

TRIBOLOGICAL PROPERTIES AND MICROSTRUCTURE OF THE METAL-POLYMER COMPOSITE THIN LAYER DEPOSITED ON A COPPER PLATE BY ELECTROCONTACT SINTERING

The properties of the electrocontact sintered metal-polymer composite materials are strongly determined by the heat flow taking place during sintering, which, in turn, is influenced by the amount and initial distribution of the polymer particles in the metal matrix. In case of the metal-polymer powder mixture in the form of a thin layer deposited on the bulk metal substrate, the influence of the latter is also taken into consideration. Thus, the model simulating the heating and sintering of the thin layer made of metal-polymer powder mixture on a metal plate is proposed. Based on mathematical calculations relating to the model describing the thermal state of the system, it is shown how heat flow fields are formed within the layer, depending on the polymer content and its distribution. These theoretical simulations seem to be useful in optimising the production of the antifriction metal-polymer layer on a bulk copper substrate by electrocontact sintering. The results of the tribological experiments and microstructural observations are in a good agreement with the theoretical model.

Keywords: metal-polymer sintered composites, electrocontact sintering, thermal state, dry lubricant, tribological properties

1. Introduction

Combinations of metals and polymers provide separate type of composite materials [1-5] which are of practical interest for many specific applications. Mostly, the polymer acts as a matrix while the metal is a filler. Thus, the methods and equipment from the conventional polymer industry can usually be used to process these composite materials. Some modern techniques, like microwave sintering [6] or 3D printing [7], may also be suitable. In the case of metal based composites, however, joining both constituents requires different fabrication processes. Typically, the sintered porous metallic structure is impregnated by the polymer or polymer is deposited in the form of a layer on the bulk metallic substrate. Since the consolidation process of metals proceeds at significantly higher temperatures than that of polymers, the direct metal-polymer composites manufacturing seems to be problematic. The reason is related to the degradation or even depolymerisation of the organic constituent at the elevated temperatures which are necessary to consolidate the metal. Therefore, to preserve the properties of polymer in the final product, nonconventional techniques of metal-polymer composites production have to be exploited.

Electrocontact sintering is a special method of powder consolidation [8-10]. The main advantage of this method is a significant reduction of time exposure to high temperature during

the sintering/consolidation process. Therefore such phenomena like grain growth, chemical interactions between components or their decomposition are strongly limited. This method is characterised by a high local concentration of the released energy in the form of resistance heat on contact points between particles, when electric current passes through the powdered material. Owing to the high heating rate and a sharp temperature gradient on metal-polymer interfaces, the hereditary structure of original polymer may be maintained [11].

Metal-polymer composites are used for numerous purposes because of their different attractive properties like mechanical, thermophysical, electrical or tribological. Since the latter are of our special interest [11-12], the current paper is also focused on tribological behaviour of the investigated composite materials. In the case of metal-polymer bearings [13-15], the metal provides mechanical strength, while the polymer acts as a dry lubricant. This construction promotes dimensional stability and improves thermal conductivity. As the polymer component, predominantly polytetrafluoroethylene (PTFE) is used, because it offers exceptionally low friction, is thermally and chemically resistant, mechanically stable and improves vibrational damping. The metal-polymer composites for bearing-type applications are generally designed to operate as self-lubricating or with marginal external lubrication. However, their main advantage is connected with their use in dry sliding conditions, where high

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purity of moving parts is required. Finally, the metal-polymer composite bearings are a cost-effective alternative for many industrial and automotive applications. All composite bearings are lead-free and, therefore, environmentally friendly and do not need any maintenance.

It is expected that the performance of conventional metal-polymer bearing-type composites may be improved if a new consolidation technique would be applied. Therefore electrocontact sintering was used in the current study. Among many different parameters influencing the sintered properties, of main importance is energy, and thus the temperature distribution within the body being electrocontact sintered. When the system consists of components considerably different in terms of electrical properties, their relative concentration and arrangement have to be taken into consideration. Additionally, when the system consists not only of the powder, but also of the bulk substrate, the latter modifies the temperature distribution. Thus, the aim of the work was to find a relation between the thermal state of the metal-polymer powder mixture during electrocontact sintering and the content and arrangement of the dispersed polymer filler, taking into account the influence of the bulk metal substrate. For this purpose mathematical modeling was used, which enabled us to define the thermal state of the system during consolidation. To verify the usefulness of theoretical calculations for the development of sintered properties, microstructural observations and tribological investigations of sintered composites were performed.

