

Investigation of ceramics based on Cu-Sn powder obtained by plasma dynamic method

Yu Shanenkova, A Sivkov, A Ivashutenko and A Tsimmerman

National Research Tomsk Polytechnic University, 30 Lenin av., Tomsk, 634050, Russia

E-mail: julia_kolganova@mail.ru

Abstract. Composites based on copper matrix are of a great interest in various applications. Copper-tin alloys are intensively investigated due to their thermal and chemical stability in combination with good mechanical properties. This work shows the possibility to obtain Cu-Sn ceramics by spark plasma sintering using nanoscale powders consisting of copper and tin, synthesized by plasma dynamic method. This method is implemented by using a coaxial magnetoplasma accelerator with copper electrodes and adding the solid precursor (tin) in the accelerator before carrying out the synthesis process. The synthesized Cu-Sn powders were investigated by X-Ray diffractometry and transmission electron microscopy. It was determined that the final material consists of phase Cu₄₁Sn₁₁. Using this product, the bulk ceramics samples were obtained by spark plasma sintering at different temperatures (150 °C, 250 °C and 500 °C). The changes in microstructure of copper-tin ceramics in dependence on the sintering temperature were also studied. After analyzing all ceramics samples by X-Ray diffractometry and scanning electron microscopy methods, it was found that the optimal temperature for sintering Cu-Sn ceramics, which was made of the powder synthesized by a plasma dynamic method, was equal to 250 °C at pressure 60 MPa. At these conditions, the ceramics sample had the lowest porosity with the smallest grain size.

1. Introduction

Sliding bearings are widely-used in rotating mechanism of different machines. The lifetime of their work strongly affects the stable operation of the responsible mechanisms. The most common their failure cause is not a breakage but the wear and damage of the working surfaces in their parts. Thus, the solution of the problems connected with the increase in the lifetime of machines depends on improving the durability and reliability of friction units and, in particular, sliding bearings [1].

There is a group of soft metals, so-called babbitt, which are used as materials for bearings [2]. These species include tin (Sn), lead (Pb), cadmium (Cd), antimony (Sb) and zinc Zn, which are characterized by the presence of solid structural components in the plastic matrix. However, these materials have low fatigue resistance. Therefore, there is a necessity to introduce different additives into material composition, used for producing the bearings.

Earlier work [3] describes a method for improving the conformability of the friction pair by using a coating made of soft anti-friction metals such as indium, copper and silver. The most known method for depositing such coatings is a method of electroerosion alloying. Another way to solve this problem is a pre-activation of copper-tin powders to improve the tribological characteristics of Cu-Sn alloy [4]. The authors of the work [5] study the change of tribological properties in materials based on copper-tin with or without the use of lead at hot pressing of samples. Furthermore, the use of intermetallic pair



copper-tin can more efficiently and selectively recover the CO₂ to CO in a wide range of potentials [6].

This paper shows a new unique method for obtaining materials based on tin-copper in a high-speed plasma jet generated by a coaxial magnetoplasma accelerator with copper electrodes [7], as well as the creation on their basis of bulk samples using a spark plasma sintering installation. Change in the density and porosity of the obtained bulk samples based on Cu-Sn, as well as their chemical and phase composition were studied with increasing sintering temperature.

2. Experimental

Plasma-dynamic method is based on a system with a coaxial magnetoplasma accelerator, which is supplied from the capacitive energy storage with the charging voltage up to 5 kV and the charging capacity to 28.8 mF. In such a way, the charging energy can have a value up to 360 kJ [8-11]. A sketch-map of the coaxial magnetoplasma accelerator and the principle of its operation are shown in figure 1.

