Cu alloys. The aim of the present work was to evaluate the influence of quench-ageing treatment on the wear resistance of ZnAl40Cu1.5Ti1.5 alloy.

2. The scope and methodology of the research

Subject of examination was Zn – 40 wt % Al – 1,5 wt % Cu – 1,5 wt % Ti 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 alloy was examined in both as-cast and heat treated conditions. More information about the techniques of casting of Zn-Al-Cu-Ti alloys can be found in the work [14]. Part of the samples were subjected to a heat treatment: solution treatment (385°C/24h) and artificial ageing (125°C). Parameters of solution treatment was selected based on previous studies and literature analysis. The optimum ageing time was calculated on the basis of hardness test. The scope of the tests included structural tests and hardness tests, the wear and roughness tests. The HITACHI S 3400N scanning electron microscope, which cooperates with the EDS X-ray spectrometer, was used in the structural tests. The Brinell hardness tests were

conducted for a f 5 ball with the load of 250 kG. Criteria of the selection of wear test conditions (loading, sliding speed, sliding distance) were selected based on the analysis of researches, in which topic of research were a wear resistance of similar Zn-Al-Cu alloys [1,2,5]. The tribological tests of Zn-Al-Cu alloys were conducted with the following parameters: rotational speed of 900 rpm, testing time: 30 min (which corresponds to the sliding distance of 1700m), load: 10N, contact temperature: 21°C. The wear test of the Zn-Al-Cu-Ti alloys was conducted for the sliding distance of 1700, 3400, 5100 and 6800 m. Schematic diagram of wear tester are presented in Fig. 1. Because the testing device does not ensure recording all the parameters, as an indicator of wear resistance was assumed weight loss. Every time before and after the tests, the samples were weighted on the RADWAG WAA 100/C/1 electronic balance (the measurement accuracy up to $\pm 0,0001$ g). Subsequently, the tests of the surface condition for the Zn-Al-Cu alloys were conducted with the use of the scanning electron microscope. For Zn-Al-Cu-Ti alloys, after wear tests, roughness profiles were measured. There was a 3D surface image made for every tested sample, as well as 2d isometric image of a surface, roughness distribution on selected sections, roughness profiles and waviness of the selected profile.

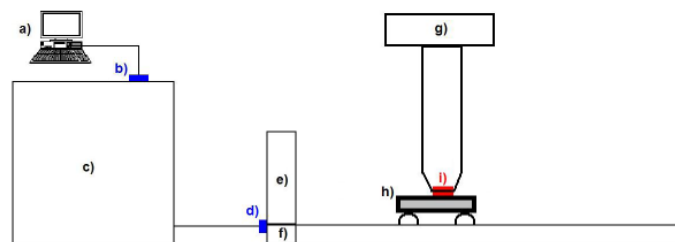


Fig. 1. Construction scheme of tribological wear tester: a) PC Computer with Microsoft Windows OS, b) serial communication interface USB, c) control unit, d) serial communication interface RS232, e) linear unit, f) step motor, g) load on sample, h) carriage with fixed sample

3. Test results

The hardness test results obtained from ZnAl40Cu1.5Ti1.5 alloy are presented in (Table 1 and Fig. 2). The results show that partial replacement of copper with titanium increase hardness in comparison with the ZnAl40Cu3 alloy, hardness of which in as-cast state for cooling in graphite form amounts to the maximum of 111 HB [9]. The results indicate also that heat treatment of the alloy contributes to the increase of its hardness in comparison to alloy as-cast. The aging at temperatures of 175°C and 150°C causes a decrease in hardness in comparison to the alloy after

TABLE 1

Brinell hardness values of the as-cast and heat treated samples of ZnAl40Cu1.5Ti1.5 alloy

Ageing temperature °C	as-cast	Solution treatment 385°C/24h	Ageing time					
			1h	3h	5h	7h	10h	24h
175	134 (2,8)	150 (1,3)	136 (1,2)	131 (1,9)	124 (1,7)	120 (2,2)	115 (1,5)	112 (1,5)
150			143 (4,2)	140 (1,8)	136 (2,0)	133 (2,1)	130 (4,6)	119 (9,8)
125			152 (2,0)	165 (1,7)	147 (1,6)	145 (3,2)	143 (5,2)	130 (5,5)

solution treatment (385°C/24h). Different results were obtained for the alloy after artificial aging at 125°C. At first, up to 3 hours of aging, can be observed hardness increase in comparison to the alloy subjected only solution treatment (Fig. 2). The best results can be obtained, in the case of solution treatment and ageing, in the following temperature and time: 385°C/24h + 125°C/3h.

