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STUDY ON NANOHARDNESS OF PHASES OCCURRING IN ZnAl22Cu3 AND ZnAl40Cu3 ALLOYS

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Zn-Al alloys are mainly used due to their high tribological and damping properties. A very important issue is determination of the hardness of the phases present in the Zn-Al-Cu alloys. Unfortunately, in literature there is lack of studies on the hardness of the phases present in the alloys Zn-Al-Cu. The aim of this research was to determine the hardness of the phases present in the ZnAl22Cu3Si and ZnAl40Cu3Si alloys. The scope of the research included examination of the structure, chemical composition of selected micro-regions and hardness of phases present in the examined alloys. The research carried out has shown, that CuZn4 phase is characterized by a similar hardness as the hardness of the interdendritic areas. The phases present in the structure of ZnAl40Cu3 and ZnAl22Cu3 alloys after soaking at the temperature of 185 °C are characterized by lower hardness than the phase present in the structure of the as-cast alloys.

Keywords: ZnAl22Cu3 alloy, ZnAl40Cu3 alloy, nanohardness, structure

1. Introduction

Zn-Al alloys are mainly used due to their tribological properties as materials alternative to bronze, cast iron and aluminum alloys in bearings and as construction materials [1-2]. Positive results are brought by the use of Zn-Al alloys in bearings exposed to high loads operating i.a in mining, milling machines, elevators, etc. The advantages of the Zn-Al alloys include the following: low melting point, good castability, high strength and hardness, good fatigue strength, low density, low coefficient of friction, low wear rate, low cost of manufacturing [3]. However, these alloys are used at moderate friction speed, which results from a significant deterioration of features after exceeding the temperature of 100°C-120°C [4, 5].

The structure and strength of the Zn-Al-Cu alloy are well known. Eutectoid ZnAl22Cu3 alloy as-cast is characterized by its dendritic structure. Interdendritic spaces are places in which eutectoid mixture and precipitation of the metastable ε phase (CuZn5 phase) occur. Eutectoid mixture initially forms two supersaturated solutions: visible as dark precipitates, the supersaturated solid solution rich in Al – phase α', and visible as a bright phase, supersaturated solid solution rich in Zn – phase β's. These phases (β', α') are formed from α and β phases in the course of slow cooling – crystallization. Moreover, during the crystallization are formed supersaturated rich in zinc η phase and the ε phase. The structure of the monoeutectoid, as-cast ZnAl40 alloy form dendrites rich in the Al – α phase and rich in Zn η phase in interdendritic spaces. The copper addition influences the formation of the intermetallic ε phases (CuZn4) in the interdendritic areas. This phase is formed in alloys containing at least 1% mass of Cu. The number and size ε phase precipitates increases with increasing of copper content in the alloy [6-7]. In the interdendritic spaces, α + η eutectoid mixture is present, where the η phase is a solid solution rich in Zn. The microstructure of the alloy monoeutectoid ZnAl40Cu3 alloy thus consists of dendrites rich in the Al – α phase, a eutectoid mixture of α + η phases and precipitates rich in Cu of T’ phase and ε phase in interdendritic spaces [8, 9].

Eutectoid and monoeutectoid Zn-Al-Cu alloys exhibit better tribological properties than bronze and cast iron in many engineering applications. In most cases, the Zn-Al-Cu alloys have a lower friction coefficient than that of bronze. Zn-Al-Cu
alloys have high resistance to seizures. Resistance to seizures increases along with increasing of the aluminum content in the alloy [10]. The main way to improve the tribological properties of Zn-Al-Cu alloys is the addition of silicon. Another important factor influencing the tribological properties of the Zn-Al-Cu alloy is a carried out heat treatment in the alloy. In the [11] study, the following were examined: monoeutectoid as-cast ZnAl40Cu2Si2 alloy and alloy exposed to supersaturating at 375°C/24h following ageing 150°C/24h for different loads and different speeds of friction. In the initial period of friction coefficient of the alloy has been growing rapidly, and then, depending on the load value, reached a stable state. An important factor influencing friction value can be found in an alloy structure. Zn rich phase (phase) has good lubricating properties and act as a natural lubricant. Load transferring capacity is attributed to the rich in the Al phase [10]. Rich in Cu and Zn phase (CuZn5) is assigned a disadvantageous influence. After grinding, there were visible deep scratches and grooves on the surface of aluminum bronzes. On the surface of Zn-Al-Cu alloy are visible smears. Blurred alloy material of the Zn-Al-Cu alloy often adheres to the surface of the counter sample. It provides protection of the cooperating surfaces, thus it reduces the friction contact surface of the samples. This causes decrease of the material removal rate and maintains the reduced consumption of material. However, the formation of smears on the surface of as-cast Zn-Al-Cu alloys can be a difficulty [6]. The material can be removed to a large extent without the formation of smears. The negative impact can be present in hard, brittle and rich in copper precipitates structures, e.g. phase (CuZn5). The presence of such particles within the friction surface causes their grinding. For as – cast Zn-Al-Cu alloys, for which in the structure are present phase and small, unevenly distributed silicon precipitates, the basic mechanism of wear is grinding. Smears are formed simultaneously on the surface of such samples, but the mechanism of their interaction is not as effective as abrasion leading to the formation of cracks and furrows.

