FUNDAMENTALS OF TECHNOLOGY OF ELECTRIC CONTACT SINTERING OF NANOSTRUCTURED METAL-POLYMERIC COATINGS OF TRIBOTECHNICAL PURPOSE

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Model-theoretical approaches to optimization of structure-technological conditions of electrocontact sintering of metal-polymer coatings are presented. It is shown that application of methods for computer simulation of zones of powder composite materials formation based on principles of mesomechanical approach using structural models, adapted to wide range of technological parameter values and properties of powder system initial components, allows determining the dependencies of effect of technological factors and structural peculiarities as well as characteristics of initial components of dispersed powder systems on processes of sintered layer structure formation. At that, consideration of local effect of thermal factors and internal stresses, appearing in process of coating formation, has the defining importance. 4 Ref., 1 Table, 9 Figures.

Keywords: *electrocontact sintering, metal-polymer composite coatings, copper matrix, computer simulation, sintering parameters, structure-technological factors, coating formation*

Application of the composite self-lubricating materials, nanostrucutred by carbon nanotubes and nano-onions, and coatings, based on powder cooper matrix [1], in friction assemblies, is a perspective direction for increase of service life and expansion of loading-speed ranges of machine and mechanism operation. However, introduction of polymer fillers and carbon nanostructures directly in powder charge, using known technological methods, and obtaining of quality metallic matrix-based materials by traditional methods of the powder metallurgy is significantly complicated due to low melting temperatures and heat resistance of polymers. This problem can be solved by electrocontact sintering method [2, 3] relating to series of high-speed and high-energy methods for production of materials and coatings from powder composites. Thus, its main peculiarity lies in the possibility of obtaining of coatings from powder materials with different physico-chemical properties.

It should be noted that properties of the composite materials with metallic matrix are caused by effect of a number of factors, i.e. properties, quantity and type of matrix and filler; type and nature of filler distribution in the matrix; composite structure and technology of its production; external impacts. Therefore, information about mechanisms, stipulating presence in the composite of that or another properties, possibility of prediction and regulation of nature of heat-transfer and structuring process development in the course of contact interaction of dispersed components of the metal-polymer systems, in particular, at high-speed heat impact by electric current, will allow rational application of existing composite materials and creation of new ones with high level of service characteristics [4].

Serious problems appear in process of formation of structure and properties of nanofilled metal-polymer powder coatings. They are related with the fact that powder metallic matrices and dispersed inclusions receive different types of thermal stresses depending on level of temperature effect and heat evolution type, determined by technological and structural factors, at high-speed impact by electric current. It is reasonable to consider such powder systems as a structural sequence, including dispersion matrix, contact interaction zone and dispersed filler. Therefore, investigation of thermal-stressed state of nanostructured metal-polymer dispersed systems at high-speed impact by electric current and determination of dependencies of structural transformations in zones of metal-polymer contact interaction is sufficiently complex and unconventional task from point of view of thermomechanics of adaptive materials.

Model-theoretical approaches to optimization of parameters of powder coating electrocontact sintering. One of the important technological parameters of powder composite electrocontact sintering is a sintering time which to significant extent influences the nature of processes of structure formation in powder layers and determines the strength characteristics and quality factors of the materials. The time of electrocontact sintering of metallic powders and composite coatings on their basis has also significant influence on the nature of accompanying electrophysical processes in powder layer. In particular, it affects the level of influence of pinch effect, which can result in distortion of surface form of powder layer, as well as skin-effect, generated by electric current and appearing in metal. The latter lies in a displacement of line of electric current passage to the surface of current conducting element and can result in preferred powder sintering on a periphery of powder layer. At that, appearance of impact waves and their dissipation is possible during release of energy at electric current passage through the powder system. In this connection optimization and determination of efficient time for sintering of powder compositions are sufficiently important in development of technology for formation of composite powder coatings by electrocontact sintering. Such a time provides for achievement of temperatures of powder system sintering and set strength characteristics of the metallic matrix.

The model-theoretical investigation of appearing physical processes was carried out in order to determine the optimum time for sintering of powder thin-layer coatings, taking into account nature of effect of some factors indicated above. Procedure for simulation of stages of electric current passage through mesofragment of bulk powder copper layer and computer structural models of zone of contact interaction electrodes — powder layer were developed for that. They describe thermal and stress-strain state of the materials during external impact as well as allow observing the development of electrodynamic and thermal processes in the mesofragments of powder layer, formed by electrocontact sintering, in real time.