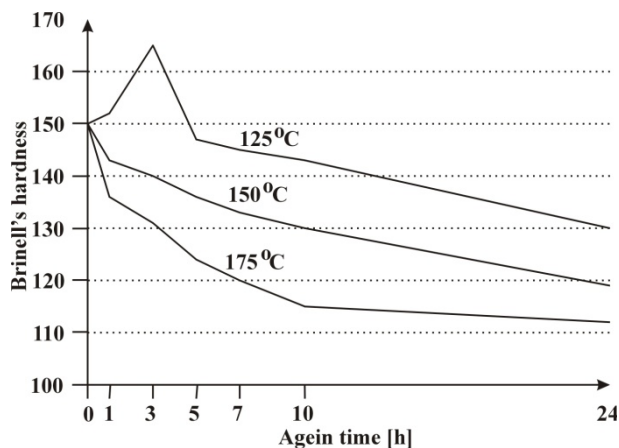


Fig. 2. Hardness versus aging time curves of ZnAl40Cu1.5Ti1.5 alloy at three different temperatures

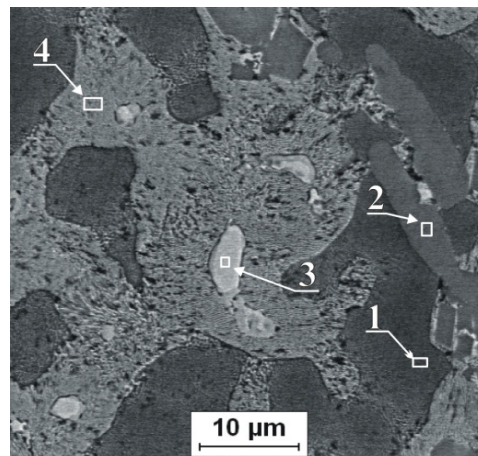
In its as-cast state, ZnAl40Cu1.5Ti1.5 alloy is characterized with a fine-grained dendritic structure (Fig. 2). Precipitates are visible inside of the dendrites, the presence of the phase rich in Cu and Zn is noted – it is, most likely, the phase ϵ -(CuZn₄) (pt 3, Fig. 2). The dendrites are created through the phase with significant amount of Zn and Al (pt 4, Fig. 2). There is a phase rich in aluminum and containing Zn to be found in the interdendritic spaces (pt 1, Fig. 2). Precipitates present in interdendritic spaces are rich in titanium and aluminum. They also contain Zn (pt 2, Fig. 2). The alloy, after heat treatment, is characterized with a different structure. There are no dendrites or Precipitates rich in Zn and Cu. There is a number of Precipitates rich in titanium and aluminium visible in the structure (pt 4, Fig. 3), as well as Precipitates rich in Al and Zn (pt. 1, Fig. 2). Apart from the divisions having Ti in their structure, there are also spaces of higher content of Al (pt. 2 and 3, Fig. 3).

The results of the study of wear resistance of the ZnAl40Cu1.5Ti1.5 alloys are presented in (Table 2 and Fig. 4). The alloy tested is characterized with low mass loss. The length increase of the sliding distance results in the mass loss. The highest wear resistance can be found in an alloy subjected to heat treatment, which also has the lowest mass loss.

TABLE 2

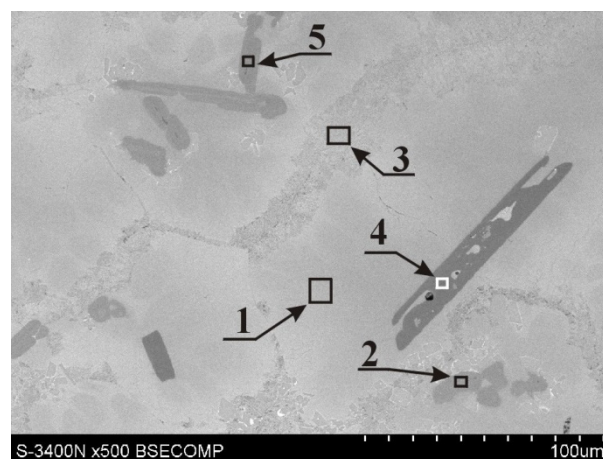
The weight loss of ZnAl40Cu1.5Ti1.5 alloy depending on the route of friction

Alloy	The weight loss for the route of friction [mg]			
	1700 m	3400 m	5100 m	6800 m
ZnAl40Cu1,5Ti1,5/ as-cast	11.4	16.9	29.4	38.2
ZnAl40Cu1,5Ti1,5/ after HT	4.0	14.9	22.1	27.7



	Zn at. %	Al at. %	Cu at. %	Ti at. %
pt 1	19.4	80.6	—	—
pt 2	15.5	60.2	—	24.3
pt 3	81.5	3.6	14.9	—
pt 4	55.2	42.1	2.7	—