2. Materials and experiments

To produce the sliding composite thin coatings the following powders were used:

- Electrolytic copper powder to form the matrix of the sliding layer, Cu content min. 99.5 mass%,
- Natural graphite powder as a filler,
- PTFE plate-like powder as a filler.

Particle size close to 50 μm was chosen for all powders. The required powders were separated by a sieve method.

Several powder mixtures were prepared by mixing in a cone agitator for 2 hours. The compositions of the mixtures are specified in Table 1.

TABLE 1

Compositions of the powder mixtures used in the experiments

No.	Copper, mass %	Graphite		PTFE	
		mass %	vol. %	mass %	vol. %
1	94	5	8.4	1	2.3
2	93			2	4.5
3	90			5	10.5
4	88			7	14.7
5	87			8	16.8
6	86			9	18.9
7	85			10	21.0

As a substrate a high purity copper plate of 0.6 mm thickness was used. The loosely packed mixtures of copper, graphite and PTFE powders, in the form of layers, were put on the plate. The thickness of the powder layer was about 0.3 mm. A pilot-plant apparatus, designated as UNP-684, was used for electrocontact sintering. The process was carried out in air at a pressure of 300 MPa and current of 12 kA. The duration of the current transmission was 2 seconds. Thus, the antifriction composite layer of about 0.1 mm thickness and of residual porosity below 3% was produced, and then the bimetallic product of 15 \times 12 mm in dimensions was directed to microstructural and tribological investigations.

Surfaces of sintered composite layers were examined directly after the electrocontact sintering has been finished and compacts have been cooled down to room temperature. It was done on a scanning electron microscope JSM-50A.

Tribotests were performed using a block-on-roller method. As a counterbody a roller made of carbon steel hardened to 44 HRC with the surface roughness $R_a = 0.63 \mu\text{m}$ was used. The criterion of wear was the length of the friction distance corresponding to the reduction by 90% of the thickness of the antifriction metal-polymer-graphite layer.

3. Defining the problem

During electrocontact sintering the electric energy is transformed into heat enabling consolidation of the powdered material. Of course, in view of the process, the latter is the most important part of the electric circuit, to which punches also belong. Thus, within the material being sintered in this way, the resistance heat is generated on the contact points between powder particles and between them and punches' surfaces. Additional heat comes from the electrical resistance of the interiors of the particles, which means that the type of the material, in terms of its conductivity, also influences the temperature distribution within the powdered material during sintering. Furthermore, some additional heat derives from the resistance of material used for electrodes-punches [8,16]. Because the current density flowing through the contact points is very high, a large amount of heat is locally generated, which has a decisive influence on consolidation.

When powder mixture that undergoes electrocontact sintering comprises components differing significantly in their electrical and thermal properties, identifying the thermal state of the sintered system becomes especially complicated. That is the case for metal-non-metal powder mixture and, in particular, for the metal-polymer system. Thus, for modeling the thermal state and simulating thermodynamical processes occurring in the metal-polymer powder system, not only the thermal characteristics of metal and polymer have to be taken into account, but also their mutual concentrations, arrangement and particles' geometry. All of the specified parameters influence heat flow and therefore the temperature distribution. The latter is of great importance, since, in view of the need to preserve the initial

properties of polymer, special attention should be focused on heating of polymer particles [17].

In the present study the plane-parallel stationary heat transfer through the system comprising powder mixture of copper, PTFE and graphite particles placed on a bulk copper plate is considered. The calculations describing the thermal state of the system were made for its nominal temperature of 1073K. Processes occurring in the system were analysed on the mesolevel [18].

4. Methodology of a heat transfer simulation

In the case in which the temperature is a function of all three coordinates, x , y , and z , the steady-state conduction is described by the Fourier law of thermal conductivity [19]:

$$q_x = -\lambda_x \frac{\partial T}{\partial x}; \quad q_y = -\lambda_y \frac{\partial T}{\partial y}; \quad q_z = -\lambda_z \frac{\partial T}{\partial z} \quad (1)$$

where q_x , q_y , q_z are the heat fluxes (heat transfer per unit area), T is the temperature of the body, while λ_x , λ_y , λ_z are the thermal conductivities (in a linear problem formulation).

The equilibrium heat flow inside the body is given by:

$$q_x = \frac{\partial}{\partial x} \left(\lambda_x \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(\lambda_y \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(\lambda_z \frac{\partial T}{\partial z} \right) = -q^B \quad (2)$$

where q^B is the rate of heat generated per unit of volume.