A very important issue is determination of the hardness of the phases present in the Zn-Al-Cu alloys. However, in the literature, there is lack of studies on the hardness of the phases present in the alloys Zn-Al-Cu. The paper [12] reports that for eutectoid ZnAl22Cu3 alloy hardness of phase is about 175HB and is much higher than for the Al-rich phase, the hardness of which is about 110HB. There is, however, lack of researches on the hardness of the phases present in the monoeutectoid alloys and examination of hardness of phases forming ZnAl40Cu3 and ZnAl22Cu3 alloys after heat treatment.

2. Scope and methodology of the researches

The aim of this research was to determine the hardness of the phases present in the ZnAl22Cu3Si and ZnAl40Cu3Si alloys. The subject of research was: Zn – 22% mass -3% mass Cu 1.5% Si and Zn –40% mass – 3% mass Cu 1.5% Si alloys. Alloys were melted in an induction furnace – type VSG O2, the company Balzers, Al2O3 crucible under an argon atmosphere under pressure in the working chamber of the furnace. Zinc was used as raw material at technical purity (99.99% Zn), aluminum grade – 3N8 (99.98% Al), oxygen – free copper, grade – M00B and silicon at technical purity and mischmetal. Alloys in a liquid state were examined and exposed to tempering at a temperature of 185°C/10h 385°C/10h. The scope of the research included examination of the structure, chemical composition of selected micro-regions and hardness testing of phases occurring in alloys. A scanning microscope Hitachi S 3400N cooperating with EDS X-ray spectrometer were used. Nanohardness test was performed using the “CSM Instruments” nanohardness device under 2mn load.

3. Analysis of the test results

ZnAl40Cu3 alloy was characterized by dendritic structure. Dendrites, visible as brighter areas (pt 1, Fig.1a, Table 1) contained more zinc and less aluminum than the interdendritic areas, visible as darker (pt 2, Fig. 1a, Table 1). Inside of the dendrites revealed the presence of precipitates rich in zinc and copper (pt 3, Fig. 1a, Table 1). Results of researches published in [13] can provide to a conclusion that it is the CuZn4 phase. Soaking of the ZnAl40Cu3 alloy at the temperature of 185°C during 10 hours caused disintegration of dendrites. In a location where earlier dendrites occurred, there was a visible lamellar structure, while in the interdendritic spaces were visible bright and dark areas (Fig. 1b). In these locations a significant decrease in zinc content and an increase in aluminum and copper (pt 1, Fig. 1b, Table 1) were observed. The decrease in the content of zinc and an increase in aluminum content were also observed in the case of the interdendritic spaces (pt 2, Fig. 1b, Table 1). In the case of phases rich in Zn and Cu there was a slight decrease in the content of copper and zinc content increase (pt 3, Fig. 1b, Table 1). The disintegration of the dendritic structure was observed in the samples exposed to soaking at a temperature of 385°C In the area of the brighter phase, formed after disintegration of the dendrites, a decrease of zinc content and an increase of aluminum content were observed, similarly as for samples soaked in the temperature of 185°C (pt 1, Fig. 1c, Table 1). The decrease in the zinc content and increase in aluminum content, however, were significantly lower than in samples soaked in a lower temperature. Within the interdendritic space, differently than for samples soaked at a lower temperature, an increase of the zinc content and a decrease of aluminum content were revealed (pt 2, Fig. 1c, Table 1). Precipitates rich in copper were also visible in the structure. A significant increase in the content of copper, zinc decrease and increase in aluminum were observed (pt 3, Fig. 1c, Table 1).
Chemical composition of ZnAl40Cu3 alloy in chosen microareas (Fig. 1)

| Chemical composition Zn/Al/Cu wt % | dendrite/phases formed after decomposition of dendrite – pt. 1 | interdendritic regions pt. 2 | rich in Cu phases – pt. 3 | other |
|-----------------------------------|-------------------------------------------------|-----------------------------|--------------------------|-------|
| Zn      | Al       | Cu      | Zn      | Al       | Cu      | Zn      | Al       | Cu      | Zn      | Al       | Cu      |
| as-cast (a) | 95,0 | 1,0    | 4,0    | 60,8 | 37,5 | 1,7 | – | – | – | – | – |
| 185 °C/10h (b) | 94,0 | 4,5    | 1,5    | 56,6 | 42,3 | 1,1 | – | – | – | – | – |
| 385 °C/10h (c) | 74,4 | 23,0   | 2,7    | 72,8 | 24,5 | 2,8 | 79,6 | 9,1 | 11,3 | – | – |