Fig. 3. As-cast microstructure of ZnAl40Cu1.5Ti1.5 alloy



	Zn at. %	Al at. %	Cu at. %	Ti at. %
pt 1	48.0	49.7	2.3	—
pt 2	41.0	59.0	—	—
pt 3	39.8	58.5	1.7	—
pt 4	6.2	62.0	—	31.8
pt 5	18.7	52.6	—	28.7

Fig. 4. Microstructure of ZnAl40Cu1.5Ti1.5 alloy after solution treatment and aging 385°C/24h+125°C/3h

The analysis of the wear traces after the tests of wear resistance point out to different ways in which the ZnAl40Cu1.5Ti1.5 alloy is used in as-cast state and after undergoing heat treatment. In the case of the alloy in as-cast state, there are a few pits created (Fig. 5 – 1700 m). Along with the increase in the sliding distance, their depth and amount increases (Fig.5 – 3400 m).

Subsequently, the next bigger pit is created (Fig. 5 – 5100 m); the continuous increase of the sliding distance results in the creation of another pit (Fig. 5 – 6800 m). Along with the increase of the sliding distance, the wear depth increases, up until the sliding distance reaches 5100 m (Fig. 6). Further increase of the sliding distance up to 6800 m does not cause such a significant increase in the wear depth (Fig. 6). The use of the alloy after heat treatment has, initially, the same course as the alloy in as-cast state. A few pits are formed (Fig. 7 – 1700 m). These pits are, however, very quickly combined into one (Fig. 7 – 3400 m). Further increase of the sliding distance evens the depths of the wear traces (Fig. 7 – 5100 m and 6800 m). The analysis of the curves of wear trace profiles of the ZnAl40Cu1.5Ti1.5 alloy

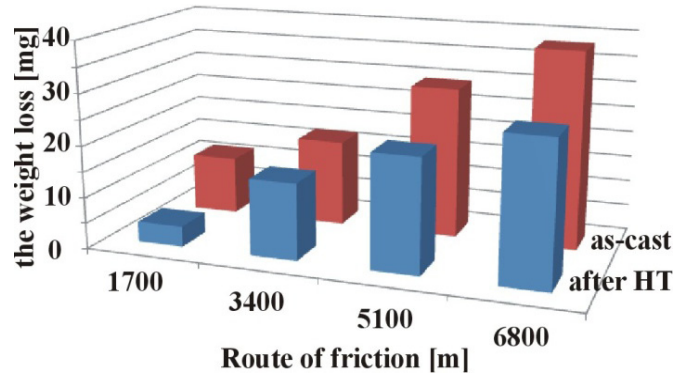


Fig. 5. The weight loss of ZnAl40Cu1.5Ti1.5 alloy depending on the route of friction

