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TRIBOLOGICAL PROPERTIES OF COPPER-BASED COMPOSITES WITH LUBRICATING PHASE PARTICLES

WŁAŚCIWOŚCI TRIBOLOGICZNE KOMPOZYTÓW NA OSNOWIE MIEDZI Z UDZIAŁEM CZĄSTEK FAZ SMARNYCH

The results of research into influence of chemical composition on structure and tribological properties of copper-based composites intended for slide bearings are presented in this paper. The study was focused on copper alloys with lubricating phase particles in form of graphite, tungsten disulphide (WS_2), molybdenum disulphide (MoS_2) and glassy carbon. The metallic matrix of composite materials was composed of alloys from Cu-Sn-Zn system. The mass content of lubricating phase particles was from 5 to 20%. The process of production of subject materials included the processes conducted with full or partial contribution of liquid phase and it was conducted by two methods. Both the method of classic powder metallurgy and stir casting method were used for the production of composites. Lubricating phase particles heated to the temperature of 200°C were introduced to liquid metal bath and then the process of stirring and casting to moulds was performed. In case of production of composites by powder metallurgy, the process included mixing of bronze powders and lubricating phase particles, and then their consolidation. Sintering process was conducted in temperature between 750÷800°C. The produced materials were tested in terms of microstructure and tribological properties with the CSM Instruments tribometer.

Keywords: copper matrix composites, bearing materials, microstructure, tribological properties, friction coefficient

W pracy zamieszczono wyniki badań dotyczące wpływu składu chemicznego na strukturę oraz właściwości tribologiczne materiałów kompozytowych na osnowie miedzi przeznaczonych na łożyska ślizgowe. Przedmiot badań stanowiły stopy miedzi z udziałem cząstek faz smarnych w postaci grafitu, dwusiarczku wolframu (WS_2), dwusiarczku molibdenu (MoS_2) oraz węgla szklistego. Metaliczną osnowę materiałów kompozytowych stanowiły stopy z układu Cu-Sn-Zn. Udział masowy cząstek faz smarnych wynosił od 5 do 20%. Proces wytwarzania badanych materiałów obejmował procesy przebiegające z całkowitym oraz częściowym udziałem fazy ciekłej i przebiegał dwutorowo. Do wytwarzania kompozytów zastosowano zarówno metodę klasycznej metalurgii proszków, jak i metodę topienia i odlewania z jednoczesnym mieszaniem tzw. *stir casting*. Do ciekłej kąpieli metalicznej wprowadzono podgrzane do temperatury 200°C cząstki faz smarnych a następnie realizowano proces mieszania i odlewania do form. W przypadku otrzymywania kompozytów na drodze metalurgii proszków proces obejmował mieszanie proszków brązu oraz cząstek faz smarnych, a następnie ich konsolidację. Proces spiekania prowadzono w temperaturze z zakresu 750÷800°C. Wytworzone stopy poddano badaniom mikrostruktury oraz oceny właściwości tribologicznych na tribometrze CSM Instruments.

1. Introduction

The possibility of use of composite materials in tribological systems depends on the required value and stability of friction coefficient and high resistance to frictional wear, both in conditions of technically dry friction and with lubrication. Development of composite materials in copper matrix with lubricating phase particles made possible to use them in tribological systems operating in conditions of intense friction. Proper selection of components provides possibility to produce composite materials suitable for difficult conditions with high unit pressures, variable temperature and atmosphere [1÷3]. The materials that are most often used as lubricants are graphite, polytetrafluoroethylene (PTFE, teflon, tarflen, fluon), molybdenum disulphide, tungsten disulphide, glassy carbon, sulphur compounds including hexagonal zinc sulphide and nitrides (h-BN) [4÷6]. The possibilities of use of other lubricants and agents limiting the frictional wear in form of mica, boric acid, borax, oxides, borides and fluorides with different effects of use were also presented in the papers [7]. The metallic matrix in these composite materials is composed of copper or its alloys from Cu-Sn composition. Introduction of lubricating particles to the composites decreases the friction coefficient, provides good self-lubricity, resistance to galling and good thermal properties [5]. The intensity of tribological wear depends not only on the properties of components from which the composite material is made, but also on their volume fraction and distribution in the metallic matrix [2, 8]. The selection of size and shape of lubricating phase particles is also important. The tribological properties of lubricating phase particles can change with the working conditions. For graphite the friction coefficient in ambient temperature is from