As – cast ZnAl22Cu3 alloy is characterized by dendritic structure. A rich in zinc, supersaturated solid solution of Al in Zn containing copper forms dendrites which are visible as the bright phase. The dendrites were much richer in Zn and poorer in Al than in the case of an ZnAl40Cu3 (pt 1, Fig. 2a, Table 2 and pt 1, Fig. 1a, Table 1). In Al -rich interdendritic spaces, eutectoid mixture composed of platelet is present- platelet are rich precipitates on the aluminum phase and richer in Zn matrix (pt 2, Fig. 2a, Table 2). In the case of the ZnAl22Cu3 alloy within the interdendritic space was observed much higher content of zinc and aluminum content than in ZnAl40Cu3 alloy. In the structure of the ZnAl22Cu3 alloy was not revealed occurrence of rich in copper and zinc CuZn5 phase precipitates. Soaking at the temperature of 185 °C resulted in the disappearance of dendrites. Within the remaining after soaking of dendrites was observed a slight increase in aluminum content and the decrease in copper content (pt 1, Fig. 2b, Table 2). Within the interdendritic spaces was revealed a decrease of zinc content and an increase in aluminum content (pt 2, Fig. 2b, Table 2).

Interdendritic space of the ZnAl22Cu3 alloy was richer in zinc and poorer in aluminum than in the case of the ZnAl40Cu3 alloy. Complete disappearance of the dendritic structure was revealed in the case of soaking of the ZnAl22Cu3 alloy at the temperature of 385 °C. In the structure were visible very small, dark and precipitates and bright matrix. Bright phase compared to the dark precipitates contained slightly more zinc than dark precipitates. (pts 1 and 2, Fig. 2c, Table 2). Both light and dark phase were significantly richer in zinc and poorer in aluminum than in the case of aluminum alloy richer in ZnAl40Cu3 alloy. Single, bright precipitates of phases rich in Cu and Zn, probably of probably of CuZn5 phase (pt 3, Fig. 2c, Table 2) were also visible.

Table 1

Table 2
As a result of a phase hardness measurement present in the ZnAl22Cu3 alloy it was found that the interdendritic areas are characterized by greater hardness than the dendrites (Table 4.1). On the curve: the force curve – the penetration depth (Fig. 4a) a certain area can be observed where the depth of penetration increases, despite the fact that the force does not increase. Similarly, on the curve depth of penetration versus time a skip distance is visible – place of rapid penetration depth growth (Fig. 4b). It can be assumed that in this place the indenter hit the void (micro pores). Next, the shape of the curves did not change significantly, suggesting that further indenter penetrated the same phase. In the structure of the alloy with addition of silicon were also present precipitates of the silicon at very high hardness. As a result of a phase hardness measurement present in the ZnAl40Cu3 alloy was also found that the interdendritic areas are characterized by greater hardness than the dendrites (Table 4.2). The hardness within the interdendritic spaces of the alloy with higher aluminum content was slightly lower, while in the dendrites area much greater. Precipitates of the CuZn5 phase were also present in the structure. However, contrary to the literature data, their hardness was not very large but close to the hardness of the interdendritic areas of ZnAl40Cu3 alloy. In addition, very hard silicon precipitates were visible in the structure.

**TABLE 3**

| Nanohardness of ZnAl40Cu3 alloy |
|---------------------------------|
| nanohardness HV |
| dendrite | interdendritic regions | precipitates |
| as-cast | 115 | 156 | Si - 677 CuZn5 - 153 |
| 185°C / 10h | 84 | 75 | – |
| 385°C / 10h | 194 | 221 | – |

**TABLE 4**

| Nanohardness of ZnAl22Cu3 alloy |
|---------------------------------|
| nanohardness HV |
| dendrite | dendrite | dendrite |
| as-cast | 60 | 160 | Si - 1054 |
| 185°C / 10h | 30 | 145 | – |
| 385°C / 10h | 168 | 195 | – |