The following conditions should be considered on the surface of the body:

$$T|_{S_T} = T^S, \quad \lambda_n \frac{\partial T}{\partial n} |_{S_q} = q^S \quad (3)$$

where T^S is the known surface temperature on the S_T ; λ_n is the thermal conductivity of the body; n is the coordinate axis in the direction of the unit vector normal to the surface; q^S is the heat flux input on the surface S_q , i.e. the heat transferred through the unit area of the surface; $S_T \cap S_q = S$, $S_T \cup S_q = 0$.

For the given system the type of imposing boundary conditions is considered. The temperature is specified at nodes, along osculating ribs of model elements, and over the outer planes. It should also be noted that convection depending on the body surface temperature and the environment temperature is another important boundary condition. In the case of linear boundary conditions,

$$q^S = \alpha(T_B - T^S) \quad (4)$$

where α is the convective heat transfer coefficient; T_B is the specified temperature of the environment, which is known, but the surface temperature T^S is unknown.

The application of the finite element method when solving heat problems is outlined in detail elsewhere [20]. Based

on the given mathematical model, this method enables us to obtain numerical data describing the temperature field, i.e. the distribution of temperature at all points of some spatial domain at a given moment of time. The choice of the calculation scheme depends on the shape and dimensions of the body and the position of boundaries.

To study the thermal processes taking place in the powder material of interest during its sintering, a small and representative part of the sintering system was considered. Thus, the calculations were made for zones (Fig. 1) comprising 20 powder particles of copper (1 in Fig. 1), graphite (2) and PTFE (3), two electrodes (4) and metallic substrate (5). Particle sizes of all powders are the same and equal 50 mm, while the numbers of particles of individual materials correspond to their concentrations in powder mixtures. Two different randomly arrangements of particles were assumed and considered, signed as "I" and "II".

For Table 1 the data of materials' properties were gathered. These data were used for simulating the heat transfer. The following boundary conditions were imposed: the temperature of external ribs of the electrodes-punches – 770 K, the temperature on contact points between metallic particles and on contact points between metallic particles and the electrode – 1073 K; the temperature of PTFE particles was assumed as 698 K, which is an onset temperature of thermal-oxidative destruction of PTFE [21].

TABLE 2

Data used for the thermal state calculations of the investigated materials during their electrocontact sintering

Component	Material	Thermal conductivity λ , W/(m×K)	Specific heat c , J/(kg×K)	Density ρ , kg/m ³
Electrode	Aluminum bronze	47	0.42×10^3	8.7×10^3
Metallic substrate	Electrical copper	395	0.41×10^3	8.94×10^3
Metallic matrix	Copper powder	390	0.39×10^3	8.93×10^3
Polymer filler	PTFE powder	0.26	0.92×10^3	2.1×10^3
Graphite filler	Graphite powder	51	1.61×10^3	2.3×10^3

ELCUT software designed for simulating the physical fields was used to calculate the effects of the composition and arrangement of the metal-polymer powder system on the thermal state of the metal-polymer-graphite powder thin layer deposited on a bulk metal substrate, when subjected to the electrocontact sintering.

5. Results and discussion

To simulate the thermal state of the system comprising the thin layer of copper-PTFE-graphite powder mixture and a bulk copper substrate during electrocontact sintering, the temperature fields appearing in the system were calculated. Because of non electrical and very low thermal conductivity of PTFE, it was