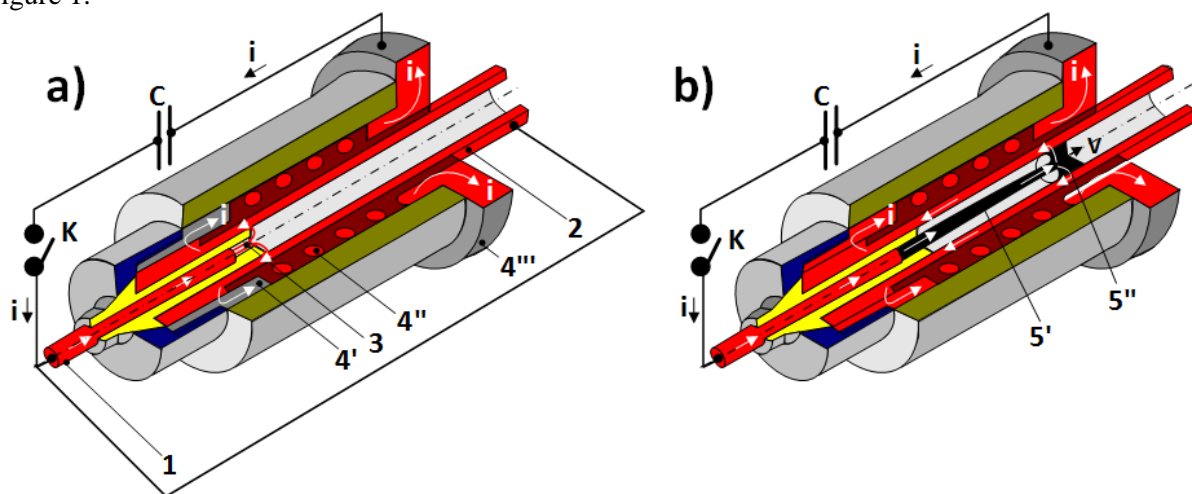


Figure 1. Sketch, elements and principle of operation of coaxial magnetoplasma accelerator: a) initial state; b) state at working: 1 - Central electrode; 2 - Electrode-barrel; 3 - Plasma formation zone; 4 - Inductor (4' – contact cylinder; 4'' – solenoid; 4''' – contact flange); 5 - Plasma structure of high-current discharge (5' – Plasma Z-pinch harness; 5'' – round plasma jumper).

Previous works have demonstrated the possibility to synthesize the nanodispersed powders with different stoichiometric and phase composition [8] using the accelerator. In order to produce the powdered materials based on copper and tin the coaxial accelerator with copper electrodes was used in order to obtain Cu precursor. Before starting the experiment, tin-containing precursor (chips of tin) was put in the plasma formation zone. A working chamber-reactor, which were used to implement plasma-dynamic process, was preliminary evacuated and filled with inert gas (argon) to prevent the saturation of the resulting material by oxygen (avoid product oxidation).

After closing the power keys (K), the discharge current starts to flow through the current channel. After rising the current up to some level, it creates a plasma arc jumper in the plasma formation zone. Due to the high velocity and temperature of plasma copper material is eroded from the wall of the accelerating channel. This copper interacts with tin, which was put into accelerator and converted to plasma state by increasing current. Thus Cu-Sn-containing plasma exits from accelerating channel into the space of the chamber-reactor, where plasma-chemical reaction is implemented. The synthesized product settles down to the wall of the chamber. After one hour, the chamber is opened and the product is collected.

Figure 2 shows the photogram of the plasma flow. The video record was carried out using a Photron Fastcam SA1.1 high-speed camera through the special protective glass. When the capacitive energy storage has the parameters as mentioned above, at the exit of the accelerator the flow speed is maximum and reaches up to 4.5 km/s.

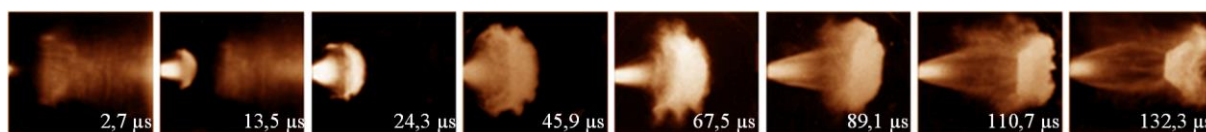


Figure 2. Photogram of plasma flow movement in working chamber.

After collecting the product of a plasma-dynamic synthesis, it was studied by means of X-ray diffractometry (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) methods. Scanning electron microscopy (SEM) images were recorded using a Hitachi TM-3000 scanning microscope with carbon substrate. X-Ray diffraction (XRD) analysis was carried out using a Shimadzu XRD 7000S diffractometer (CuK α -radiation). The database PDF-2 and the software PowderCell 2.4 were used to make full-profile structural analysis and estimative calculations. Transmission electron microscopy (TEM) images of the product were made using a Philips CM-12 microscope.

