International Journal of Engineering Trends and Technology
ISSN: 2231 – 5381 /doi:10.14445/22315381/IJETT-V69I10P227

Volume 69 Issue 10, 211-216, October, 2021
©2021 Seventh Sense Research Group®

Electrocontact Alloying As A Method For Obtaining Composite Materials Based On Immiscible Copper-Lead Alloys

Sergey Grigorievich Ponomarev[1], Maxim Vitalievich Kornyushin[1,2], Victor Victorovich Rybalchenko[1,2]

[1]*Mobile Solutions Engineering Center, MIREA-Russian Technological University, Vernadskogo prosp. 78, Moscow 119454, Russia*

[2]*Moscow Polytechnic University, Bolshaya Semyonovskaya str. 38, Moscow 107023, Russia*

[1] ponomariov.2021@mail.ru, [2] kornyushin.m@inbox.ru, [3] rybalchenko_viktor@bk.ru

Abstract - *The fusion zone formation is considered during electrocontact alloying of a copper (Cu) plate with lead (Pb). Under the electric current influence,the low-melting Pb component is rapidly heated in a closed volume, which leads to its accelerated propagation in the copper matrix with the formation of a copper-bronze composite. The influence of the current duration and the specific amount of Pb on the structure of the fusion zone, its size, and the ratio of components in the alloying zone was studied. The possibility of obtaining a concentration of the alloying component from 2 to 70 vol.% in the fusion zone is shown. In this case, the thickness of the doped layer can vary from 0.1 to 3 mm. For example, on a copper plate with a size of 40x40x4 mm, an area with 14x11x0.3 mm was obtained, the composition of which corresponded to the bronze of the CuPb30 brand. The value of the sliding friction coefficient for this region corresponded to a similar value for CuPb30 bronze.*

Keywords — *immiscible alloys, monotectic reaction, adiabatic shear bands, electrocontact alloying, copper-lead composite material.*

I. INTRODUCTION

The development and research of new metal alloys and composite materials are among the most critical topics in metallurgy and materials science. Over the past four decades, progress in modern materials technologies has made it possible to artificially create an increasing number of new metal alloys in systems that do not mix in thermodynamic equilibrium. This possibility of alloying elements between which there are no alloys in nature opens up great opportunities for many areas of physics, chemistry, and materials science. One of the obvious questions that need to be answered is which new alloys can be obtained and which areas of practical application their properties will be most in demand [1]. In addition, successful approaches were demonstrated to improve and modify the functional properties of new metal alloys made of immiscible components by reinforcing them with ceramic [2], [3] or carbon [4], [5] particles.

Developing methods for surface alloying of copper with heavy fusible elements is an essential task for developing new anti-friction materials. To obtain composite materials based on systems with limited solubility in the liquid state, including the copper-lead system, a contact doping method was proposed [6], based on the application of the phenomenon of abnormally fast mass transfer of a liquid-phase system through a solid single-phase or multi-phase system, provided that a monotectic reaction occurs between them. The essence of this phenomenon [7] is that when energy sufficient to initiate a monotectic transformation is brought into the contact zone of such systems (while maintaining the refractory phase in the solid-state), an abnormally fast mass transfer of the liquid-phase system to the solid-phase one is observed. Energy can be supplied to the contact zone, for example, by heating, shock-wave loading. Depending on the method and speed of energy supply, the continuity of the solid-phase system may be preserved or broken during the mass transfer process [14]. The technology based on the mentioned phenomenon can be applied to a relatively broad class of systems with stratification in the liquid state. At the same time, a significant number of metal systems that are important for practical application and do not undergo a monotectic transformation remain beyond their capabilities.

Further studies [8], [9] have shown that contact doping, which essentially reduces to mutual mass transfer of substances across the boundary of their contact, can occur not only in the reverse monotectic reaction and not only in monotectic systems. Thus, it turned out that intense pulsed effects of various nature on the contact zone of two solid metallic substances, depending on the energy, pulse duration, as well as size and shape of the contact zone, can lead to:

- to the abnormal mass transfer of one substance to another without breaking the continuity of the latter;
- to mutual mass transfer and creating a region with a homogeneous distribution of components in the contact zone.

