

B. JUSZCZYK*, J. KULASA*, W. MALEC*, SZ. MALARA*, M. CZEPELAK*, L. CIURA*

MICROSTRUCTURE AND TRIBOLOGICAL PROPERTIES OF THE COPPER MATRIX COMPOSITE MATERIALS CONTAINING LUBRICATING PHASE PARTICLES

MIKROSTRUKTURA ORAZ WŁAŚCIWOŚCI TRIBOLOGICZNE MATERIAŁÓW KOMPOZYTOWYCH NA OSNOWIE MIEDZI Z UDZIAŁEM CZĄSTEK FAZ SMARNYCH

The paper presents results of the studies into influence of individual particles of lubricating phase on microstructure and tribological properties of copper based composite materials for slide bearings. The studied material was composed of copper alloys with lubricating phase particles, e.g. in a form of graphite and glassy carbon. The metallic matrix of composite materials consisted of Cu-Sn type alloys. Production of the examined materials included processes with complete or partial participation of liquid phase and was conducted in two ways. In production of composites both classical powder metallurgy technology was applied and a method of melting with simultaneous mechanical stirring in liquid state (stir casting). Particles of lubricating phases were heated up to the temperature of 200°C and introduced into a liquid metal and then stirring process at constant rate of 1500 rpm rotational speed was applied. To improve wettability of graphite and glassy carbon particles titanium was introduced into the metallic matrix.

In production of the composites by powder metallurgy methods the process consisted of mixing of bronze powders and particles of non-metallic phases and then their consolidation. Both quantitative and qualitative structure analysis of the produced composites was performed. Also through evaluation of tribological properties (friction coefficient, wear) with CSM Instruments high temperature tribometer THT was conducted.

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

W pracy zamieszczono wyniki badań dotyczące wpływu poszczególnych cząstek faz smarnych na mikrostrukturę oraz właściwości tribologiczne materiałów kompozytowych na osnowie miedzi przeznaczonych na łożyska ślizgowe. Przedmiot badań stanowiły stopy miedzi z udziałem cząstek faz smarnych m.in. w postaci: grafitu oraz węgla szklistego. Metaliczną osnowę materiałów kompozytowych stanowiły stopy z układu Cu-Sn. 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 z jednoczesnym mieszaniem mechanicznym w stanie ciekłym (stir casting). Do ciekłego metalu wprowadzono podgrzane do temperatury 200°C cząstki faz smarnych, a następnie prowadzono proces mieszania stosując stałą prędkość obrotową na poziomie 1500 obr/min. W celu poprawy zwilżalności cząstek grafitu i węgla szklistego do osnowy metalicznej wprowadzono tytan.

W przypadku otrzymywania kompozytów na drodze metalurgii proszków proces obejmował mieszanie proszków brązu oraz cząstek faz niemetalicznych, a następnie ich konsolidację. Wytworzone materiały kompozytowe poddano analizie struktury zarówno w ujęciu ilościowym, jak i jakościowym. Dokonano również szczegółowej oceny właściwości tribologicznych (współczynnik tarcia, zużycie) przy wykorzystaniu tribometru wysokotemperaturowego THT firmy CSM Instruments.

1. Introduction

Durability and reliability of machines and equipment are often determined by the operational properties of the applied bearings which results in a need for constant improvement of those components of the equipment. Limitation of friction forces by application of materials of antifriction properties can significantly reduce mechanical destruction of structural elements.

The conducted analysis of state of the art in the area of copper-based bearing materials shows a need for elimination of lead from antifriction materials, such as tradi-

tional copper alloys, which are still used for slide bearings and sliding components. Cast copper alloys, mainly of CuSnPb and CuSnPbZn groups, have been widely used in production of those components. Some examples of those alloys are covered by the European Standard EN 1982: i.e. CuSn5Pb20, CuSn7Pb15, CuSn10Pb10, CuSn5Pb9, CuSn7Zn4Pb7, CuSn5Zn5Pb5, CuSn3Zn8Pb5 grades. The wide area of applications results from their undeniable merits. The existing limitations for lead application resulting from its harmfulness, however, increasingly dictate a need for intensive search for its substitutes. To solve that problem it is necessary to develop a substitute in which particles of some

* INSTITUTE OF NON-FERROUS METALS, 5 SOWIŃSKIEGO STR., 44-100 GLIWICE, POLAND

other, harmless to environment, substance can play the role of the emergency solid oil, instead of lead [1, 2].