After that, the obtained nanodispersed Cu-Sn powder was sintered using the installation for spark plasma sintering (SPS 10-4 Advanced Technology). According to literature data [12], the initial sintering conditions were chosen. The resulting product of a plasma-dynamic synthesis was pre-sifted through a sieve (500 mesh). After that, it was laid in a graphite mold under a pressure of 60 MPa and was sintered at a temperature of 150 °C under high vacuum. After receiving the first ceramics sample, it was decided to raise the temperature up to 250 °C (sample 2) and then up to 500 °C (sample 3), which were at the same pressure and in the same atmosphere.

3. Results and discussion

The results of XRD analysis of the product obtained by plasma-dynamic synthesis, as well as reference cards of the estimated phases are shown in figure 3. It is possible to see that the composition of the synthesized material contains such phases like copper Cu (card No. 4-836), the intermetallic copper-tin Cu₄₁Sn₁₁ (card No. 30-510) and lead Pb (card No. 4-686). The appearance of lead in the product can be explained by the fact that tin, which was put in the plasma formation zone, was not a pure product. It has in its composition 10% of lead. The main phase in the product is copper, due to its erosion wear from the surface of the accelerating channel, and the excess mass of submitted material. Also there is the required phase of the intermetallic compound Cu₄₁Sn₁₁. Moreover, it is worth noting that the most intense peaks at 43-44 and 48-50 degrees are sufficiently broadened. Upon closer examination, their separation into two peaks is clearly seen. These broadened peaks include the reflections of both phases (copper and intermetallic Cu₄₁Sn₁₁).

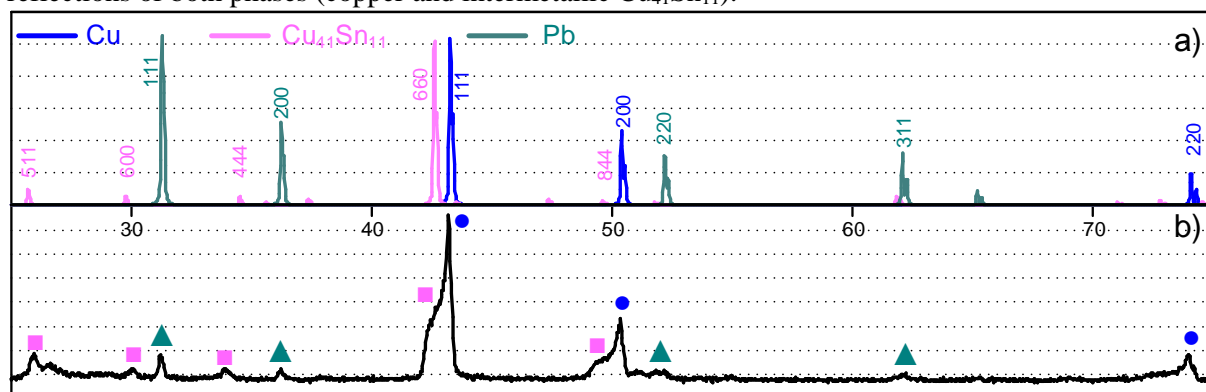


Figure 3. XRD patterns of (a) reference cards, (b) plasma dynamic synthesis product.

In order to investigate the particle morphologies a transmission electron microscope analysis was carried out, the results of which are presented in figure 4. This figure shows that the electronic microdiffraction from the selected area (SAED) has a point-ring character. The phases found at decrypting this diffraction are in a good agreement with XRD data. The bright-field image shows a

typical cluster of particles in the product. Dark-field images are obtained in the light of diffracted beams by shifting the diaphragm aperture in the area of corresponding reflexes. The indices of the reflecting crystal planes are indicated on dark-field images and their numbers are indicated on SAED.