The investigations were carried out for the case of coating formation with 300 μm thickness of bulk layer from copper powder of PMS-1 grade of 100 μm particle size on a surface of copper substrate using electrodes, manufactured from M1 grade copper, when electric current density makes 400 A/mm^2. The algorithm for solving of specified problem is the following, namely detailed description of model with statement of investigation object and specification of bonds of system components; model formalizing; model programming with statement of selected means; testing of the model and receiving of reliable results. The table shows the physical characteristics of materials necessary for simulation. Temperature resistant coefficient for copper corresponded to 0.0068 deg^{-1} value and heat-transfer coefficient made 5.2 W/m^2 deg at 0.2 m/s of velocity air flow for closed spaces.

In general case, if the electric current is passed through the powder layer, the whole process can be divided on a number of stages and consider sintering of powder material on each stage as a separate process, the initial parameters of which are the final calculated parameters of a previous stage.

The first stage of up to 0.3 s duration has significant importance in electrocontact sintering. Rapid current increment takes place when applying difference of potentials to sintered powder layer. The time during which current increment takes place has no dependence on form and cross-section area of pressing, but at the same time depends on its height, namely rise of the height promotes increase of the increment time. However, it should be noted that the time of current increment significantly reduces with the increase of applied force and supplied stress.

The typical peculiarity of the first stage is preferred heat evolution on interparticle contacts, caused by current passage through the surface low-conductivity layers (Figure 1, *a*).

Properties of calculated model elements for mesofragment of electrocontact sintering zone of powder layer

Model element	Material	Thermal conductivity coefficient λ, W/(K·m)	Specific heat capacity *C*, J/(kg·K)	Specific electric resistance ρ, Ohm·m	Density γ, kg/m^3
Electrode	Copper M1	390	$0.38\cdot10^3$	$1.68\cdot10^{-8}$	$8.93\cdot10^3$
Powder	Copper PMS-1	365	$0.39\cdot10^3$	$1.6\cdot10^{-8}$	$7.2\cdot10^3$
Oxide layer	Cu_2O	1.013	$0.429\cdot10^3$	$2.14\cdot10^{-4}$	$6\cdot10^3$
Pores	Air	0.027	$1.009\cdot10^3$	–	1.293

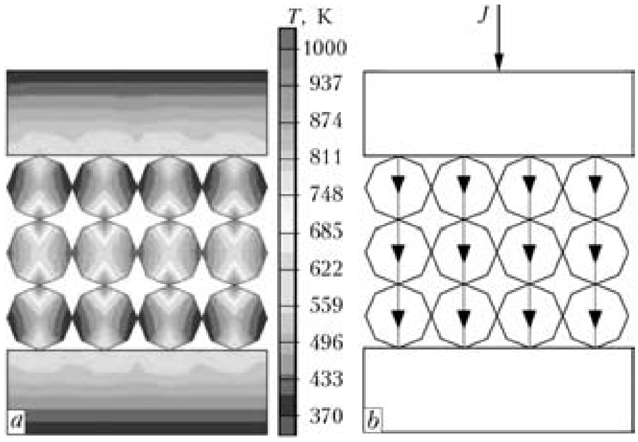

Figure 1. Results of simulation (*a*) and scheme of electric current passage (*b*) on the first stage of process of powder copper layer electrocontact sintering at sintering time 0.3

At the some time possible formation of sparking should be noted. The electric current on the first stage flows parallel to electric field intensity lines forming at that separate chains (Figure 1, *b*). At that, current in each chain has approximately similar value. Thus, it should be noted that there is no heating of the particles at the beginning of sintering process and preferred heat evolution takes place at contact resistance. The average temperature of powder layer on the first stage does not exceed 573–623 K. In the case, when intensity of heat evolution at current passage through the powder layer exceeds the heat input spent for metal heating in zone of contact interaction of particles in solid phase up to melting temperature, as well as for convective heat exchange with ambient environment and heat transfer in the electrodes, then part of metal can liquate.