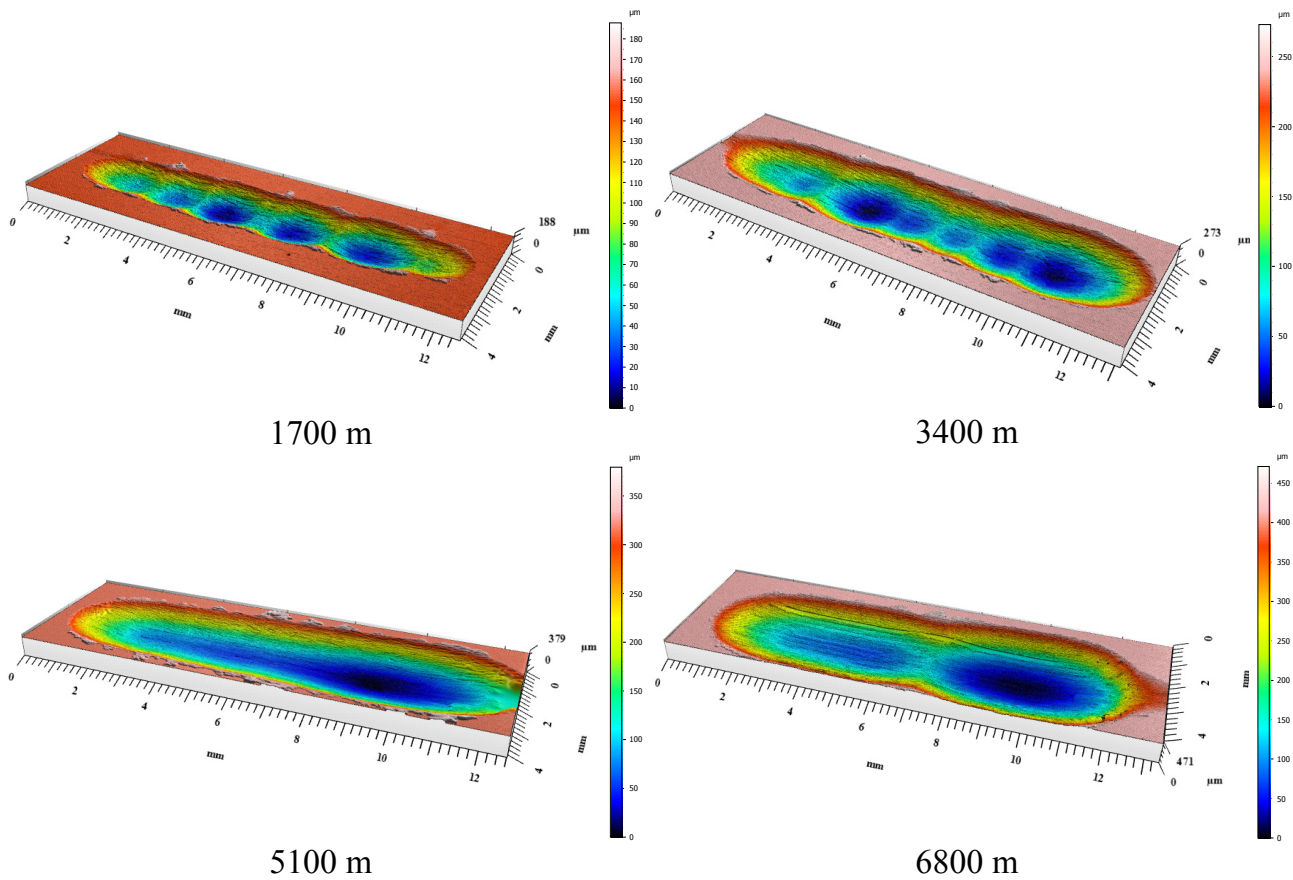


Fig. 6. 3D view of the surface of the as cast ZnAl40Cu1.5Ti1.5 alloy after wear tests

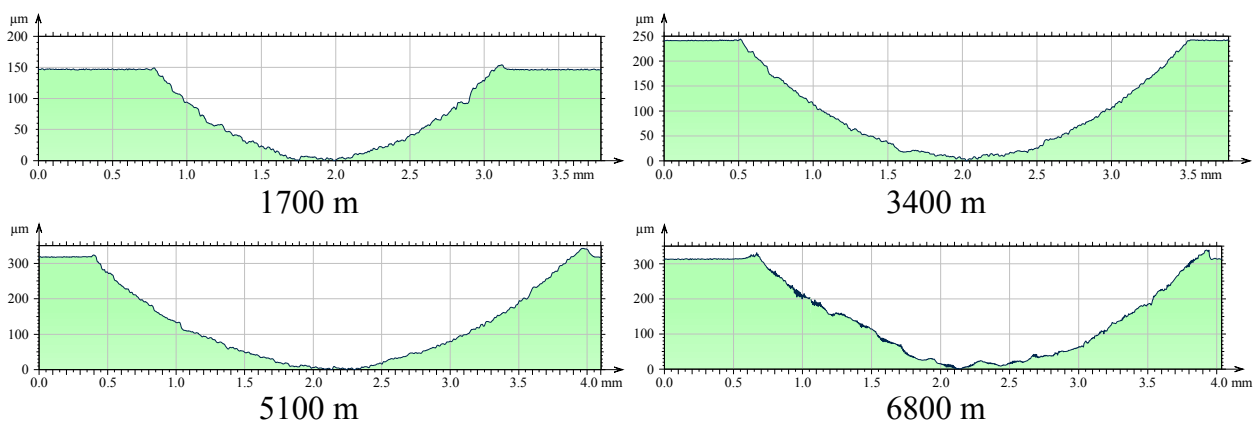


Fig. 7. Profile traces of wear curves as-cast ZnAl40Cu1.5Ti1.5 alloy after wear tests