Possibilities of application of other than lead element of similar properties are very limited and bismuth seems to be the only element of similar properties which can be used in practice. That is why, following the example of fittings alloys which are intended for machining, also tin-bismuth alloys for slide bearings were introduced, produced by powder metallurgy methods. Among cast bearing alloys also C89320 grade, which contains 6% of tin and 5% of bismuth, was registered by the Copper Development Association. The materials are mostly intended for operation in demanding conditions, under variable and impact loads.

To reduce friction between mating surfaces and, in consequence, reduce their wear, some lubricants are applied. For that purpose solid, plastic and lubrication oils are used. The latter are mostly applied in hydrodynamic bearings which represent one of the most commonly used groups of slide bearings for transmission of radial load. When there is no possibility to apply oil lubrication or to provide its constant supply to the friction node the friction forces rise and the wear increases. That problem can be addressed by application of composite materials with lubricating phases, as in the examples of copper based composites with particles of non-metallic phases. Those materials are becoming more and more widely used in the conditions of dry friction and in friction with lubrication, because of the low friction factor. The most widely used lubricating agents are graphite, polytetrafluoroethylene (PTFE, Teflon, Tarflen, Fluon), molybdenum disulfide, tungsten disulfide, glassy carbon, sulfur compounds including hexagonal zinc sulfide and nitrides (h-BN) [3-8].

One of the important conditions when designing a new antifriction material is to develop a method for its production which would guarantee easiness of its application in production of sliding components of various types. Composite materials for slide bearings are usually produced by powder metallurgy methods. Also methods of classical metallurgy are used with application of liquid metal stirring and simultaneous introduction of non-metallic phase particles [9-13]. There is a problem, however, to provide a proper dispersion of graphite particles in the metallic matrix. Tests of centrifugal casting [14-15] resulted in production of a gradient distribution of particles of non-metallic phases in the cast components.

The objective of this study was to evaluate influence of particles of graphite and glassy carbon on microstructure and tribological properties of copper-based composite materials intended for slide bearings.

2. Experimental

In the paper studies into metal-based materials with particles of lubricating phases in a form of graphite and glassy carbon are described. The metallic matrix of the materials was composed of alloys of Cu-Sn system. The weight percentage of the lubricating phases ranged from 0.5 to 6%. Precise chemical compositions of the investigated materials are presented in Table 1. Process of production of the examined materials covered operations with complete and partial participation of liquid phase and was conducted in two ways. The applied pro-

duction technology was based on powder metallurgy method and on classical metallurgy with melting and casting.

The metallic matrix of composite materials produced by powder metallurgy was CuSn10 bronze formed in laboratory conditions. Particles of lubricating phases in the amount of 0.5÷6 wt. % were introduced into the produced Cu + Sn10 powder mixture. Grain size of the powders used in the study was: 20 μm for graphite and $\sim <12 \mu\text{m}$ for glassy carbon, respectively. The mixing was conducted in a ball mill of horizontal axis of rotation for 2 hours. To increase mixing efficiency and to prevent agglomeration of non-metallic phase particles a wetting agent in a form of kerosene was applied. Mixing process was conducted in the atmosphere of air in room temperature. Then the mixture of powder components CuSn10/C(graphite) and CuSn10/C(glassy) was consolidated and sintered. Double-side cold pressing was applied with the pressure of 400 MPa, while high-temperature sintering was performed in the temperature of the range 750-800°C. Sintering process was conducted in a continuous laboratory furnace in the atmosphere of mixture of gases: NH_2 (5% H_2). During the pressing cylindrical samples of dimensions $\varnothing 10 \times 15$ and $\varnothing 40 \times 10$ mm were produced. The sinters were then subjected to additional pressing with pressure of 700 MPa to produce highly homogenous material of low porosity. The final operation consisted of relief-recrystallization annealing conducted in temperature of 800°C for 1 hour.

The second method of production of the examined composite materials was based on melting with simultaneous stirring, in literature known as stir casting. The process consisted of: melting operation in crucible induction furnace, transfer of liquid metal with the crucible to a resistance furnace and its homogenizing in temperature of 1100°C, introduction of heated up to temperature of 200°C particles of lubricating phases, stirring of metallic bath, removal of the crucible with the suspended material and its casting into a mould. The CuSn10PTi2 alloy was used as the basic materials for composite matrix. Application of a carbide-forming element in a form of titanium addition in the amount of <2 wt. % was performed for improvement of graphite particle wettability. In the process of CuSn10PTi2 alloy melting pure metals (Cu, Sn) and master alloys (CuP14.7, CuTi25) were used as charge materials. Stirring of the composite bath was conducted at constant rate of 1500 rpm for 120 s.