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0.1 to 0.2, and the lower values can be observed in more humid environment. The absorbed on the edges of crystal lattice thin oxygen and water vapour films facilitate significant decrease of resistance to the movement of graphite layers, while in the vacuum environment, the friction coefficient of graphite may reach the value of even 0.5, and its wear is considerably increased. Above the temperature of 500°C, graphite starts to oxidize, and its friction coefficient starts to increase. Composites with soft graphite particles have lower tribological wear and friction coefficient in comparison with matrix [9÷10].

Development of effective and efficient method for production of finished slide elements from those materials is an important aspect in designing of new bearing materials. Composite materials for slide bearings are most often produced by powder metallurgy method. The techniques of classic metallurgy with stirring of the liquid metal and simultaneous introduction of non-metallic phase particles are also used [11]. However, the main problem is to provide proper dispersion of graphite particles in metallic matrix. Centrifugal casting trials [12÷15] showed that such method of production results in gradient distribution of non-metallic phases particles in the cast elements. Content of lubricating phase particles changes in a cast sleeve cross-section from zero at its outer wall, to a dozen or several dozen at the inner wall. Such type of dispersion may be beneficial in bearing materials which require only thin sliding layer [16].

Extreme diversity of tribological properties may be achieved in hybrid (heterophase) composites containing both hard particles (e.g. SiC, Al_2O_3) and soft particles (graphite, glassy carbon) which play a role of a lubricant during friction process. The double reinforcement is performed to achieve beneficial mechanical and tribological properties at the same time [17÷23]. An example of hybrid composite in copper matrix is Cu-TiO_2-H_3BO_3 composite [24÷25]. Titanium oxide (TiO_2) of great hardness, characterized also by good thermal resistance and frictional wear resistance plays in these materials the role of "hard" particles. Boric acid H_3BO_3 of perfect sliding properties is used as soft phase particles. Application of heterophase hardening provides possibility to control both abrasive and sliding properties of the produced composites.

The aim of this paper was the evaluation of the influence of individual lubricating phases on microstructure and tribological properties of copper-based composite materials for slide bearings.

2. Experimental

The subject of the research presented in this article was focused on copper-based composites with lubricating phase particles in form of graphite, tungsten disulphide (WS_2), molybdenum disulphide (MoS_2) and glassy carbon. The metallic matrix of composite materials was composed of alloys from Cu-Sn-Zn system. The weight content of lubricating phase particles was from 5 to 20%. The process of production of the materials included operations conducted with full or partial contribution of liquid phase and it was conducted by two methods. The applied production technology was based on both powder metallurgy and classic metallurgy using melting and casting processes.

The metallic matrix of composite materials achieved in powder metallurgy process was composed of bronze, CuSn10, produced in laboratory conditions. The lubricating phase particles in the amount of 5-20 wt. % were introduced into the produced Cu + Sn10 powder mixture. Granularity of powders used for research was: 20 μm for graphite, ~3 μm for tungsten disulphide and molybdenum disulphide and <12 μm for glassy carbon, respectively. The mixing process was performed for 2 hours in a ball mill with horizontal rotation axis. In order to increase the effectiveness of mixing process and to prevent agglomeration of non-metallic phases particles, a wetting agent in form of kerosene was used. The mixing process was conducted at room temperature in air atmosphere. Then, the mixture of powder components CuSn10/C(graphite), CuSn10/C(glassy), CuSn10/WS_2 and CuSn10/MoS_2 was subject to compacting and sintering. Double-sided cold pressing with constant pressure of 400 MPa and high-temperature sintering in temperature between 750÷800°C were performed. The sintering process was conducted in laboratory furnace in hydrogen atmosphere. Cylindrical samples of Ø10×15 and Ø40×10 mm were produced in result of sintering. In order to achieve the material with high level of homogeneity and low porosity, the produced samples were subjected to additional high-pressure processing, using pressure of 700 MPa. The final operation consisted of stress relieving and recrystallization annealing conducted in temperature of 800°C for 1 hour in hydrogen atmosphere.