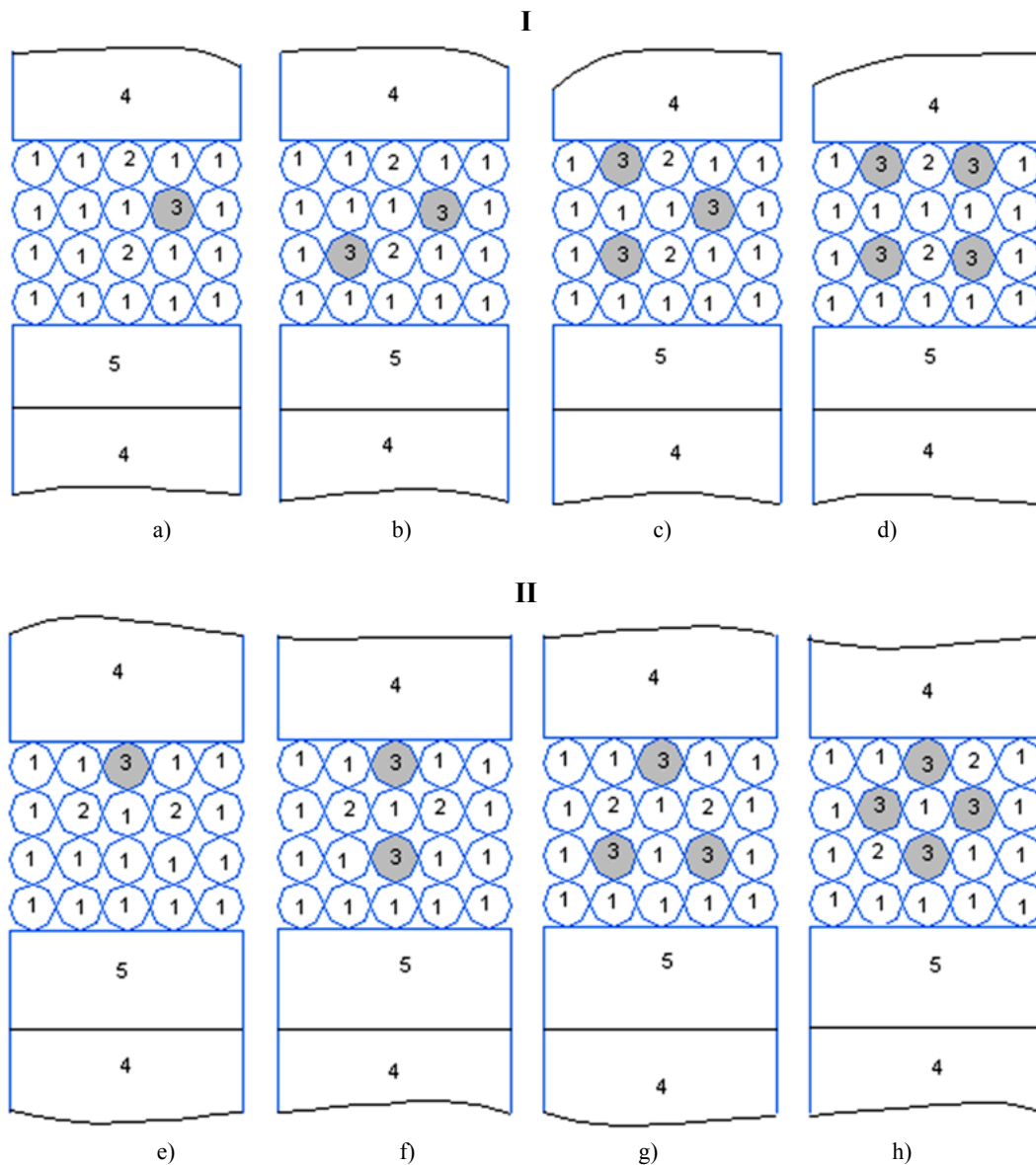


Fig. 1. Schemes used for simulating the thermal state of sintering zones of metal-polymer-graphite-bulk substrate systems subjected to electro-contact sintering: graphite concentration – 5 mass% for all powder mixtures, contents of PTFE filler – in a) and e) 2 mass%, in b) and f) 5%, in c) and g) 7%, in d) and h) 10%. Note the different arrangement of powder particles in upper (I) and lower (II) rows. Particles: 1 – copper, 2 – graphite, 3 – PTFE. Electrodes – 4, copper plate – 5

expected that the polymer particles may have the decisive influence on the temperature distribution. Figure 2 demonstrates the effects both of PTFE particles concentration and their arrangement within the layer on the temperature fields. In fact, it can be seen that the number of copper particles that are fully heated up to 1073 K (isothermal sintering temperature of the system) decreases when the concentration of PTFE particles rises. In this case both general thermal loading of the powder layer and that of the upper electrode is reduced. Thus, the temperature of the upper electrode drops considerably which, in turn, affects essentially the temperature of particles and heat transfer in the layer (Fig. 2-I).

At low PTFE particle content of 2 mass% (Fig. 2-I-a) the temperature distribution in the sintered powder mixture layer is, in general, uniform. However, at contact points between PTFE and copper particles, the temperature of the latter is reduced. In layers containing more, i.e. 5 and 7 mass%, of nonconductive

polymer particles (Fig. 2-I-b and 2-I-c) the number of metal-metal contacts decreases, which results in a smaller amount of heat generated, and thus, in a lower number of copper particles heated up to the nominal sintering temperature. It can be expected, therefore, a lower mechanical strength of the sintered metallic matrix and, of course, of the composite layer. At all contact points the estimated temperature reaches only 829-878 K. As a consequence, further increase of polymer concentration in the powder mixture up to 10 mass% (Fig. 2-I-d), the negative influence on heat generation and heat transfer and, in this way, on sintered properties is enhanced.

Considering the sintering process of the powder layer with arrangement II of the PTFE particles (lower row in Fig. 2), it can generally be stated that the isotherm pattern indicates some higher temperatures of the metal particles than those observed for arrangement I systems.