Soaking at the temperature of 185°C/10h caused a significant decrease in hardness of the phases present in the tested alloys (Table 4.1 -4.2). In the case of the alloy with lower aluminium content in the harder phase (the interdendritic phase) this decrease was not as large as in the case of dendrites. The cause there can be an increase in the Zn content of the dendrites due to soaking at the temperature of 185°C/10h. In the case of an alloy with a higher aluminium content, a significant decrease both in the dendrites and interdendritic areas was observed (Table 4.2). The hardness of dendrites for the ZnAl40Cu3 alloy was, however, higher than for the ZnAl22Cu3. Soaking at a temperature of 185°C/10h of the ZnAl40Cu3 alloy causes disintegration of dendrites – present in their place precipitates are much poorer in Zn than dendrites in an alloy with a lower aluminium content. On curve of the force – penetration depth (Fig. 4.9a-4.10) and the depth of penetration as a function of time (Fig. 4.9b-4.10b) can be observed similar skip distances as shown in Figure 4.1a and 4.1b, probably in these locations the indenter came across the micro pores during the measurement performance.
Soaking at a temperature of 385°C/10h of the ZnAl22Cu3 alloy caused hardness increase mainly within the dendrites – phase richer in Zn. Within the interdendritic space, growth was significantly lower (Table 4.1). In the case of the ZnAl40Cu3 alloy, a significant increase was observed both in the hardness of the interdendritic phase and richer in Zn (Table 4.2).

4. Analysis of results

Analysis of the literature indicates that after exceeding 3% by mass copper in the structure of the Al-Zn-Cu alloy, ε – CuZn4 phase occurs. However, carried out researches pointed out that the as-cast phase is formed only in the case of richer in Al, ZnAl40Cu3 alloy. For the ZnAl22Cu3 alloy, a significant amount of copper is dissolved in the dendrites, contributing to their strengthening. However, CuZn4 phase occurs only after soaking at a temperature of 385°C. According to [7, 9] studies, the presence of precipitates in copper – rich structure increases the tendency of the alloy cracking, as these precipitates are harder and more brittle than the matrix. This process is accompanied by a decrease in elongation with the increase of copper content due to the formation of hard, brittle and rich in copper intermetallic precipitates along the grain boundaries. In the case of the ZnAl40Cu3 alloy, copper amount is not very large, and the ε phase precipitates cannot be formed at grain boundaries, but inside dendrites. It was expected that CuZn4 phase will be a hard phase. However, researches pointed out that the hardness of this phase is close to the hardness of the interdendritic areas of the ZnAl40Cu3 alloy. Therefore, the presence of ε – CuZn4 phase cannot exert such a significant influence on the strength properties of the ZnAl40Cu3 alloy. The results of researches showed difference in the hardness of the dendrites and interdendritic areas; the difference is greater for an alloy with a lower content of aluminium. The cause can be found in the much higher zinc content in dendrites of the ZnAl12Cu3 alloy than in the dendrites of the ZnAl40Cu3 alloy. In the case of friction, it can be expected that lower hardness characterizing dendrites present in the structure of the ZnAl12Cu3 alloy will act as a natural lubricant and harder dendrites present in the ZnAl40Cu3 alloy structure will fulfill these tasks much worse. Present in the interdendritic spaces harder eutectoid mixture will transfer loads. Soaking at a temperature of 185°C caused a significant decrease in the hardness of both in the area of dark phase (interdendritic areas ) as well as the bright phase. The bright phase was characterized by a harder ZnAl40Cu3 alloy where 185°C soaking did not cause a more complete disintegration of dendrites. A lower hardness of the phases present in the structure of the tested alloys can be responsible for the observed deterioration in tribological properties after exceeding approximately 120°C [5].

The phases present in the structure of the alloys tested after soaking at 385°C were characterized by greater hardness than the phases present in the as-cast alloy structure. This may cause a greater ability of Zn-Al-Cu alloys for transferring loads. The presence of the harder phases, including silicon precipitates in the as-cast alloys, may have an impact on the wear mechanism in the alloy during friction. Tearing off of hard particles can cause the formation of grooves and scratches. Moreover, having a high hardness, bright phase formed after soaking at 385°C can no longer play the role of the lubricant, which may help to reduce the seizure resistance of the tested alloys.

5. Conclusions

Carried out researches allow to formulate the following conclusions:

- As-cast CuZn4 phase is present only for the ZnAl40Cu3 alloy, in the case of the ZnAl22Cu3 alloy presence of this phase was not found.
- CuZn4 phase is characterized by a similar hardness to the hardness of the interdendritic areas.
- Present in the of ZnAl40Cu3 alloys structure dendrites are less harder than the interdendritic areas.
- The phases present in the structure of ZnAl40Cu3 and ZnAl22Cu3 alloys after soaking at the temperature of 185°C are characterized by lower hardness than the phase present in the structure of as-cast alloys.
- The phases present in the structure of ZnAl40Cu3 and ZnAl22Cu3 alloys after soaking at the temperature of 385°C are characterized by greater hardness than the phases present in the structure of as-cast alloys.

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