The second method for production of the composite materials was based on the process of melting with simultaneous stirring known in literature as stir casting. The method included: process of melting in induction crucible furnace, transfer of the metal bath together with crucible to resistance furnace and homogenization in temperature of 1100°C, introduction of the heated to 200°C graphite particles, stirring of metal bath, taking the crucible with the suspended matter out and casting into a mould. The basic material of composite matrix was CuSn10Zn7PTi alloy. Application of carbide forming element in a form of titanium addition in the amount of 1÷4 wt % was aimed at the improvement of wettability of graphite particles. Pure metals (Cu, Zn, Sn) and master alloys (CuP14,7, CuTi25) were used as charge materials in the process of alloy melting. The process of stirring of composite bath was performed at constant speed of 1500 rpm during 120 s.

The microstructure was characterised with a use of light microscope Olympus GX71F. The evaluation of tribological properties was conducted on the basis of abrasion tests performed in room temperature with CSM Instruments Pin-on-Disc tribometer. A pin in form of ball with 6 mm diameter made of 100Cr6 bearing steel was used for research. The study was conducted with constant load of 10 N. The sliding distance was 2160 m, rotational speed 0.9 m/s, and the radius was 5 mm. Examination of wear depth was conducted with Taylor Hobson Surtronic 25 profilometer.

3. Results and discussion

Microstructure of the obtained composites, depending on the type and amount of non-metallic phases, is presented in Figures 1÷4. Microstructure of composites shows typical microstructure of material after consolidation. The basic structural component is solid α solution of tin and phosphorus in copper, with individual fine recrystallized grains and characteristic annealing twins (Fig. 1÷4). Distribution of particles of non-metallic phases in matrix is irregular. There are clusters of lubricating phases of various size and shape, and their amount increases with the increase of their content (Fig. 1b÷4b). The arrangement and morphology of graphite and glassy carbon particles is similar. With smaller content (5 wt %), they create individual clusters in the matrix, occurring mainly next to grain boundaries (Fig. 1a, 2a), while with higher content, they occur in form of compact agglomerates (Fig. 1b, 2b). As the result of the increase of content of particles of these phases, one can observe the increase of their size and level of concentration in triple contact points of grains of metallic matrix. Tungsten disulphide and molybdenum disulphide particles create a thick, discontinuous or continuous lattice around the areas of solid α solution (Fig. 3, 4). The analysis of microstructure shows also that the metallic matrix tightly adheres to the introduced lubricating phase particles. Boundaries between particles and matrix are clear and there are no impurities.

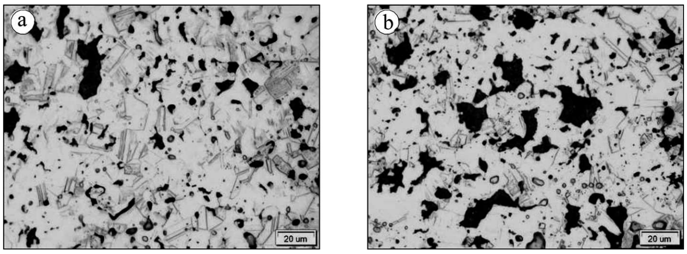

Fig. 1. Microstructure of CuSn10/C composites containing 5 wt % of graphite (a), 20 wt % of graphite (b) sintered in temperature of 800°C

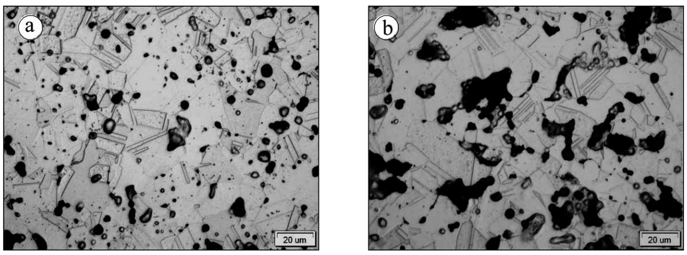

Fig. 2. Microstructure of CuSn10/C_{glassy} composites containing 5 wt % of glassy carbon (a), 20 wt % of glassy carbon (b) sintered in temperature of 800°C