TABLE 1
Chemical composition of the investigated materials

Produce method	POWDER METALLURGY		MELTING AND CASTING (STIR CASTING)	
	graphite	glassy carbon	graphite	glassy carbon
Metallic matrix	CuSn10		CuSn10PTi2	
Lubricating phase	graphite	glassy carbon	graphite	glassy carbon
Content of lubricating phase, wt.%	1,5	0,5	1,5	1,5
	3	1,5		
	4	2,5	3	3
	6	3,5		

Structural characteristics were made with Olympus GX71F light microscope. Evaluation of tribological properties

was based on the tests performed in room temperature with application of high-temperature CSM Instruments tribometer of Pin-on-Disc type. In the tests a pin in a form of a ball of diameter 6 mm, made of 100 Cr6 bearing steel, was used. The tests were conducted at constant load of 10 N. The distance of friction was 2160 m, rotational speed was 0.9 m/s, and the radius 5 mm.

3. Results and discussion

Microstructure of the composites produced by powder metallurgy process is presented in Figures 1 and 2. The microstructure shows typical features of the material after consolidation. The basic structural component is a solid α solution of tin in copper. Also individual, fine recrystallized grains and characteristic twins which were generated during the final annealing are conspicuous (Fig. 1, 2). Distribution of graphite grains in the metallic matrix is moderately homogenous, however some individual clusters of particles of that phase were observed, and their number increases with the increase of graphite content in the composite material (Fig. 2). Distribution of particles of glassy carbon is diversified and considerably depends on its content. At the lower content (0.5 wt. %) it occurs in a form of individual particles or small clusters (Fig. 2 a) while at higher (3.5 wt. %) it creates chain precipitates along grain boundaries (Fig. 2 b). The clusters are composed of strongly adherent spherical particles and create a broken or continuous lattice around the areas of the solid α solution. Analysis of microstructure of the produced composites showed their structure to be compact and homogenous in the whole volume. Also high sintering degree was observed. The metallic matrix is strongly adherent to the introduced particles of lubricating phases, while the boundaries between particles and the matrix are distinct with no accumulation of impurities.

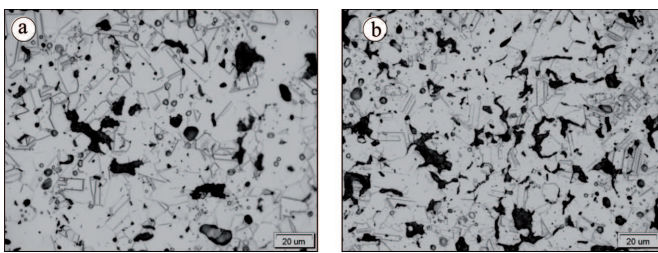


Fig. 1. Microstructure of CuSn10/C composites containing 1.5 wt. % of graphite (a), 6 wt. % of graphite (b) sintered in temperature of 800°C

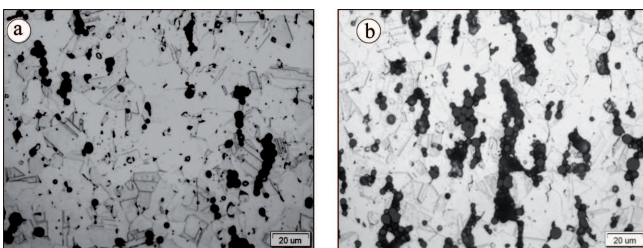


Fig. 2. Microstructure of CuSn10/C composites containing 0.5 wt. % of glassy carbon (a), 3.5 wt. % of glassy carbon (b) sintered in temperature of 800°C

To characterize precisely the microstructure of the produced composite materials a quantitative analysis was performed based on the images registered with light microscope. Surface area analysis of graphite particles showed that the size of the particles in the composite material is comparable, regardless of its content. The majority (80%) of the analyzed particles has surface area below 20 μm^2 , while in the rest of the examined objects that parameter was of the range 30-100 μm^2 , which is very advantageous when considering tribological properties. Quantitative assessment of glassy carbon particle size showed that more than half (54%) of the examined population has surface area below 20 μm^2 . The remaining part of the particles in the composites has surface area of the range 30-200 μm^2 . The particles of glassy carbon have slightly larger size, when compared to the graphite containing composites, which results from a tendency for agglomeration.