On the second stage, the temperature of contact surfaces of powder material particles significantly exceeds the temperature of particles and it is enough for melting of oxide film and part of the metal due to heating taking place durin electric current passage according to Joule–Lentz's law. Quick evolution of large quantity of heat energy in vicinity of the interparticle contact can result in chipping of the smallest particles being in solid phase. However, this phenomenon has not significant effect on sintering process. Repulsive forces, appearing as result of heat expansion, reduce more than 10 times in melting of oxide layer and insignificant part of metal being in contact interaction. The liquid-metal bridges are formed as a result of part of metal melting. It should be noted that the specific electric resistance of liquid copper exceeds the specific electric resistance of solid copper in several times. In particular, heating of copper to 970 °C promotes rise of specific electric resistance up to $9.6 \cdot 10^{-8}$ Ohm·m. Loss of stability and destruction of the liquid-metal bridges take place during temperature increase, reduction of pressure and, as a consequence, increase of electric resistance in particle contact. This inevitably leads to change of path of electric current over powder layer, and current passes through unmelted contacts which have lower resistance. Thus, similar liquid-metal bridges appear on other contacts of the powder particles.

Duration of the second stage starts on 0.3 s and finishes on 0.6 s. At that, results of computer simulation showed that the average temperature in powder layer on this stage exceeds 623 K. Since, the second stage of electrocontact sintering of powder material is characterized by large number of changes in electric current paths, it should be divided on several stages during simulation.

The paths of electric current lines and model of thermal state of mesofragment of zone of powder layer electrocontact sintering on the first step of the second sintering stage are shown in Figure 2, Figure 3 shows the second step of the

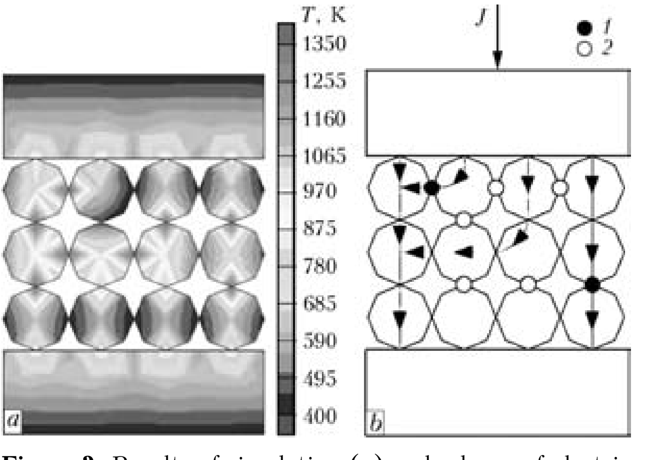

Figure 2. Results of simulation (*a*) and scheme of electric current passage (*b*) on the first stage of the second step of process of powder copper layer electrocontact sintering at sintering time 0.4 s: *1*, *2* — contacts in which metal is in solid-liquid and liquid state, respectively

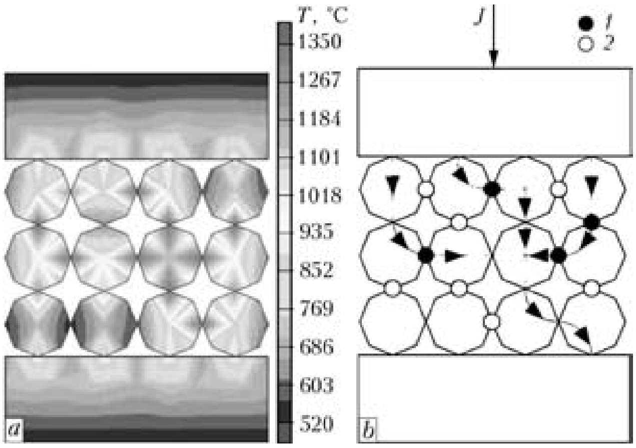

Figure 3. Results of simulation (*a*) and scheme of electric current passage (*b*) on the second stage of the second step of process of powder copper layer electrocontact sintering at sintering time 0.5 s (marks *1*, *2* are the same as in Figure 2)

second stage and Figure 4 represents the third step of the second sintering stage.

It can be seen in the represented models that the electric current paths cover all the contacts at increase of sintering time, melt them, thus promoting joining of cooper particles and sintering of powder system. At that, the results of computer simulation of thermal state of copper powder layer in the process of electrocontact sintering showed satisfactory correlation with the results of experimental investigations. As current has passed through the interparticle contacts, their melting is accompanied by increase of electric resistance and described above process repeats again up to melting of all metal particles or stop of current supply. The metal in particle contact areas transforms in molten or much softened state. The particles of powder system begin insignificant displacement relatively to each other that result in compacting of composite material.