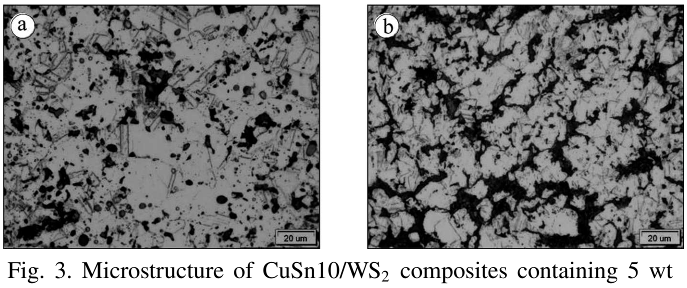

Fig. 3. Microstructure of CuSn10/WS_2 composites containing 5 wt % of tungsten disulphide (a), 20 wt % of tungsten disulphide (b) sintered in temperature of 800°C

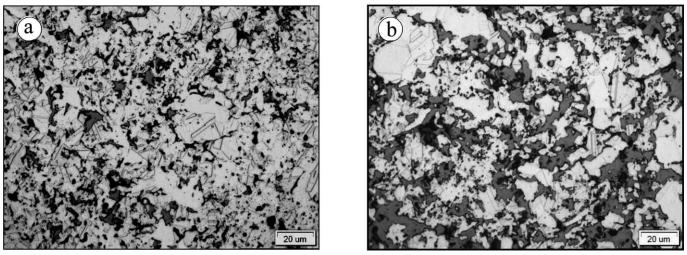

Fig. 4. Microstructure of CuSn10/MoS_2 composites containing 5% of molybdenum disulphide masses (a), 20% of molybdenum disulphide masses (b) sintered in temperature of 800°C

The attempts to obtain composited with graphite contribution in the process of stir casting brought positive results. The presence of titanium addition in alloy limited the flow of graphite particles to the metal surface and caused its distribution in the entire volume. The research showed that in the graphite/metal interface a very thin layer of titanium carbide is created, which causes wetting of the surface of graphite particles and its good adhesiveness in the interface. The measurements of volumetric fraction of graphite particles showed that together with the increase of titanium contents in alloy, the amount of introduced graphite also increases. Its maximal amount is 14 vol % for alloy with addition of 4 wt % of titanium. Figure 5 presents the microstructure of composites with various contents of titanium and graphite. Samples received from the tested composite materials did not show porosity. The basic structural component of metallic matrix is solid α solution (solution of tin and zinc in copper). Distribution of graphite particles in metallic matrix at their lower contents is quite uniform (Fig. 5a). At higher contents a tendency to agglomeration of particles in microstructure (Fig. 5b) can be observed. In both cases, the graphite particles were well connected to the metallic matrix.