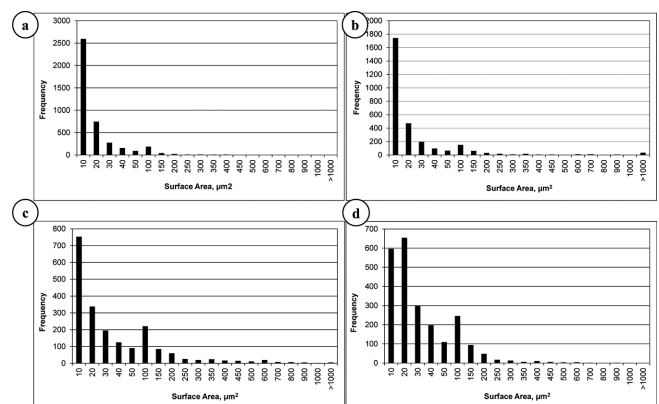


Fig. 3. The statistical distribution of the surface area of lubricating phase particles in composite materials: CuSn10/1.5 wt.% C_{graphite} (a), CuSn10/6 wt.% C_{graphite} (b), CuSn10/0.5 wt.% C_{glassy} (c), CuSn10/3.5 wt.% C_{glassy} (d)

Tests for production of composites with graphite and with glassy carbon by casting and simultaneous stirring (stir casting) brought positive results. Titanium addition in the alloy limited rising of the particles of lubricating phases up to the metal surface and resulted in its distribution throughout the whole volume. Figures 4 and 5 show microstructure of composites with graphite and with glassy carbon produced by casting. When graphite was added its content in the ingot was quite uniform along the whole length of the ingot at relatively low tendency for segregation, and only individual clusters of that phase in the metallic matrix were registered.

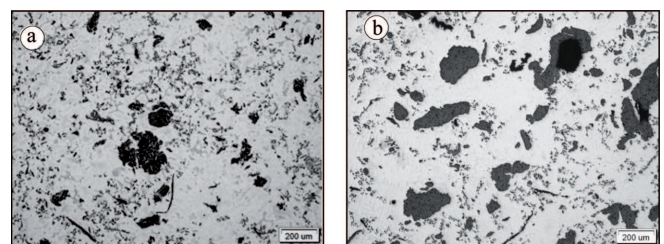
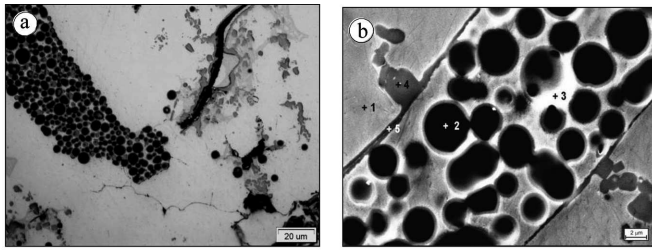


Fig. 4. Microstructure of CuSn10PTi/3 wt. % C_{graphite} (a), CuSn10PTi/3 wt. % C_{glassy} (b) composites



Point	Chemical composition, wt. %					
	Cu	Sn	P	Ti	C	O
1	84,1	7,2	-	-	8,7	-
2	14,3	1,7	-	14,0	70,0	-
3	20,5	6,8	-	33,8	38,9	-
4	5,5	-	17,7	60,8	16,0	-
5	29,3	3,2	4,2	36,7	14,8	11,8

Fig. 5. Microstructure of CuSn10PTi/C_{glassy} (a, b) composites and the chemical composition of the points indicated in the Figure 5 b

Composites with glassy carbon addition had more diversified microstructure. In those composites a noticeable tendency for formation of agglomerates was observed (Fig. 4b). The generated agglomerates of spherical glassy carbon particles (Fig. 5a) are often interconnected by a layer of titanium carbide (Fig. 5b). The connection is relatively durable and prevents breaking of the agglomerates into smaller fragments. The basic structural component of the metallic matrix is a solid α solution (tin and zinc solution in copper). Beside particles of titanium carbide TiC, which were observed on the outer surfaces of glassy carbon and graphite, in the microstructure presence of titanium oxide (usually in a form of films) and CuTiP and TiP compounds was registered.