Insignificant quantity of liquid phase is formed and intensive sintering of powder system takes place as the result of processes described above. Increase of powder system average temperature, which achieves 1073–1123 K values and corresponds to temperatures of copper matrix sintering, should be noted on the final third stage which starts on 0.6 s and finishes in 1.1–1.3 s time range. Finishing of the processes of powder layer compacting by means of plastic deformation (Figure 5) also takes place on this stage. Increase of powder system pressure by force application to the electrode promotes rise of the stress in particles and their elastic deformation. After stresses in the particles exceed the material yield strength, their plastic deformation takes place. Material of the particles tends to fill initial interparticle pore space. Density of the material increases as a result. At that same time, reduction of contact resistance between the particles takes place with increase of contact surface. Herewith, reduction of equivalent stresses by Mises, the maximum values of which make around 112–156 MPa, occurs. The cooper metallic matrix,

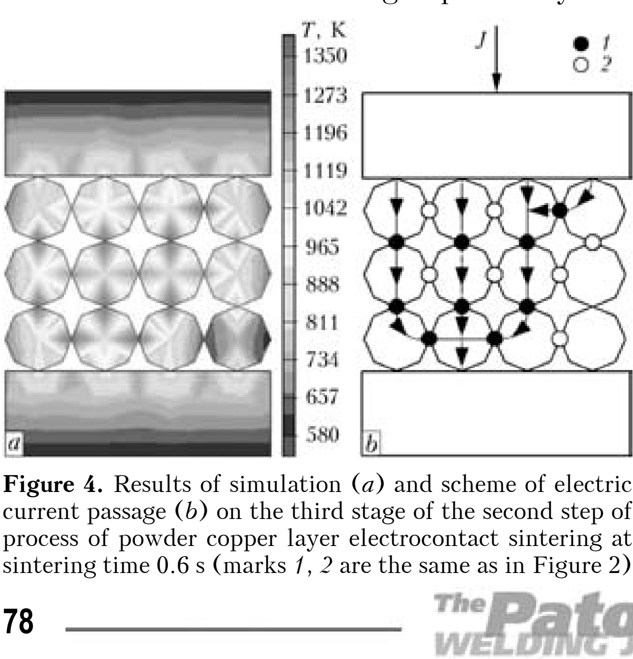

Figure 4. Results of simulation (*a*) and scheme of electric current passage (*b*) on the third stage of the second step of process of powder copper layer electrocontact sintering at sintering time 0.6 s (marks *1*, *2* are the same as in Figure 2)

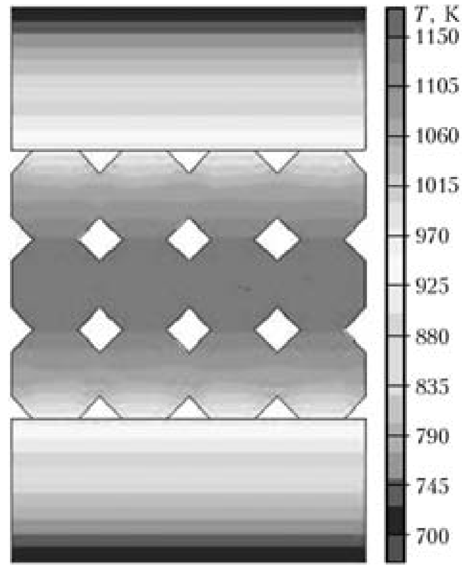

Figure 5. Model of combined thermal and strained state, formed by powder copper layer electrocontact sintering on the expiry of sintering time, making 1.2 s, under effect of 150 N compressive load on mesofragment