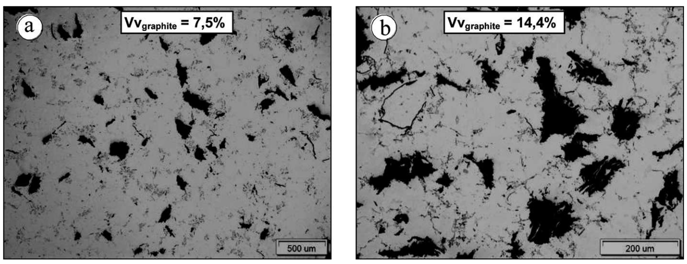

Fig. 5. Microstructure of CuSn10Zn7PTi/C (a), CuSn10Zn7PTi4/C (b) composites

The main criterion deciding on the usefulness of the studied group of materials can be seen in the results of tribological tests. Friction and abrasion are the basic problems related to the design of bearing materials. Analysis of the achieved results (Fig. 6÷9) showed that both composites produced by powder metallurgy and by stir casting method are characterized by considerably better sliding properties in comparison with materials commonly used for bearings, such as CuSn5Zn5Pb5 and CuSn10 bronze. The lowest medium values of friction coefficient on the level of 0.1 were achieved with the composites containing 20 wt % of graphite, tungsten disulphide. Similar values of friction coefficient were reached with CuSn10Zn7PTi+C composites (Fig. 8). While analysing the course of changes of values of friction coefficient, one can observe stable course of changes in the entire examined section of the composites is stable and that is varies from the other tested materials and standard alloys. Only in the initial stage of friction of the composites with molybdenum disulphide, the dynamic character of changes of friction coefficient can be observed, which stabilizes in the permanent value of 0.05 after reaching the distance of 1000 m (Fig. 7). It is probably related to the fact that the products of abrasion created in the initial stage in a form of chipped particles of molybdenum disulphide form an additional sliding layer. On the basis of the results of the conducted tribological studies, it can be established that the friction coefficient depends both on the type of lubricating phase and its contribution (Fig. 9).

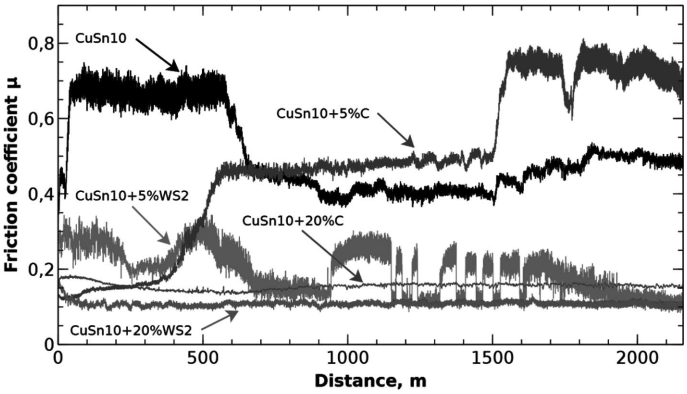

Fig. 6. Relation of friction coefficient as a function of sliding distance of composites produced by powder metallurgy method

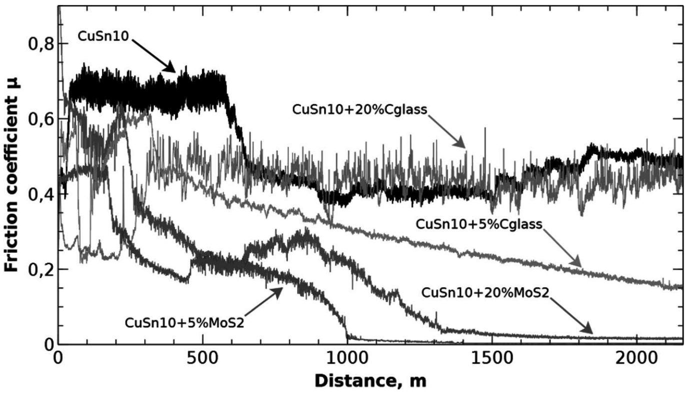

Fig. 7. Relation of friction coefficient as a function of sliding distance of composites produced by powder metallurgy method

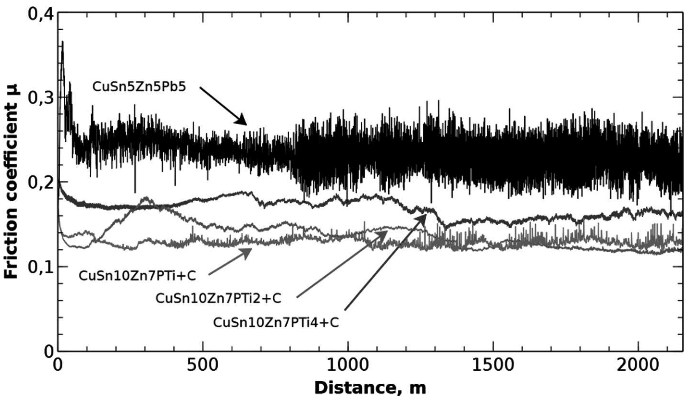

Fig. 8. Relation of friction coefficient as a function of sliding distance of composites produced in stir casting process