Preliminary studies have shown that the action of current pulses with a duration of 0.01-1.00 s, a density of (1-4) × 103 A/cm2 on contacting different metal reagents leads to the formation of a region of pulsed fusion of components and penetration of alloying components into the matrix metal to a considerable depth [10]. The zone of pulsed fusion of components formed in the central part of the assembly has a shape close to an ellipsoid and, as a rule, a homogeneous structure. Therefore, to control the alloying process, it is necessary to have information about the influence on the size and structure of the fusion zone, such values as the duration of the current pulse, the characteristic dimensions, and the composition of the assembly. This work was carried out to identify such relationships using contact alloying of copper with lead as a perspective immiscible components system for new anti-friction materials.

II. EXPERIMENTAL SETUP

Fig. 1 shows the experimental setup scheme. Between two rectangular copper plates, "A" there is an electrically insulating plate "B" with a thickness of L, in which there is a round hole "C." An alloying (low-melting) component "D," such as lead, is placed in cavity "C" formed by the insulator and the copper plates so that it provides electrical contact between the metal materials of the assembly. The entire system is subjected to compression with a force P to prevent the melts from leaving the fusion zone. The copper plates are connected to the contacts of an electric pulse unit, which outputs current pulses with a 50 Hz frequency and a duration of τ from 0.01 to 1 s. As a result of the electro-pulse action, rapid local heating of the alloying component occurs, which leads to a sharp increase in pressure in the metal contact zone. As a result, mutual penetration and mixing of the components are observed with the fusion zone "E," schematically shown in Fig. 2.

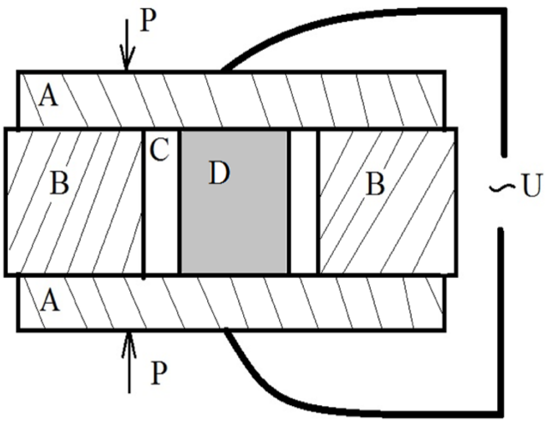

Fig 1: Scheme of the experimental setup

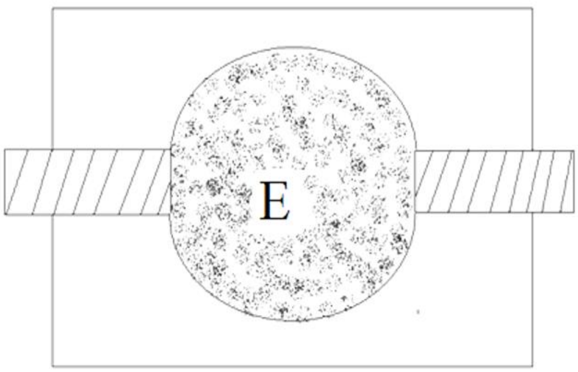

Fig 2: Fusion zone (schematically)