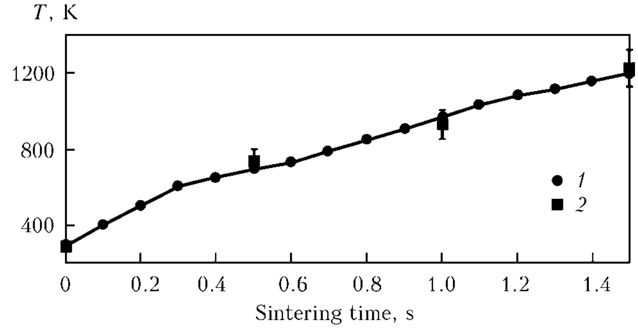

Figure 6. Dependencies of temperature in powder layer on sintering time under electric current impact: *1* — results of computer simulation; *2* — experimental value

having relative density 80–90 %, is formed as a result of electric current impact and pressure application. It should be noted that resistance of pressing increases with reduction of geometry of sintered powder system particles. This phenomenon can be explained by the fact that increase of quantity of specific volume components of the system promotes directly proportional rise of quantity of electric contacts due to what powder layer conductivity is reduced.

Figure 6 shows the temperature dependencies of powder layer, obtained as the result of computer simulation of thermal state of zone of copper powder layer electrocontact sintering using developed structural model. The latter considers structural peculiarities of the formed powder composite as well as results of experimental investigations. Determination of temperature in the powder layer was carried out on specially designed operating prototype of the unit at its joined application with seam resistance welding machine MSh-3207 in mode of spot sintering. Copper powder layer was loaded only by effect of electrode force. Registration of temperature in sintering zone was performed with the help of chromel-alumel thermocouple by electronic potentiometer Memograf with automatic signal processing. It is equipped with RS485 interface for feature determination and data transfer in the computer.

As can be seen, the difference between temperature values, received as a result of experimental investigations and computer simulation, does not exceed 10–15 % in the whole range of changing of sintering time that can be considered sufficiently acceptable in the case of formation of powder layers using given high-speed electrocontact sintering method.

Model-theoretical description of structural-technological factor effect on thermal state of zone of formation of metal-polymer powder copper-based coatings in process of electrocontact sintering. The issues of theoretical description and investigations of processes of transfer and distribution of heat in coating formation zones gain a particular importance in electrocontact sintering of powder metal-polymer systems. At the same time, it should be considered that quick evolution of heat energy in vicinity of the interparticle contact due to electric current passage, and, in particular, when dielectric spaces (air, dielectric filler, oxide film, etc.) are present between the adjacent metallic particles, can result in appearance of different phenomena, determined by electric, thermalphysical and mechanical characteristics of the components. Investigation of thermal state of the electrode-dies also provokes a scientific interest, since dimensions of area of contact with sintered material and nature of powder composite system have significant influence on processes of heat distribution in them. It should also be noted that theoretical description, examination and analysis of temperature distribution fields, temperature gradient and heat flows as well as obtaining of proper investigation results allow optimizing and predicting temperature distribution, heat flows and temperature gradient inside the composite met-