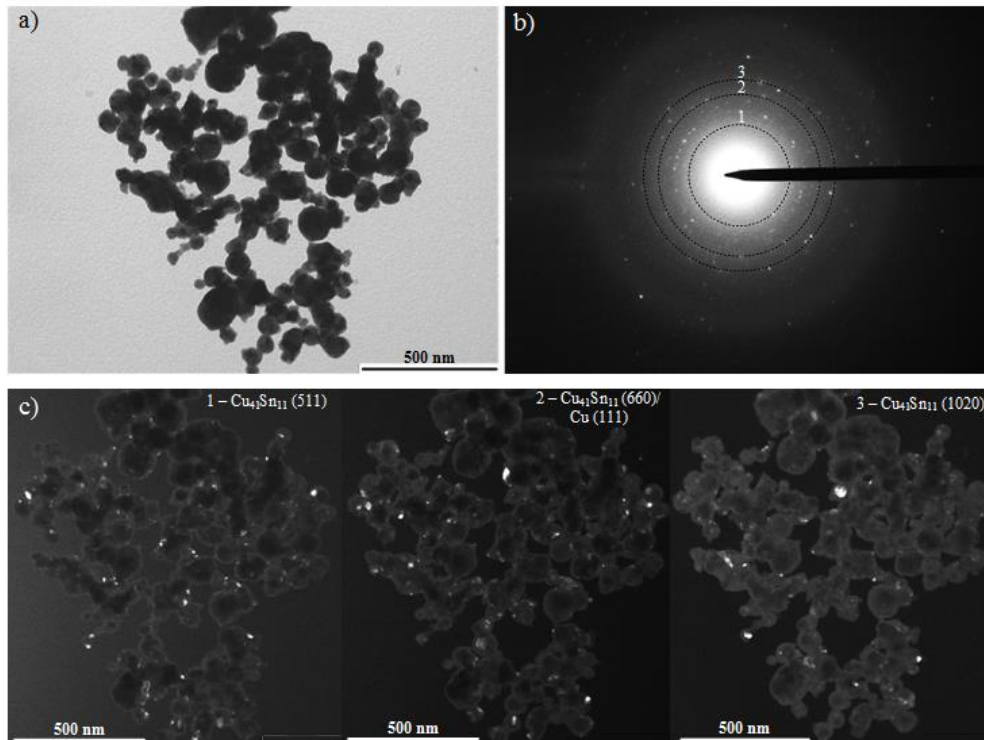


Figure 4. TEM-images of synthesized product: a) bright-field image; b) SAED; c) dark-field images in the light of different reflexes.

The use of transmission microscopy allows accurately finding that the particle sizes in the material range from about 10 nm to ~ 200 nm. The reason for this is the pulsed nature of the plasma dynamic process, during which the current and the electrodischarge plasma parameters change in a very wide range. Such broad particle size distribution can have a positive effect, when creating the bulk materials by spark plasma sintering. During sintering and compacting the fine fraction fills the space between the larger particles that provides obtaining the high-density ceramics.

XRD patterns of samples sintered at different temperatures are presented in figure 5. XRD pattern of the bulk metal material obtained at 150 °C (figure 5b) is almost identical to the diffraction pattern of the initial powder (figure 3b) both at the location of the main peaks and at the intensity of their phases in comparison with each other. Some changes in intensity are seen with increasing in sintering temperature of the bulk material up to 250 °C. In this case, there is an increase in the yield of the phase of the intermetallic compound (figure 5c). However, such increase in sintering temperature on 100 °C does not show significant changes in the product structure. Dramatic changes in XRD pattern are visible for the product sintered at a temperature of 500 °C. The peaks, which are responsible for a phase of the intermetallic compound $\text{Cu}_{41}\text{Sn}_{11}$, almost disappear, while reflexes of lead increase dramatically. It can be explained by a known phase diagram in Cu-Sn system. At temperatures about 500 °C, tin dissolves in copper, and the sensitivity of XRD analysis becomes not enough to clearly identify intermetallic compound.

The results of scanning electron microscopy are shown in figures 6-8. At sintering the powdered product at a pressure of 60 MPa and a temperature of 150 °C (figure 6), a huge number of pores in the obtained sample is seen even with a slight magnification (1.0k). This is also confirmed at the magnification of 5.0k for a more detailed analysis. Moreover, at this magnification it is clear that the grain size varies from several microns to 40 microns. According to this, it can be concluded that the obtained bulk sample under such conditions has not a sufficient quality due to the significant number

of pores. The presence of such amount of pores can be explained by too low sintering temperature of the sample.