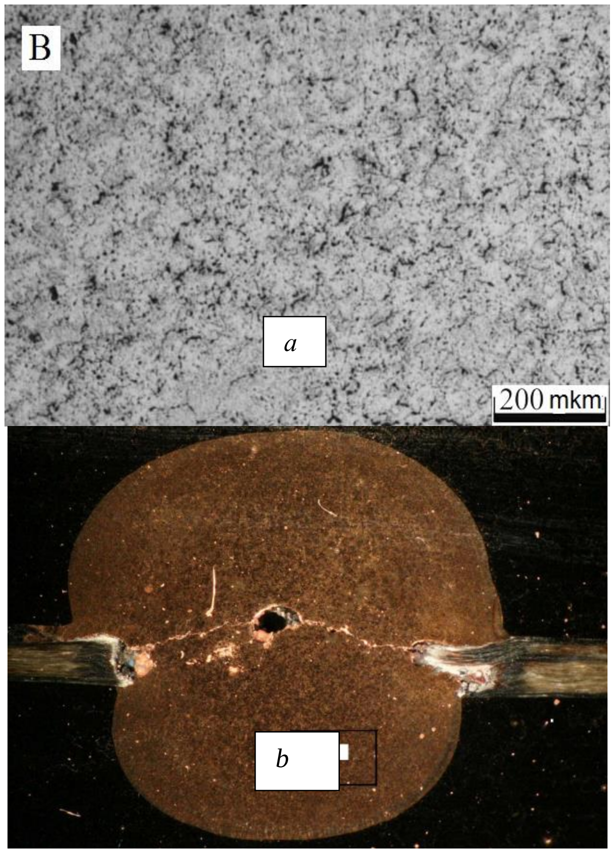

Fig 3: a) – the fusion zone microstructure; b) – the fusion zone of Cu-Pb

For example, Fig. 3 shows the fusion zone formed on two copper plates with dimensions of 25x25x4 mm under the action of an electric current pulse with a duration of τ =0.8 s and an amplitude of 4000 A. The thickness of the insulator L=0.4 mm, the parameter δ =0.09. The fusion zone has a clearly defined boundary in each plate and is close to the paraboloid of rotation in shape. Fine rounded inclusions of a copper-lead alloy with a high lead content are relatively evenly distributed inside the copper array. The maximum interaction depth is 2 mm. The average lead content in the fusion zone is 20 wt.%. The accelerated penetration of liquid lead into solid copper to a considerable depth is explained by the presence of two factors. With such duration of the electric current, the temperature of the monotectic interaction is reached in the contact zone of lead and copper. At the same time, in cavity 2 (see Fig. 3) lead develops overpressure caused by thermal expansion. The combination of high temperature and overpressure contributes to the penetration of lead into copper. Thus, with such an alloying contact scheme, a composite in the form of a copper plate containing an alloy region is obtained.

When conducting experiments [7], [11-12] on electrocontact alloying, it was assumed that a particular fusible material (for example, lead) was used as an alloying component. This component is heated and melts under the action of current pulses while its expansion occurs. It leads to the appearance of excessive pressure in the interaction area, which contributes to the penetration of the fusible component into the alloyed material. The value of this pressure is directly related to the degree of filling of the cavity. To characterize this effect, when using whole samples, convenient to use the parameter δ, which is calculated by the following formula [11]:

$$\delta = 1 - V_1 / V_2$$

where V_1 - is the alloying component initial volume, V_2 - is the cavity volume. It was evident that the lower the value of δ, the greater the pressure develops in cavity 2 during thermal expansion. However, there is a threshold value δ* at which there is no excess pressure caused by thermal expansion. It should be noted that at $\delta > \delta^*$, the electrical contact in the assembly can be preserved since the surface tension forces can prevent the melt from spreading. For example, if the alloying component is lead, then without taking into account the thermal expansion of the insulator, we have $\delta^* \sim 0.1$. If the fusible component is such that $\delta < \delta^*$, then the excess pressure caused by thermal expansion can lead to the adiabatic shear bands (ASB) regions formation [13]. Such highly localized structures are characterized by an increase in temperature by several orders of magnitude, which contributes to the rapid penetration of the low-melting component into the refractory one to a considerable depth. Consequently, by changing the degree of filling of cavity 2 with a low-melting component, it is possible to influence the development of electric pulse fusion and the microstructure of the resulting composite materials.

The amount of energy supplied also has a significant influence on the microstructure of the fusion zone. Its value is determined by the duration of the electric pulse τ. For short (the temperature of the fusion zone is significantly lower than the temperature of the monotectic interaction) pulse, it is possible to form ASB regions where the low-melting component penetrates with the formation of alloys nonelectric composition. These formations have a strongly elongated structure and, as a rule, coincide with the grain boundaries of the refractory component. A longer pulse leads to heating of the entire fusion zone to the temperature of the monotectic interaction. In this case, the low-melting component is part of rounded inclusions consisting of an alloy with different components. The distribution is relatively uniform and finely dispersed. If we take an even longer pulse, this will lead to small particles of the alloy beginning to enlarge, forming structures of arbitrary shape. Thus, there are three parameters for controlling doping: the pulse duration τ, the degree of filling of the cavity δ, the thickness of the insulator L.

III. EXPERIMENTAL RESULTS

Table 1 shows the results of several experiments on the electric pulse fusion of copper and lead. It can be seen that by changing the thickness d, the diameter D1 of the lead disk, and the duration of the current pulse, it is possible to control the depth of penetration of lead into copper, as well as the ratio of components in the fusion region.

Table 1: Conditions of Electrocontact Alloying

Sample number	Pulse duration τ, s	Sample thickness d, mm	D_1/ D	Pb concentration in the fusion zone η, aт%	The greatest alloying depth, mm
1	0.02	0.80	0.8	70	0.1
2	0.04	0.80	1.0	31	0.4
3	0.04	0.40	1.0	16	0.5
4	0.14	0.40	0.9	9	1.1
5	0.2	0.40	0.9	6	2.5
6	0.14	0.80	0.9	10	1.7

Let us consider the results of the first series of experiments in which the average temperature of the fusion zone remains below the temperature of the monotectic reaction.