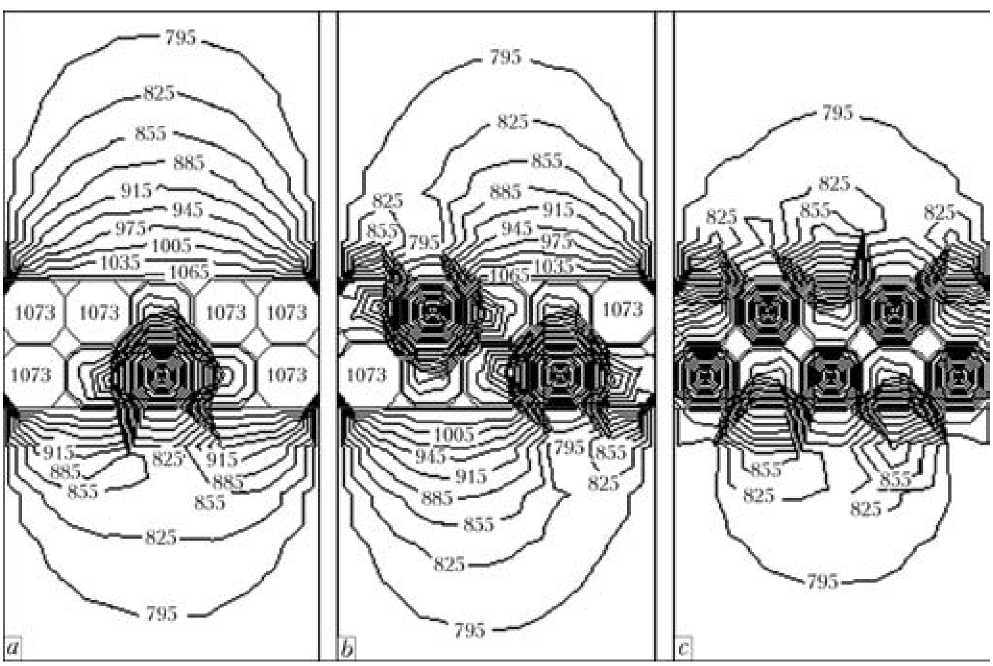

Figure 7. Models of temperature field distribution in mesofragments of zones of metal-polymer powder layer electrocontact sintering with different level of filling of copper matrix by PTFE particles: *a* — 10 vol.%; *b* — 20; *c* — 50

al-polymer powder material at change of structure-technological conditions.

In view of mentioned above, a computer plane-parallel problem of stationary heat transfer was solved for electrocontact sintering of metal-polymer powder systems with copper matrix, when the temperature between two electrodes and in the sintering zone achieves 1073 K, i.e. sintering temperature of copper powder.

Lets' consider the distribution of temperature fields in zone of formation of powder layer for sintering scheme, when two electrodes are in contact with the whole sintered surface of material — copper powder composite and 10, 20 and 50 vol.% of PTFE, equally distributed in the metallic matrix (Figure 7).

Simulation results showed that the largest electrode heating is observed in sintering of composite with PTFE 10 vol.% (Figure 7, *a*) and it is smaller in sintering of composite containing 20 (Figure 7, *b*) and 50 vol.% (Figure 7, *c*). It is also seen that copper particles, having no contact with polymer, are completely heated to 1073 K temperature, i.e. to sintering technological temperature. Surface area of upper electrode which has no contact with PTFE particles, will also be more heated than lower electrode, where break of isotherms is observed. At that, the level of temperature fields in lower electrode in the zone of contact with polymer PTFE particle is 10–15 % smaller, than in the zone of electrode contact with copper particles. The break of isotherms in the electrodes is observed as well in presence of 20 vol.% of PTFE polymer particles (Figure 7, *b*) in sintering zone. Copper particles, contacting with polymer particles, also have lower temperature in comparison with the particles making not contact with PTFE particles. It can be seen that the temperature loading in central part of zone of metal-polymer material sintering reduces with increase of content of the polymer filler in metallic powder matrix at simultaneous displacement of the regions of electrode temperature equilibrium to periphery areas.

If equal quantity of copper and polymer particles are present in the sintering zone (Figure 7, *c*), than certain temperature stabilization in powder metal-polymer composite layer, significant reduction of heating of both electrodes, increase of quantity of zones of isotherm breaking, but insignificant heating of copper particles for quality sintering of metallic matrix are observed.

Mechanisms of evolution and distribution of heat in volume of the metal-polymer powder system and, in particular, on the boundaries of dispersed metal-dispersed polymer have significant effect on processes of composite powder coating structure formation. It is extremely difficult to evaluate the nature of heat flow distribution in volume of the powder metal-polymer systems as well as distribution of temperature fields and temperature gradients on dispersed metal-dispersed polymer interface by experimental methods due to short-term of the electrocontact sintering process. At the same time, investigation and determination of dependencies of heat transfer processes in such powder systems is sufficiently important on stage of their development.

The structure simulation approaches applying finite-element digitization were used for evaluation of properties of powder composite materials of this class, in particular, in zones of their contact interaction polymer-metal, which are more susceptible to temperature difference between the current-conducting copper particles and non-conductive particles of the polymer. Figure 8 shows the models for temperature field distribution in area of investigation of mesofragment of metal-polymer powder system formation zone at different time of electric current impact in the process of electrocontact sintering. It should be underlined that the peculiarity of given problem is consideration of time of staying of composite powder system in the sintering zone, i.e. non-stationary heat transfer problem is solved. It is assumed in accordance to earlier obtained data that the time of electric current impact on metal-polymer powder system in zone of electrocontact sintering makes from 0.3 to 1.2 s. Current intensity, supplied to heat evolution source, is 12 kA.

The detailed analysis of obtained results allowed determining the following. In consideration of the heating case, when the time of sintering is 0.3 s, the temperature in contact zones between metallic particles of metal-polymer powder system achieves 623 K (Figure 8, *a*) and it makes from 601 to 623 K on the rest of surface of copper particles in the investigated mesofragment.