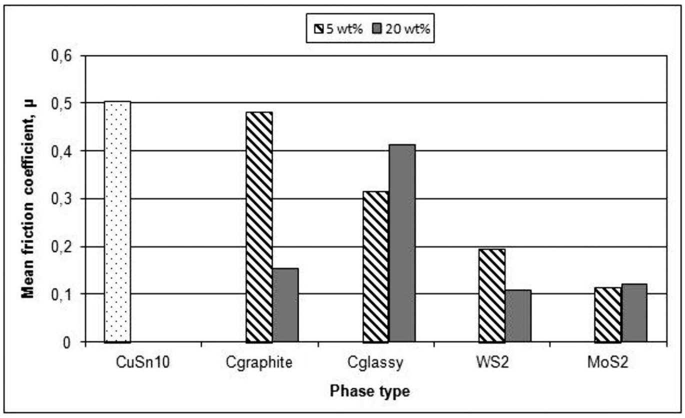

Fig. 9. Average value of friction coefficient of the tested composite materials, depending on the type of lubricant

Small wear is a characteristic feature of the tested composite materials. In Figure 10, sample traces of abrasion on the surface of tested composite materials are presented as well as distribution of the wear depth. The lowest level of wear was observed in composites containing 20% of graphite. One could observe a uniform, relatively shallow trace with the depth of abrasion of about 10 μm and width of about 0.524 mm, which is the result of beneficial interaction of composite material which contains graphite as lubricating phase (sample) and bearing steel (counter-sample). A similar image of abrasion was achieved for composites containing 20% of WS_2 where the width of abrasion was about 0.9 mm and the depth about 30 μm. The average field of abrasion for composites containing 20% of lubricating phase in form of graphite was 3491 μm^2, and was much lower in comparison with the commonly used CuSn10 bronze. In the other tested composites slightly higher level of wear was observed but the profile of their abrasion indicates a rather smooth wearing process. No clear signs of extraction of material particles and grooving were observed on the analysed surfaces. The traces of abrasion show regular course which is also proved by the distribution of wear depth (Fig. 10). When comparing the results from measurement of the depth of wear (Fig. 11) with tribological characteristics (Fig. 9) of the tested materials, one can notice a correlation between the amount of used lubricating phase and the value of friction coefficient and level of wear. Increase of content of lubricating phase particles in form of graphite and WS_2 results in a significant decrease of friction coefficient and level of wear. In the case of composite with glassy carbon, the friction coefficient increases together with the increase of content of lubricant with the simultaneous decrease of wear of material. Glassy carbon is characterized by great hardness comparable with the hardness of ceramic materials such as: SiC, Al_2O_3, therefore it is assumed that the composites with increased content of C_{glass} should interact in metal-ceramics system or in the conditions of friction with lubrication. Moreover, the composites with 5 wt % of C_{glassy} were characterized by the less rough surface in comparison with composites containing 20 wt % C_{glassy}, which also influenced the decrease of value of resistance to friction.