Results of tribological tests are the main criterion determining usability of the examined group of materials. That is why tests were performed for evaluation of sliding properties of the produced materials. Results of the tests, showing changes of friction coefficient as a function of sliding distance, are presented in Figures 6 and 7. The analysis of the results showed that graphite containing composites, both produced by powder metallurgy process and by stir casting method are characterized by better sliding properties than the materials with glassy carbon. The lowest friction coefficient at the level of 0.1 was reached with graphite containing composites produced by powder metallurgy method (Fig. 6 a). Similar values of friction coefficient were reached with CuSn10PTi+3C_{graphite} composites (Fig. 7) produced by stir casting process. In the analysis of the changes of friction coefficient with sliding distance one can observe that the course of changes in the whole examined sector is stable and different from the other examined materials. It was only in the initial stage of the process of friction of the composites with 1.5% graphite content where dynamic character of changes of friction coefficient was observed,

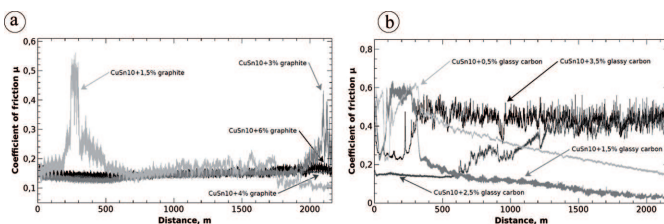


Fig. 6. Relation of friction coefficient as a function of sliding distance of CuSn10P/C_{graphite} (a) and CuSn10PTi/C_{glassy} (b) composites produced by powder metallurgy method

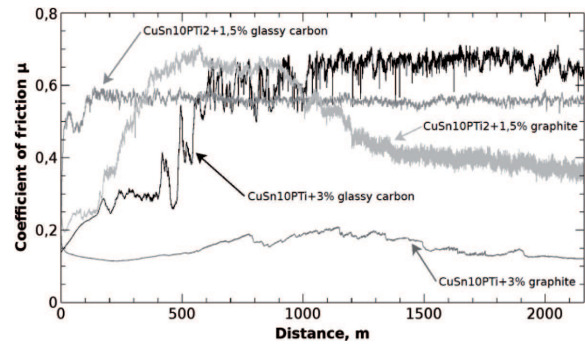


Fig. 7. Relation of friction coefficient as a function of sliding distance of composites produced in stir casting process

which after reaching 500 m distance stabilized to a constant value (Fig. 6 a).

Higher values of friction factor were registered with glassy carbon containing composites, however that does not disqualify them as bearing materials. It can be anticipated that those materials, because of high thermal stability of glassy carbon at the level of 3000°C, can perform well when operating at elevated temperature. Additionally, the glassy carbon is characterized by high hardness which is comparable to ceramic materials, such as: SiC, Al₂O₃. Therefore it can be assumed that composites with that material should operate properly in a system metal – ceramics or in conditions of friction with lubrication. Based on the performed tribological tests it can be established that friction factor depends on the type of the applied lubricating phase and on its content.

4. Conclusions

Based on the conducted studies it was established that the composite materials produced by powder metallurgy methods are characterized by compact structure and their metallic matrix adheres tightly to the introduced particles of lubricating phases.

In the cast composites the cast material mostly presented the required quality and homogeneity. There is a tendency for formation of clusters (agglomerates) with small size particles of glassy carbon. The generated agglomerates of spherical glassy carbon particles are usually interconnected by a layer of titanium carbide which prevents their breaking and their uniform distribution. Metallic matrix of the tin bronze based cast composites is characterized by presence of α phase (solid solution of tin in copper) and δ phase (Cu₄₁Sn₁₁). Also presence of a series of phases with titanium and phosphorus with possible copper content was observed as well as titanium carbide (mainly at the boundary graphite/carbon glassy – matrix) and titanium oxides (in a form of fine films mainly).

Examination of tribological properties showed that the produced graphite-containing composites have very good tribological properties. The friction factor is at the level of 0.1. The reached very good tribological characteristics of the materials significantly exceed the sliding properties of the matrix material (CuSn10 bronze) as well as the materials still widely used for bearings, such as CuSn5Zn5Pb5 bronze. The reason can be seen in the fact that wear mechanism in those materials is mainly limited to the processes of destruction of particles of lubricating phases without significant interference

into matrix material. The level of tribological properties of the produced composites meets the requirements of the materials for bearings. It forms a basis for design and optimization of the materials intended for the components of sliding connections operating in the conditions of dry friction or in friction with limited lubrication.

Acknowledgements

The study was conducted as part of Innovative Economy Operational Programme's Strategic Project 01.01.02-00-015/09-00 entitled "Advanced materials and their production technologies". The Project is co-financed from European Regional Development Fund resources as part of Innovative Economy Operational Programme, 2007-2013.

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