Smoothing of isotherms takes place at removal from the surface of copper particles to their center. Concentration and localizing of large quantity of isolines is observed in areas of copper particle contact that confirms the observable typical reduction of temperature in given area to 530 K at 25 μm distance from the surface of copper particle to its center. It can be seen in area of contact interaction copper particle — PTFE particle that removal from contact surface to the center of polymer particle promotes temperature reduction from 440 to 390 K, whereas temperature in copper particle increases from 440

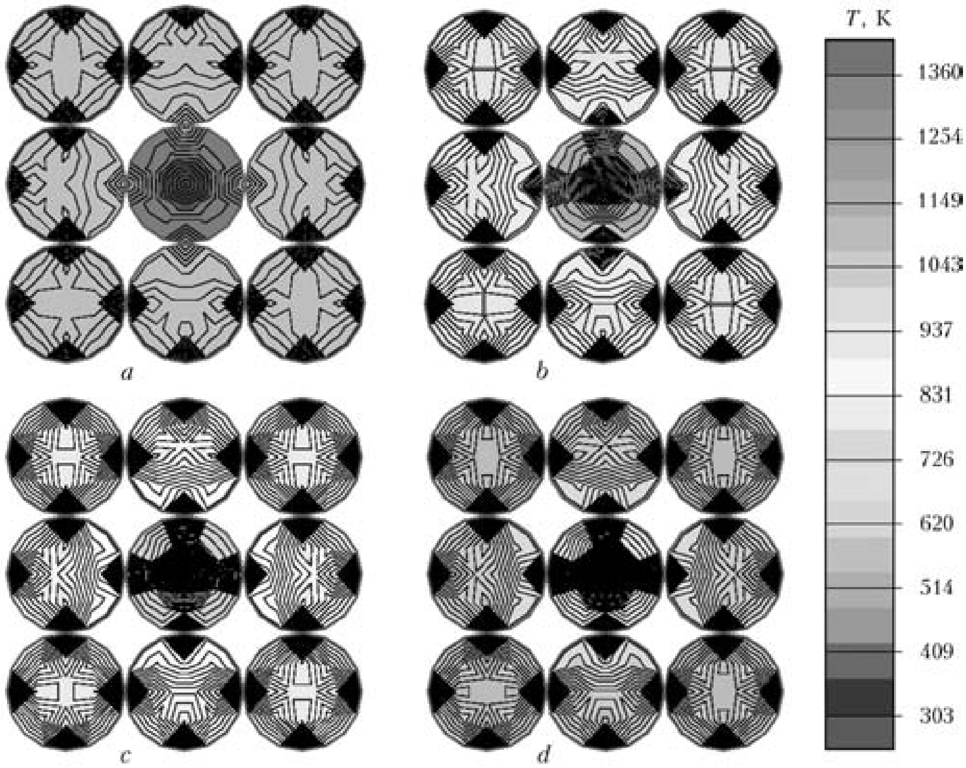

Figure 8. Models of temperature field distribution in zone of contact interaction copper-PTFE at different sintering time: *a* — 0.3 s; *b* — 0.6; *c* — 0.9; *d* — 1.2

to 495 K at consideration of zone of removal from the contact point per 25 μm. At that, the presence of pores in examined mesofragment has significant effect on the level of heat condition in periphery areas.

Increase of level of ohmic heating of metal-polymer powder system is observed at rise of sintering time up to 0.6 s. At that, temperature in zones of contact interaction copper–copper makes around 923 K (Figure 8, *b*) and from 770 to 912 K on the rest of copper particle surface. Change of temperature condition in the copper particles having no contact with PTFE particle occurs in the direction from their surface to the center in such way that temperature at 25 μm distance from its surface makes around 695 K. Reduction of temperature from 584 to 495 K in the direction from the contact surface to the center of polymer particle is observed in area of contact interaction copper particle-polymer particle. At the same time, an opposite picture, characterizing by temperature increase from 589 up to 695 K in consideration of zone of removal from the contact point per 25 μm, is marked in the copper particle.