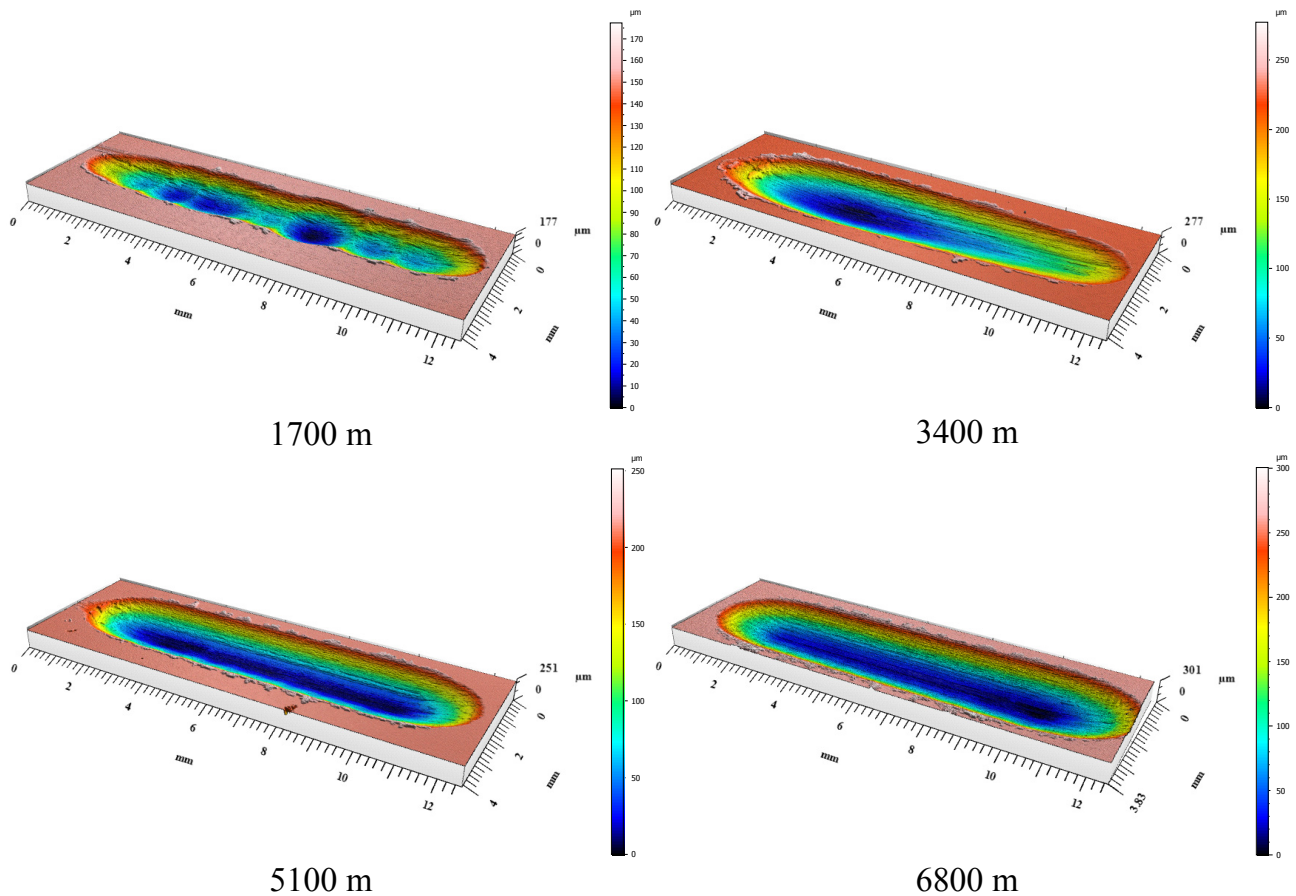


Fig. 8. 3D view of the surface of the ZnAl40Cu1.5Ti1.5 alloy (after heat treatment) after wear tests

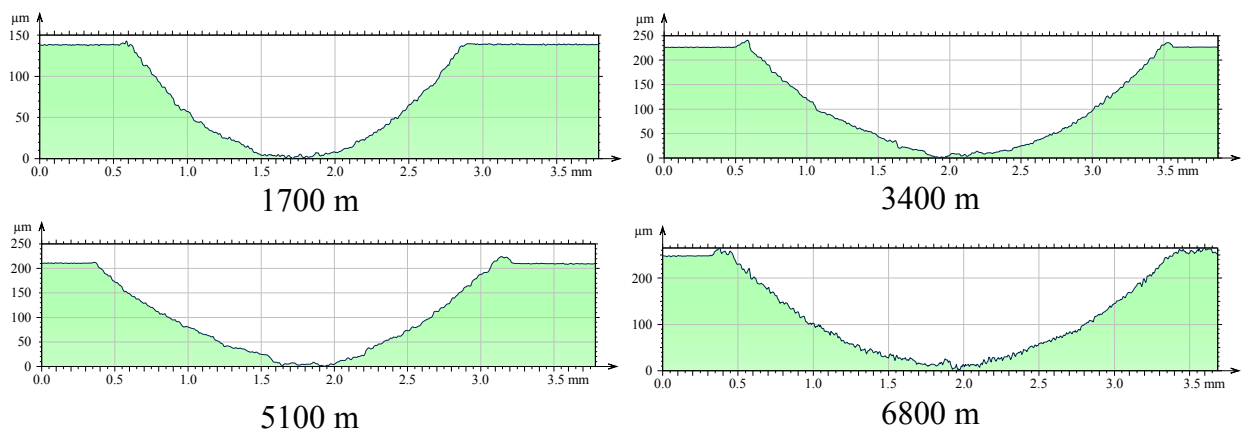


Fig. 9. Profile traces of wear curves ZnAl 40Cu1.5Ti1.5 alloy (after heat treatment) after wear tests

indicates that the increase in depth of the wear traces comes gradually: the highest increase can be observed among sliding distances from 1700 m to 3400 m, and then between 5100 m and 6800 m (Fig. 8). In contrast to the alloy in as-cast state, the depth of wear traces after heat treatment is lower.