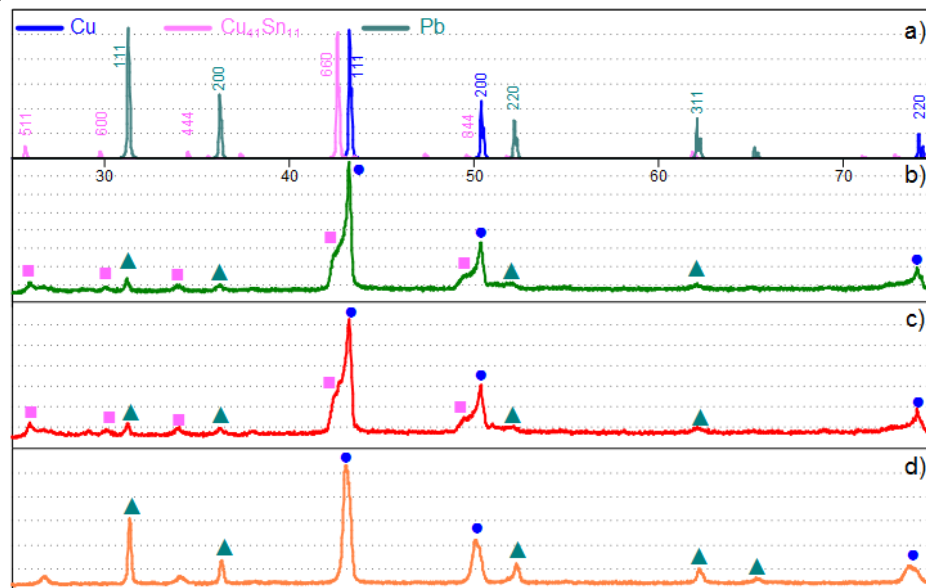


Figure 5. XRD patterns of: a) reference cards of phases; b) bulk sample, sintered at 150 °C; c) bulk sample, sintered at 250 °C; d) bulk sample, sintered at 500 °C.

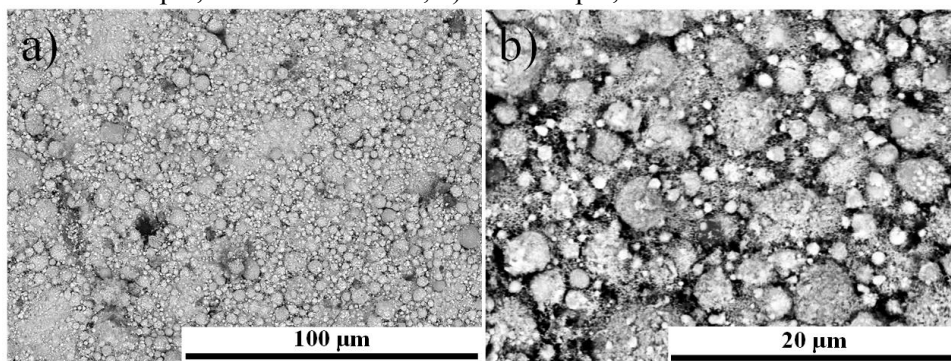


Figure 6. SEM-images of sample sintered at 150 °C with different magnification.

The further increase in the sintering temperature leads to a decreasing in pore amount in the sample and the creation of grain boundaries (figure 7). Nonetheless, the quality of the bulk metal sample was not satisfactory. Thus, the decision was made to increase the value of the sintering temperature up to 500 °C (figure 8).

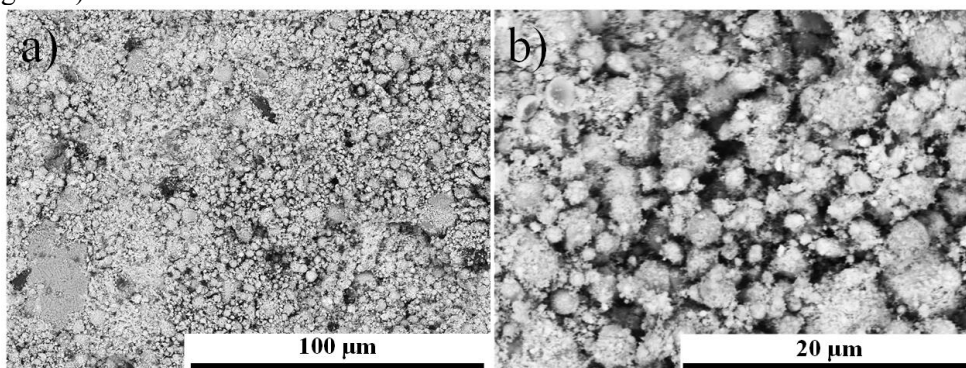


Figure 7. SEM-images of sample sintered at 250 °C with different magnification.

Figure 8a shows that the obtained material has a less porous structure than the previous samples. This product mainly consists of grains of gray color (~ 95 volume %) that are likely to be copper

(according to XRD). However, there are impregnations (white color), which fill material in the intergranular space, reducing the number of pores. The white material seems to be the intermetallic lead, because no reflexes of intermetallic $\text{Cu}_{41}\text{Sn}_{11}$ were found according to XRD data. At higher magnification (x5.0k), it is shown that the grain size varies from 1-2 μm to 20 μm .