In the copper-lead system, the processes of liquation and monotectic transformation play an important role. It is known that under certain conditions, liquid lead penetrates solid copper to a considerable depth. The process starts if the copper-lead mixture's temperature reaches the temperature Tm of the monotectic reaction. At the same time, an alloy of a monotectic composition appears at the Cu-Pb contact boundary. If there is some force (for example, gravity or pressure force due to thermal expansion), then the lead melt under the influence of this force penetrates the copper array. At T close to Tm, there are three phases: an alloy containing about 36 wt.% Pb, Cu crystals, and liquid with 92 wt.% Pb [11], [12]. An alloy layer forms around the lead. Under the influence of gravity, the lead sinks, pushing the alloy out of the interaction area. Depending on the cooling rate, the ratio of the component in the alloy may vary. Excess liquid lead from the alloy is deposited on the melting drop. Copper crystals float up. Externally, it looks like the passage of lead through a volume of copper material without signs of any destruction of the latter. Depending on the cooling rate, the ratio of components in the alloy may vary.

Fig. 4 shows the view of the fusion zone in Experiment No. 1. The copper-lead alloy in extended (about tens of micrometers) regions is distributed in a copper matrix. There is an occurrence of short ASB regions that look like small dark inclusions in light areas. The light areas are copper, and the dark areas are copper-lead alloy with high lead content. Cu-Pb alloy inclusions in the copper array range from 0.1 microns to several tens of microns. The pulse's energy was enough to melt the lead and form an alloy with eutectic composition. However, the pressure caused by thermal expansion was small, preventing the lead from penetrating the copper array to a significant depth. The thickness of the fusion zone, in this case, was only 0.1 mm.

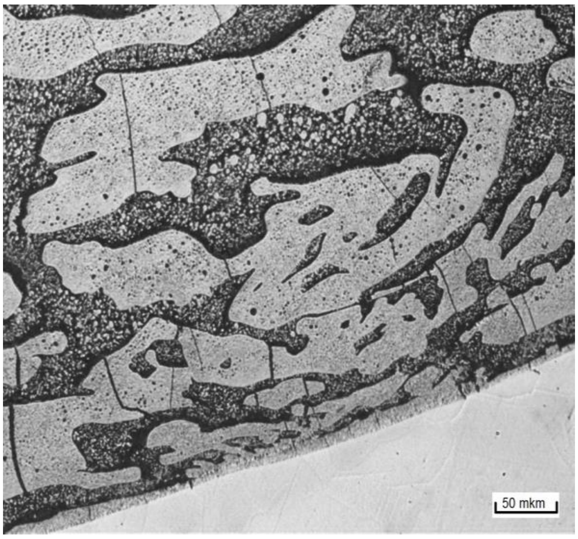

Fig 4: Microstructure of the fusion zone in experiment №1

As the pulse duration increases, the amount of energy supplied increases. Fig. 5 shows the section of the fusion zone in experiment No.2. In this case, initially, the entire cavity "C" (Fig. 1) is filled with lead. It leads to significant pressure in the fusion zone.It can be seen that the length of ASB and their number are increasing. At the same time, lead spreads to a greater depth, and its concentration in the fusion zone decreases. The inclusions of the alloy have a characteristic size of 0.01-0.1 microns (experiment No. 3 in Table 1). In experiments No. 2 and No. 3, the duration of the current action (i.e., the amount of energy) was fixed, and it was enough for all the lead to react. At the same time, the average temperature in the interaction zone did not reach the temperature of the monotectic reaction.