Heat treatment of the ZnAl40Cu1.5Ti1.5 alloy has great effect on the volume decrease of the empty space (measured for the same sliding distances) developed as a result of friction (Table 3). Thus, it confirms the results of the mass measurement, pointing to better resistance to the wear use of the ZnAl40Cu1.5Ti1.5 alloy after heat treatment. The volume of the empty space de-

veloped as a result of V_{es} (volume decrease of the empty space) friction increases along with the sliding distance. This increase is, however, smaller in the case of the ZnAl40Cu1.5Ti1.5 alloy after heat treatment (Table 3). The arithmetic mean deviation of the inequality's profile R_a and the inequality's height R_z of the ZnAl40Cu1.5Ti1.5 alloy in as-cast state decreases along with the increase of the sliding distance for the alloy in as-cast state and they greatly increase along with increase of the sliding distance for the alloy after heat treatment (Table 3).

Test results of surface layer structure after the tribological tests are shown in (Figures 10-13).

Selected roughness parameters of trace of wear after the wear tests of ZnAl40Cu1.5Ti1.5 alloy

	Roughness parameters of trace of wear/road of friction							
	1700 m		3400 m		5100 m		6800 m	
	as-cast	after HT	as-cast	after HT	as-cast	after HT	as-cast	after HT
V_{es}	$32,8 \times 10^6$	$28,5 \times 10^6$	$71,5 \times 10^6$	$59,2 \times 10^6$	$116,9 \times 10^6$	$66,2 \times 10^6$	$153,0 \times 10^6$	$101,0 \times 10^6$
R_z	10,6	7,7	11,0	9,9	11,8	15,0	12,4	17,2
R_c	4,2	3,0	5,8	4,9	6,4	8,0	6,6	8,1
R_a	2,2	2,9	2,1	2,7	2,1	2,1	2,0	1,1
R_{sk}	-0,675	-0,609	-0,580	-0,603	-0,217	-0,580	-0,057	-0,467
R_{ku}	2,4	3,7	2,7	3,0	2,7	2,4	2,7	2,2

V_{es} – volume decrease of the empty space [$\mu\text{m}^3/\text{mm}^2$], R_z – maximum height of roughness profile [μm], R_c – the average height of roughness profile elements [μm], R_a – deviation of averages arithmetic roughness profile [μm], R_{sk} – roughness profile asymmetry, R_{ku} – roughness profile kurtosis

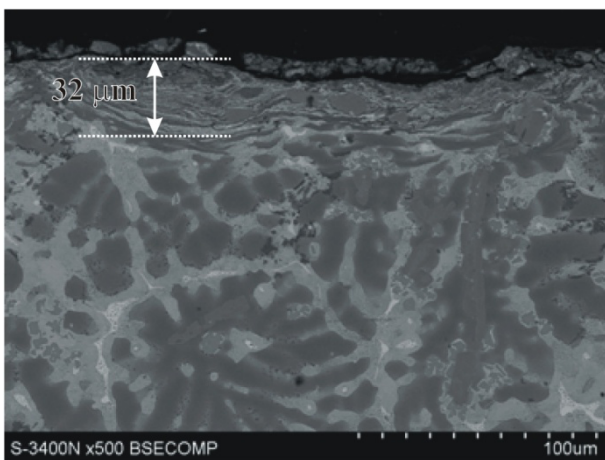


Fig. 10. Structure of surface layer of as-cast ZnAl40Cu1.5Ti1.5 alloy, after wear resistance tests

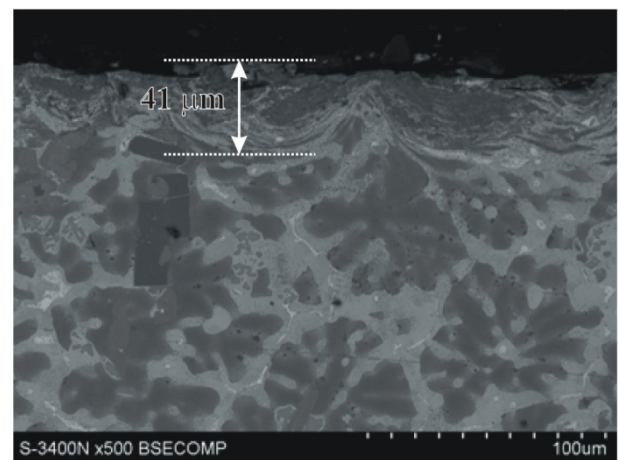


Fig. 11. Structure of surface layer of as-cast ZnAl40Cu1.5Ti1.5 alloy, after wear resistance tests (1700 m)