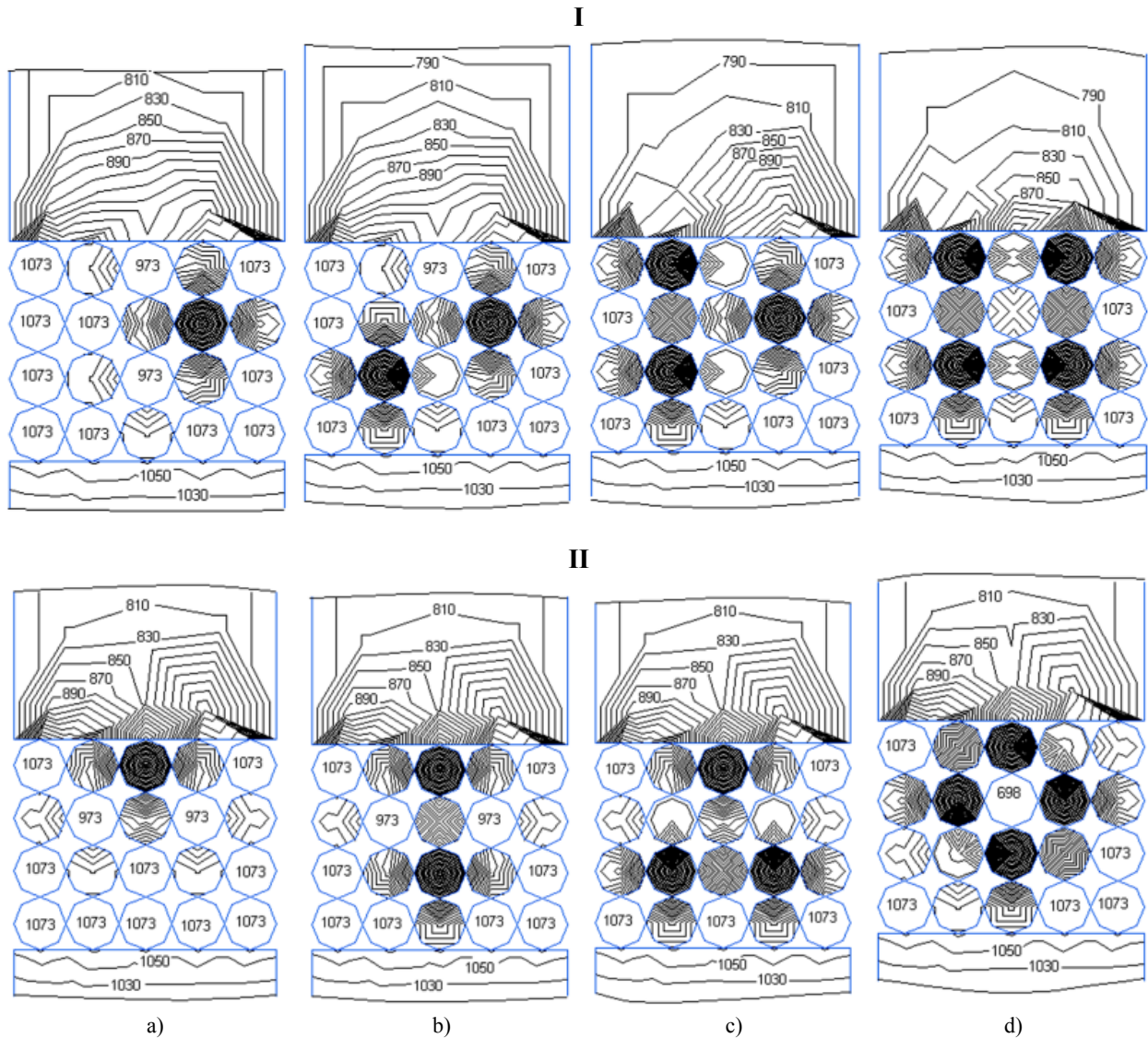


Fig. 2. Schematic representations of temperature fields in sintering zones of copper-polymer-graphite powder mixture layers on a copper substrate: graphite content 5 mass%, polymer filler content: a) – 2 mass%; b) – 5; c) – 7; d) – 10 wt.%; Note the different arrangement of powder particles in upper (I) and lower (II) rows. PTFE particles marked as dark grey

To understand more comprehensively the mechanism of thermal state variations of metal-polymer powder mixture, the distribution of heat transfer through the layer during its sintering should be considered (Fig. 3). In general, the intensity and direction of the heat flow is strongly influenced by the polymer particles content and their distribution. Furthermore, the heat flow is directed towards the polymer particles.