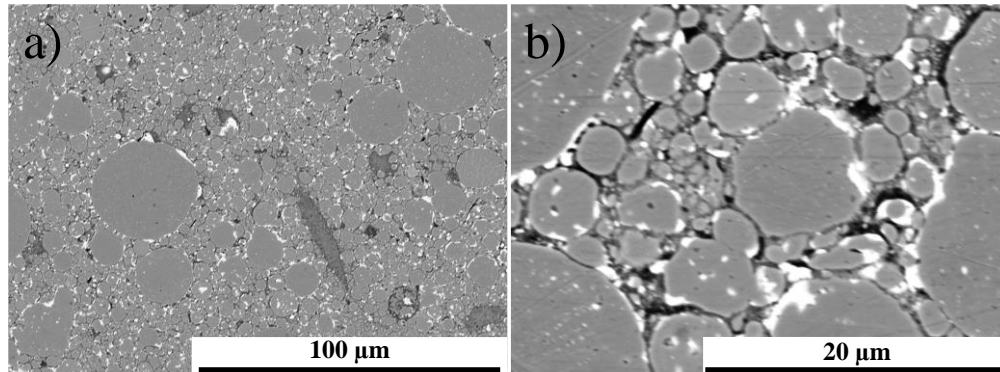


Figure 8. SEM-images of sample sintered at 500 °C with different magnification.

4. Conclusion

As a result of this work, the powder based on copper and tin was obtained using a high-power pulsed system based on the coaxial magnetoplasma accelerator with copper electrodes. Obtaining the intermetallic compound is confirmed by XRD results and analysis by transmission electron microscopy. According to these data, the main phases in the synthesized product are copper and intermetallic compound $\text{Cu}_{41}\text{Sn}_{11}$. The particle sizes vary from 10 to 200 nm.

The results on spark plasma sintering show the possibility to obtain the bulk material on the basis of such synthesized copper-tin powder. The influence of the sintering temperature on the resulting products shows that ceramics, obtained by using plasma dynamic synthesis product Cu-Sn, can be sintered even at 150 °C. However, the mean pressure and low temperature did not allow achieving the high quality of bulk material. The increase in the temperature up to 500 °C reduces the number of pores, thereby increases the sample density. However, the increase in sintering temperature at the same time led to the decrease in the content of intermetallic copper-tin phase. Thus, further research is required to find the optimal conditions of sintering for obtaining high-quality bulk samples, which will save the initial phase composition.

Acknowledgements

This work was supported by the Russian Science Foundation (grant № 15-19-00049).

Reference

- [1] Lebedev O V et al. 2009 *Nauchnyj zhurnal Bratskogo gosudarstvennogo universiteta: Sistemy, metody, tehnologii* **2** 20-23
- [2] Guo X, Zhang G, Li W, Gao Y, Liao H, Coddet C 2009 *Appl. Surf. Sci.* **255(6)** 3822
- [3] Tarelnik V B, Martzinovskij V S, Dzuba A V 2013 *Kompressornoe i jenergeticheskoe mashinostroenie* **1** 49
- [4] Vityaz P A et al. 2014 *Vestnik Vitebskogo gosudarstvennogo universiteta* **26** 110
- [5] Popescu I N, Ghiță C, Bratu V, Navarro G P 2013 *Appl. Surf. Sci.* **285** 72
- [6] Sarfraz S, Garcia-Esparza A T, Jedid A, Cavallo L, Takanabe K 2016 *ACS Catalysis* **6(5)** 2842
- [7] Sivkov A, Shanenkova Y, Saigash A, Shanenkov I 2016 *Surf. Coat. Technol.* **292** 63
- [8] Sivkov A, Ivashutenko A, Shanenkova Y and Shanenkov I. 2016 *Adv. Powder Technol.* **27(4)** 1506
- [9] Sivkov A, Saigash A and Kolganova Y 2013 *Russian Electrical Engineering* **84(8)** 418
- [10] Sivkov A, Saigash A, Kolganova J, Shanenkov I 2014 *IOP Conference Series: Materials Science and Engineering* **66(1)** 012048
- [11] Kuzenov V V, Ryzhkov S V, Frolko P A, Shumaev V V 2015 *Trudy MAI* **82** 1
- [12] Ileskina G S and Psarev V I 1980 *Powder Metallurgy and Metal Ceramics* **19(7)** 463