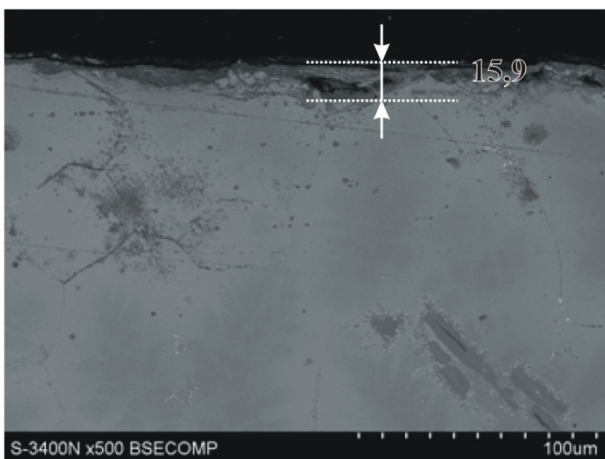


Fig. 12. Structure of surface layer of ZnAl40Cu1.5Ti1.5 alloy after heat treatment, after wear resistance tests (1700 m)

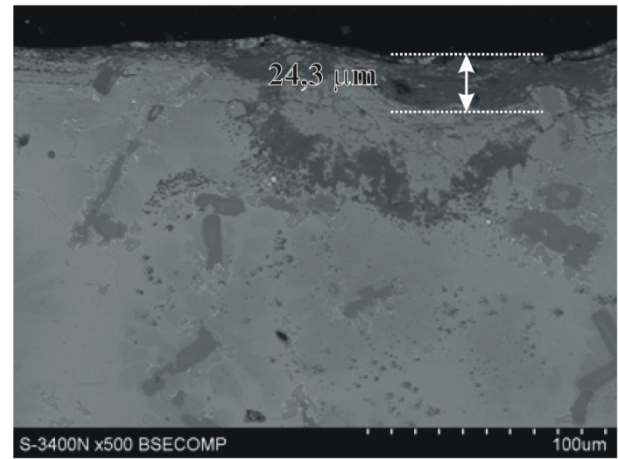


Fig. 13. Structure of surface layer of ZnAl40Cu1.5Ti1.5 alloy after heat treatment, after wear resistance tests (3400 m)

The surface layer of the ZnAl40Cu1.5Ti1.5 alloy, similarly like in the case for Zn-Al-Cu alloys (without titanium) and the tribological tests can be distinguished three sublayers:

- “tribolayer” – the upper-most region
- deformed region – the transition region between tribolayer and unaffected bulk material
- unaffected bulk material

A more accurate description of these layers was published in [5] by Savaskan.

For the as-cast alloy the first layer is discontinuous and cracked (Fig. 10). Increasing of the friction distance from the 1700 to 3400 m causes increase the thickness of the deformed layer. No friction layer was observed on the surface of the wear samples until a sliding distance of 5100 m was reached. Further

increase of friction distance to 6800 m, leading to a recurrence of “tribological layer.” In the case of the alloy after heat treatment “tribological layer” is continuous and adheres well to the base (Fig. 12). Compared to the as-cast alloy is observed lower thickness of the deformed layer. As the distance of friction increases thickness of the deformed layer increases (much slower than the for as-cast alloy). A characteristic feature of the alloy after heat treatment is the occurrence of voids near the surface of the friction distance equal 3400 m, which may suggest the formation of smears.

4. Discussion of the results

The analysis of the results of structural tests points to the possible presence of the phase ϵ - (CuZn_4) within the structure of the ZnAl40Cu1.5Ti1.5 alloy. The analysis of works indicates that Precipitates of this phase may be developed in Zn+Al alloys after exceeding the 2% of mass of Cu. The presence of Precipitates, due to high content of copper, negatively influences hardness of the alloy. The mechanism of the Precipitates development requires further research. Contrary to copper, titanium in Zn-Al-Cu alloys creates precipitates and does not take part in the process of precipitation hardening. Complete replacement of copper with titanium may be aimless. Phases rich in Ti and Al, which are not present in the alloy’s structure in as-cast state, may be observed in the alloy’s structure after heat treatment. Literature data [15-17] shows that rich in Ti and Al precipitates present in the microstructure of as-cast alloy is Ti_2ZnAl_5 phase and after heat treatment of the alloy rich in Ti and Al precipitations forms TiAl_2 and $\text{Al}_{1,6}(\text{Cu, Zn})_{1,2}\text{Ti}_{2,7}$ phases. During the heat treatment process, phase changes are possible to occur and this phenomenon requires further research. An advantageous property of the alloy’s microstructure after heat treatment is complete disappearance of precipitates rich in Zn i Cu.