It is significant that with increasing PTFE content in the powder mixture from 2 to 10 mass% the heat flow is redistributed and its intensity decreases (Fig. 3-I), which is clearly marked in layers containing 7 (Fig. 3-I-c) and 10 mass% (Fig. 3-I-d) of PTFE particles. A similar situation arises when the heat flow is redistributed in the metal-polymer layer containing polymer particles of modified arrangement (Fig. 3-II). It is worth adding that the modified arrangement of PTFE particles is preferred in view of the thermal state of the powder mixture during sintering and the need to maintain the hereditary structure of the polymer filler. At higher PTFE contents in the powder mixture that un-

dergoes an electrocontact sintering, the thermal severity of the system is reduced, just by the polymer particles, which inhibits their thermal-oxidative destruction.

The usefulness of the theoretical simulations of the thermal fields for the production of the electrocontact sintered layered antifriction materials was increased by measurements of tribological properties of sintered specimens. As it can be seen in Figure 4-a, the PTFE concentration in the sintered layer is beneficial for the reduction of the friction coefficient from 0.26 at 1 mass% of polymer content to 0.13 at 7%. Further rise of the PTFE content up to 10 wt.% affects insignificantly the friction coefficient of the layer (0.11).

Figure 4-b demonstrates the minimum of wear rate of 0.1×10^{-9} for the material containing 7 mass% of PTFE. Usually, the tribological behaviour of any material is determined by the competition of several factors. In the case of the sintered metal-polymer materials, wear rate is mainly influenced by their composition, porosity and bond strength of the metallic