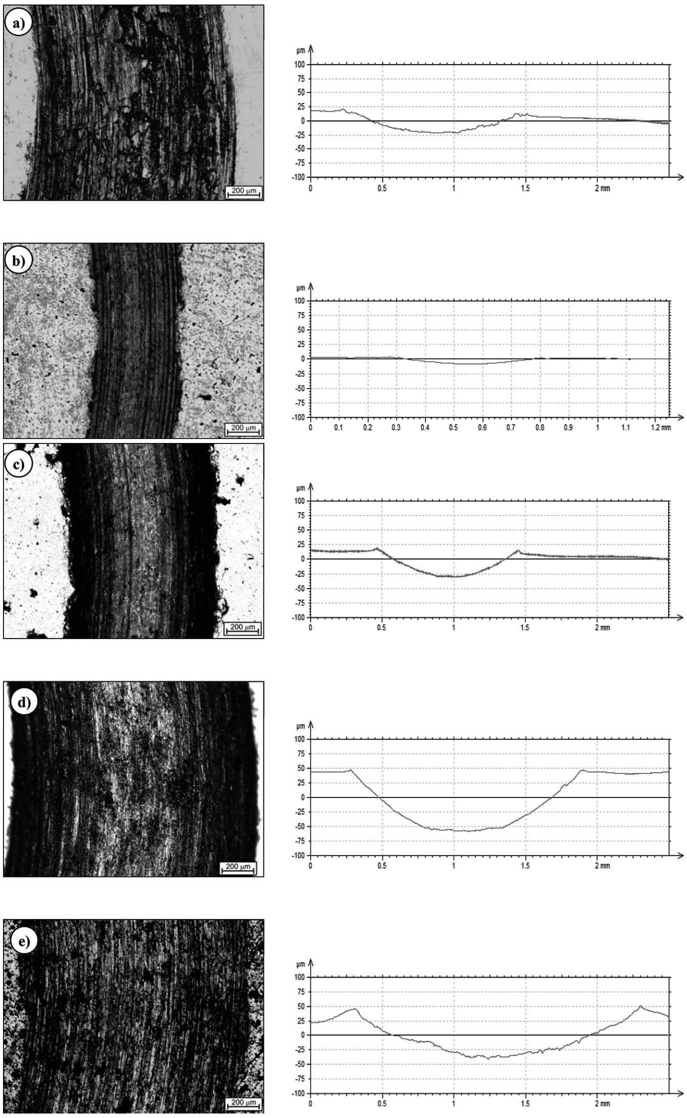

Fig. 10. Abraded surface of tested materials after interaction with steel pin and distribution of wear depth of composites: CuSn10 (a), CuSn10/20C (b), CuSn10/20WS$_2$ (c), CuSn10/20MoS$_2$(d), CuSn10/20C$_{glassy}$ (e)

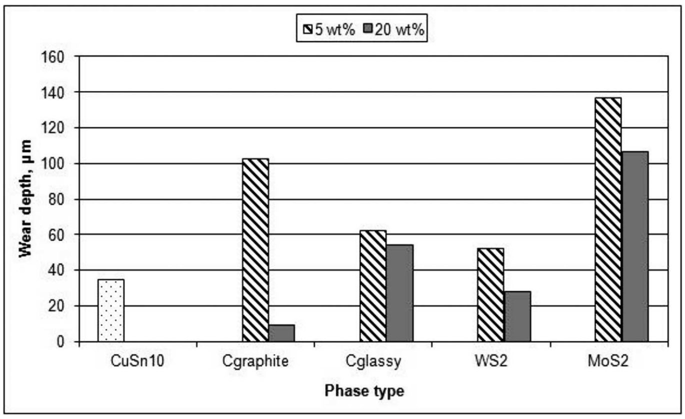

Fig. 11. Wear depth of tested composite materials created in the process of powder metallurgy, depending on the type and amount of used lubricant

4. Conclusions

On the basis of the conducted research it can be stated that there is a possibility of production of good quality composites with large contribution of lubricating phase particles, both in the process of powder metallurgy and stir casting. Produced materials are characterized by compact structure and their metallic matrix tightly adheres to the introduced lubricating phase particles. Boundaries between particles and matrix are clear and there are no impurities. Application of titanium addition provided possibility to introduce graphite particles to liquid alloy, to reach their relatively uniform distribution in metallic matrix and good connection in the boundaries, which may also protect from thermal degradation in the future. Relatively high stability of liquid mixture of CuSn10Zn7PTi/C composite creates good grounds for production of semi-finished products. Studies into metal/graphite interphase indicates presence of a thin layer, probably of TiC carbide. It was stated that the concentration of titanium in composite matrix is much lower in comparison with initial alloy. These results show that the amount of graphite introduced to the composite depends not only on the initial content of titanium in metal bath, but also on development of graphite surface.

The achieved results of research fully confirm the usefulness of tested composite materials for the application in bearings. Composites are characterized by low friction coefficient and high resistance to wear. It results from the fact that the mechanism of wear in these materials is limited mainly to the processes of destruction of lubricating phase particles, without any interference with matrix material. The best results were achieved with materials containing graphite and tungsten disulphide particles. It was established that the friction coefficient and wear depend mostly on the contribution of the particles. With the increase of mass fraction of lubricating phase particles, the abrasion wear decreases. It was also observed that in all of the tested materials addition of 20 wt % of lubricating phase particles causes considerable decrease of friction coefficient in comparison to matrix material, which was CuSn10 bronze. The produced tribological characteristics indicate that the tested composite materials can constitute good sliding materials. The achieved results form a basis for designing and optimisation of materials for sliding elements operating in conditions of dry friction or friction with limited lubrication.

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