The temperature in zones of metal-metal contact interaction makes 1223 K (Figure 8, *c*) and from 736 to 1111 K on the surface of copper particles, if metal-polymer powder system is heated during 0.9 s. The temperature reduces at removal from the surface to the center of copper particles, having no contact with polymer particle, and achieves 934 K value at 25 μm radial distance. It can be seen in area of contact interaction copper particle-polymer particle that the temperature decreases to 553 K at removal from the contact surface to the polymer particle center, whereas it rises to 896 K in the copper particle at consideration of zone of removal from the contact point per 25 μm.

When temperature of ohmic heating of powder system achieves 1356 K, that is provided by 1.2 s sintering time (Figure 8, *d*), the copper particles are almost uniformly heated over the whole area up to sintering temperature, corresponding to 1073 K, and areas of local heating up to melting temperature are observed in the points of contact interaction of copper dispersed particles. It is also determined that exceeding of thermal-oxidative degradation temperature of the polymer is observed in local areas of their contact interaction with copper particles at radial distance not exceeding 18–20 μm from the surface of PTFE particle to their center.

The dependencies characterizing effect of time of electrocontact sintering on changing of temperature in typical points of mesofragment of powder metal-polymer system (Figure 9) were built based on obtained results of the model-theoretical investigations.

It should be noted in the conclusion that the proposed model-theoretical approach allows de-

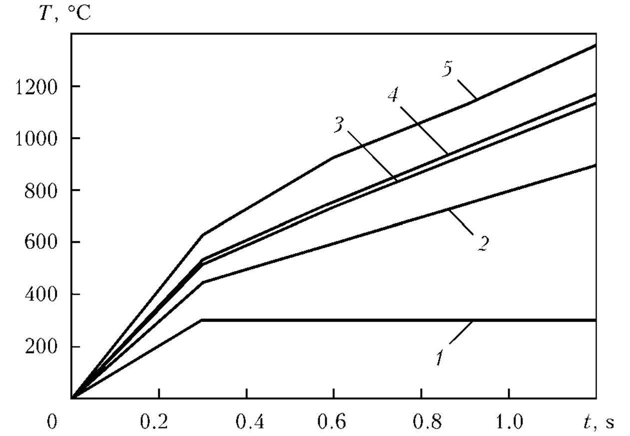

Figure 9. Dependencies of effect of time of metal-polymer powder system electrocontact sintering on temperature change in typical points of composition: *1* — center of PTFE particle; *2* — contact point copper-PTFE; *3*, *4* — center of copper particle, contacting and not contacting with PTFE particle, respectively; *5* — contact point copper–copper

veloping the computer structural models of zones of contact interaction electrodes-powder layer. They describe thermal and stress-strain state of the materials at application of external impact (density of electric current and compression force of the electrodes) under conditions of non-stationary heat transfer. These conditions differ from existing ones by possibility of consideration of effect of electrocontact sintering time, contact interaction of the surfaces and peculiarities of particle structure in powder layer (presence of oxide layer and pore space) on formation of temperature fields, component deformation, temperature distribution and thermal and mechanical stresses. The time of powder system staying in sintering zone at electrocontact sintering, making 1.1–1.3 s, was optimized based on such an approach and complex of carried out investigations at consideration of experimental correlation for specified technological conditions of formation of nanostructured metal-polymer powder coatings with bulk layer thickness 300–500 μm. It provides for the achievement of 1073–1123 K sintering temperature of metallic copper matrix, completion of processes of bulk powder layer compacting by plastic deformation and reduction of equivalent stresses by Mises to 112–156 MPa thickness values in the formed powder coating of 90–100 μm at simultaneous effect of specified loading.

It is shown for the first time that the temperature in diametric section of the copper particles reduces 1.4–1.5 times, at the same time as the temperature in diametric section of the polymer particle decreases 2.8–3.0 times during formation of coatings by electrocontact sintering, when the temperature achieves the values providing extreme conditions of thermal ohmic heating and heat transfer in the powder metal-polymer system. Established effect promotes «relay-race» development of heat transfer processes with appearance of the local thermal stresses in zones of physical contact metal-polymer and concentration of heat energy in surface layer of dispersed polymer particles. Redirection of heat flow distribution takes place due to low values of heat conduction of the polymer filler particles in comparison with the metallic matrix particles as well as high (800–900 °C/s) speed of heating of the composite powder system and short-time of sintering process (around 1.1–1.3 s). This in whole reduces the thermostressed state at dispersed polymer-dispersed metal interface due to what the processes of thermal-oxidative degradation virtually do not develop in the direction to polymer particle center.

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