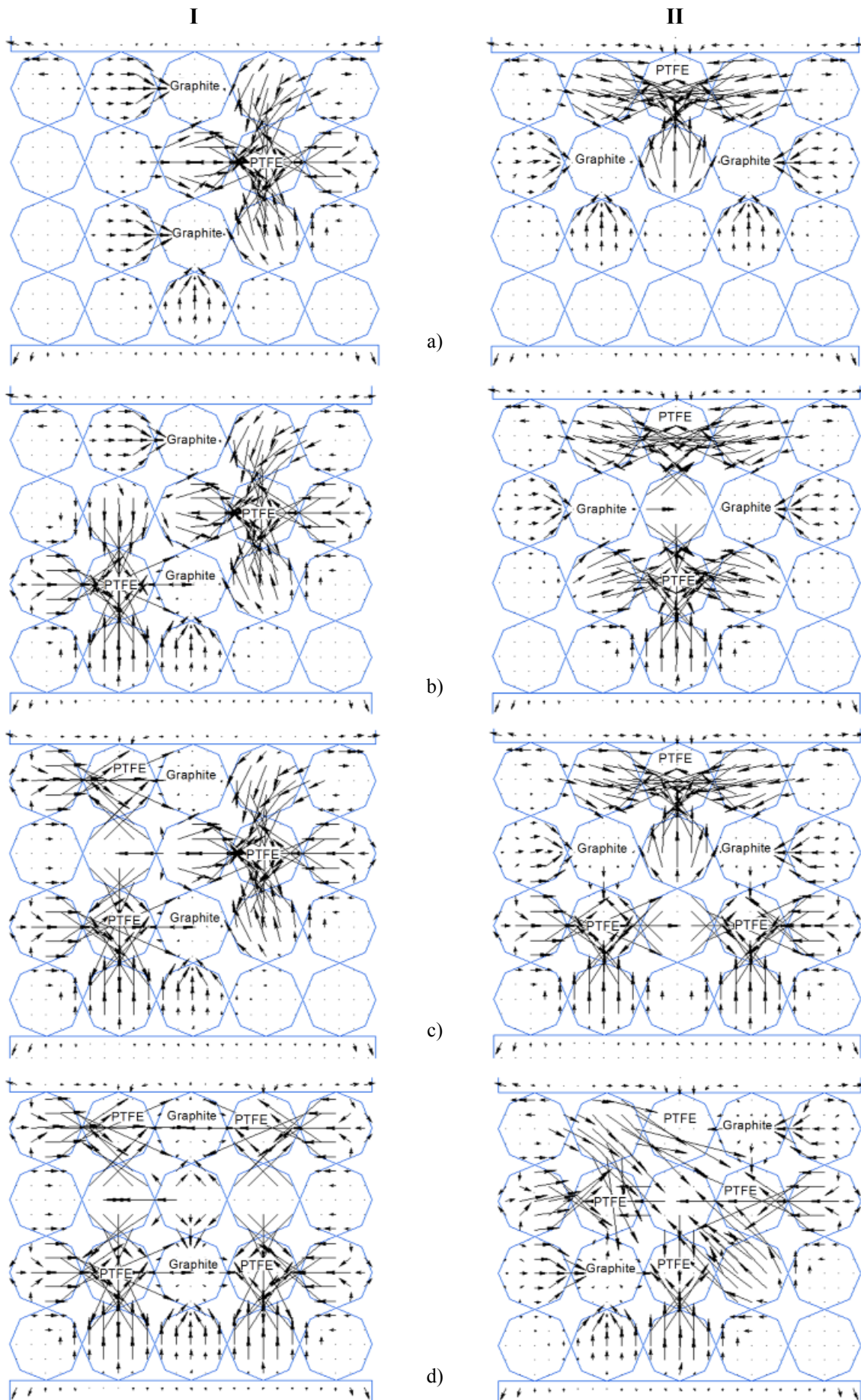


Fig. 3. Distribution of heat flow during sintering of metal-polymer powder mixture layer containing 5 mass% graphite and different polymer filler contents: a) – 2 mass%; b) – 5%; c) – 7%; d) – 10%. Arrangements of PTFE particles I and II correspond to those shown in Figure 1

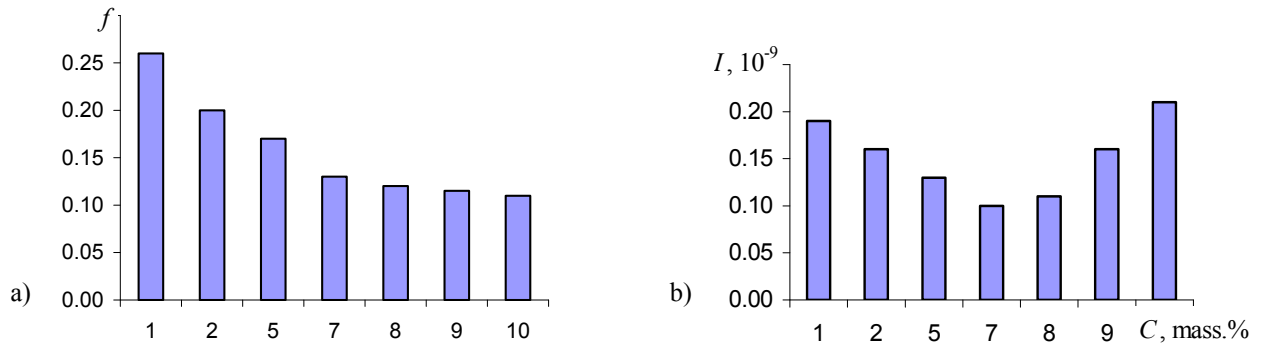


Fig. 4. Friction coefficient (a) and wear rate (b) of the sintered copper-polymer-graphite layer on a copper substrate as a function of PTFE content

matrix. Considering the composition, not only the type and contents of constituents, but also their arrangement have to be taken into account. In particular, the presence and distribution of the polymeric and lubricating filler and its stability within the metallic matrix are of special importance. Of course, the final sintered properties are also affected by the manufacture conditions which, in turn, influence the formation of thermal fields during electrocontact sintering. Furthermore, the chosen production parameters should preserve the initial properties of the polymer, even though the temperature of its degradation is lower than the temperature required for effective sintering of the metallic matrix. It should be noted that, because of the strongly reduced time of consolidation, electrocontact sintering is very useful for metal-polymer powder mixtures.

To explain the wear behaviour of the investigated materials, their microstructures were examined. In Figure 5 the representative SEM microstructures are shown. It can be seen that the thermal-oxidative destruction of this component is limited (Fig. 5-c vs. 5-a and 5-b) for the same technological regimes of electrocontact sintering in materials of higher polymer content, which is of particular importance regarding the friction and wear properties of the sintered composite layer.

Microstructure examinations have also revealed that the concentration of PTFE component in the sintered materials is lower than that in the starting powder mixtures. The amount of loss is influenced by the initial concentration of polymer: in materials containing 2 and 5 mass% of PTFE in the powder

mixture, due to electrocontact sintering, the polymer content is reduced by 30-40%, in the case of the powder mixture with 7% PTFE – by 10-15% and for 10% PTFE it does not exceed 5%. It is also noticeable that, with increasing PTFE content in the initial powder mixture, the porosity of the sintered layer is lowered: porosity of the sintered layer made of powder mixture containing 2 and 5 mass% of PTFE is about 8-9%, for that made of 7% PTFE mixture – 4-5% and for 10% PTFE – 2-4%. Both, partial loss of the polymer and porosity of the layer, are influenced by the thermal-oxidative destruction of polymer particles developed during electrocontact sintering. However, thermal state of the material is responsible for the extent of polymer destruction. As it was already indicated by the simulation procedure, the temperature distribution and, in general, thermal fields, are determined by the polymer content and its arrangement. Thus, in the case of materials investigated, the polymer constituent should be recognised as a factor affecting the sintered properties, not only by its presence in the final material, but also by its influence on the modification of the sintering process itself.