The results published in [17] indicates that for high-aluminum Zn-Al alloys already small addition of Ti increases the hardness. The higher hardness of the ZnAl40Cu1.5Ti1.5 alloy from the ZnAl40Cu3 alloy can be explained by the presence of precipitates rich in Ti and Al within the structure. Higher hardness of the alloy after heat treatment may be a result of the complete disappearance of the phase rich in Cu and Zn and of development of new, hard phases rich in Ti and Al. It may be assumed that after the 3-hour ageing process, the process of developing phases containing copper starts, which causes the decrease of hardness; that phenomenon requires further research as well.

Test results of structure of surface layer show the different mechanism of ZnAl40Cu1.5Ti1.5 alloy wear than the “classic” Zn-Al-Cu alloys, without titanium. Present in Zn-Al-Cu alloys on the surface soft oxide operates like a sliding mean [5]. A similar role in the structure of the alloy fulfills soft phase forming dendrites. These phases are characterized by good lubricant features. As a result, on the surface of Zn-Al-Cu alloys (both as-cast and heat treated) undergoing friction is very often observed so called smears [5,12]. The presence of hard phases in Zn-Al-Cu alloys

causes very often occurrence of cracks. Study [1] indicates that the plastic processing (pressing) changes the wearing from abrasive into sliding. Based on the results of carried out test can be concluded that the ZnAl40Cu1.5Ti1.5 alloy takes place sliding wear mechanism. Phases rich in Ti and Al operate as carrier phases. During abrasive action phases are not subjected chipping so that no cracks are formed. The analysis of the results of wear research points to high wear resistance of the alloy which is indicated by low mass losses. Solution treatment and ageing causes significant increase of wear resistance. The research results point to a different mechanism of the alloy use in as-cast state and after heat treatment. Gradual use of the alloy in as-cast state is probably the result of the presence of dendrites. Presence of Precipitates rich in Zn and Cu may influence the decrease of dendrites’ hardness. In this situation dendrites, characterized by low hardness, are the first to be used by forming characteristic pits. What is left are harder Precipitates rich in titanium which, with time, fall out and the process beings again. In the case of the alloy after heat treatment, there are no dendrites or Precipitates of phases rich in Cu to be found in the microstructure. Copper is, however, present in the matrix which increases the effect of precipitation hardening. The hardness difference between these spaces and Precipitates rich in Ti and Al is too significant and, initially, these spaces are used as first. Hardness of these spaces is, probably, higher than hardness of dendrites for the alloy in as-cast state; another factor can be found in the presence of a much greater amount of Precipitates rich in Ti. As a result, the profile of wear depth is evened and further process of use continuous in a very slow manner.

The test results on roughness of samples after conducting the wear tests may, first of all, point out to the creation of smears in the case of the alloy’s wear in as-cast state and cracks after heat treatment. It must be remembered, that R_a has nature of amplitude and does not give full information on the profile’s shape. Further analysis of the remaining parameters characterizing the roughness of wear traces is necessary. The average height of the elements of roughness for both, the alloy in as-cast state and after heat treatment, increases (Table 3). It may be an effect of influence of single hard particles breaking away from the wear surfaces in the wear process. The asymmetry of the roughness profile (the indicator of the skewness of the roughness profile) for both, the alloy in as-cast state and after heat treatment has negative value (Table 3). As the sliding distance increases, the asymmetry of the roughness profile R_{sk} starts having more positive value (closer to zero). In the case of the alloy in as-cast state, this increase is far more significant than in the case of the alloy after heat treatment, which may point to the development of smears in the case of the alloy in as-cast state and cracks in the case of the alloy after heat treatment. The analysis of kurtosis of the roughness profile (the measure of tailedness of the roughness profile) leads to the same conclusion. As the sliding distance of the alloy in as-cast state increases, the kurtosis value slowly decreases. In the case of the alloy after heat treatment, the kurtosis value significantly increases along with the sliding distance (Table 3).

5. Conclusions

On the basis of the results of conducted tests, the following conclusions may be drawn:

- The ZnAl40Cu1.5Ti1.5 alloy is characterized with good wear resistance.
- Heat treatment of the ZnAl40Cu1.5Ti1.5 alloy causes the increase in wear resistance.
- Partial replacement of copper with titanium causes the increase in the alloy's hardness.
- Heat treatment of the ZnAl40Cu1.5Ti1.5 alloy causes the increase in the alloy's hardness. The highest hardness can be achieved through solution treatment and ageing of 385°C/24h+125°C/3h.
- Titanium has no effect on the precipitation hardening of ZnAl40Cu1.5Ti1.5 alloy, but participates in the formation of new intermetallic phases.

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