Based on microstructural observations, the high friction coefficient and low wear resistance of sintered layers produced from the powder mixtures containing from 1 up to 5 mass% of PTFE filler, may be explained by its significant loss during electrocontact sintering. The higher concentration of the polymer in a sintered layer is beneficial in view of its friction behaviour, represented by the low friction coefficient. From the other side, however, at higher PTFE content, the mechanical strength of

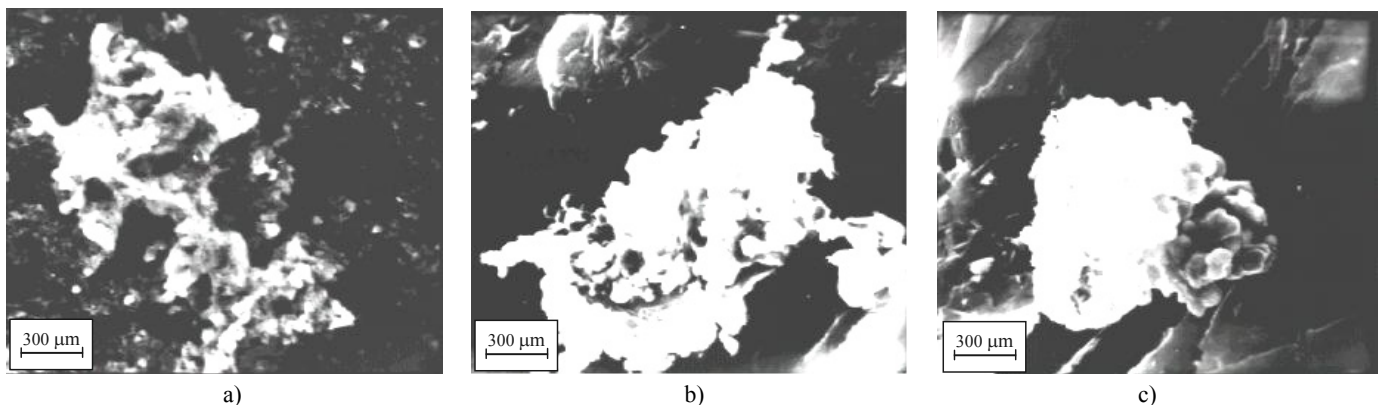


Fig. 5. Micrographs of PTFE particles showing their thermal-oxidative destruction occurring during electrocontact sintering in materials with different polymer content: a) – 2 mass%; b) – 7%; c) – 10%

the sintered layer becomes low, which results in enhanced wear. Thus, the intermediate starting concentration of 7 mass% of PTFE in the powder mixture seems to be optimal because the sintered layer then produced shows the best combination of low friction coefficient and low wear rate.

6. Conclusions

It was shown that electrocontact sintering is a possible method for the fabrication layered antifriction components comprising a copper plate as a substrate and a copper-PTFE-graphite composite as a sliding layer. In the case of metal-polymer powder mixture used for fabrication the self-lubricating components, the main advantage of sintering in this way is connected with the limited thermal-oxidative degradation of the polymer.

Theoretical simulations related to the thermal state of the metal-polymer powder mixture layer deposited on the bulk metal substrate during electrocontact sintering are useful to optimise the composition of the starting powder mixture in relation to the tribological properties of the sintered material. The concentration of the polymer particles and their arrangement in the powder mixture are responsible for the shape of thermal field forming in the material during sintering and thus, for the metallic joints development between copper particles from one side, and for the polymer degradation from the other. Therefore, the tribological properties of the final sintered layer result from the competition between both the mentioned processes. The best combination of a low friction coefficient and low wear rate was obtained for the composite layer produced from the powder mixture containing 7 mass% of PTFE. The thermal field appearing in this material produces metallic matrix of sufficient mechanical strength and is beneficial for the polymer, in terms of its initial properties preservation.

Based on theoretically generated thermal fields, the microstructures of the sintered copper-PTFE-graphite layers may be predicted with a good agreement. The same is also valid for the tribological properties. Both suggest the usefulness of the method used for the heat transfer simulation in the metal-polymer powder mixture layer during electrocontact sintering.

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