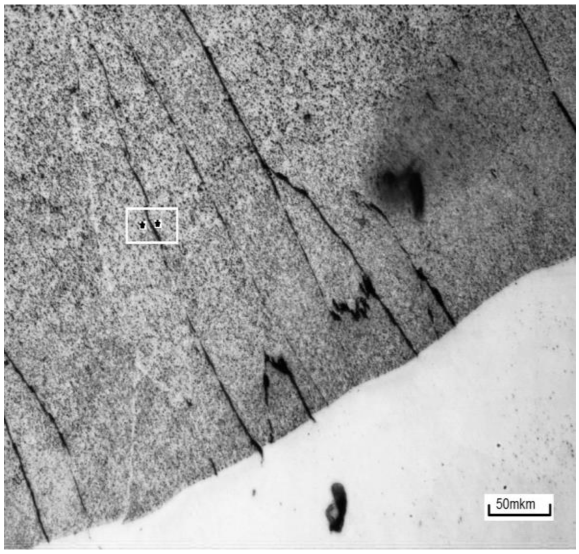

Fig 5: Microstructure of the fusion zone in experiment №2

At the same time, most of the fusion zone is a homogeneous formation containing a copper-lead mixture with a specific ratio of components. In Fig. 5, two points (*) are highlighted with a white frame. A step-by-step measurement of the copper and lead content was carried out along the straight line connecting these points. The scanning was performed with a spatial step of 0.1 microns depending on the distance. Fig. 6 shows the results of these measurements. It can be seen that there are no areas in the entire studied section of the fusion zone where the concentration of any of the components significantly differs from the average concentration throughout the entire zone. That also applies to areas containing ASB, which are displayed as dark lines in the figure. In the entire fusion zone, including the ASB regions, lead is evenly distributed, and the characteristic size of the alloy inclusions and the pure copper region does not exceed 0.1 microns.

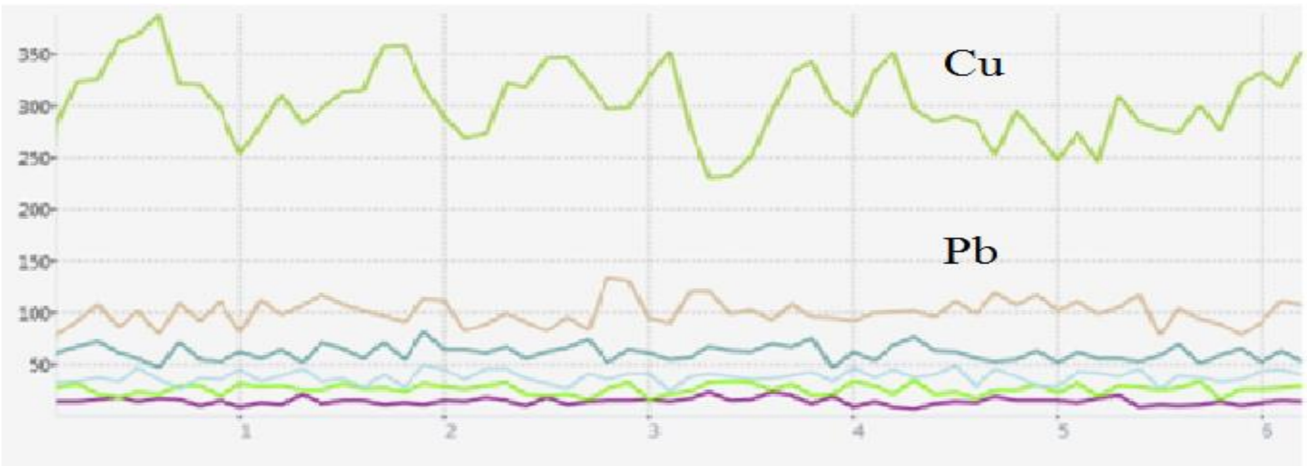

Fig 6: Change in the Cu and Pb content between two points in the fusion zone

In the next series of experiments, the average temperature in the zone of electric pulse fusion reaches the temperature of the monotectic reaction. Thus, in experiment No. 4, as a result of a long-term action of an electric current, additional heating of the fusion region occurred. It led to the destruction of the ASB regions. There was an enlargement of the structural elements of the alloy with the appearance of some local texture (see Fig. 7); lead began to concentrate along the boundaries of the copper grains.

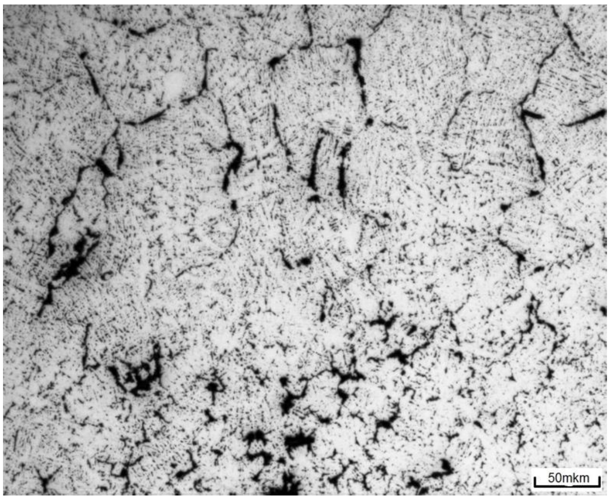

Fig 7: Microstructure of the fusion zone in experiment №4

There is a significant change in the shape of the boundary of the fusion zone. It becomes regular and closes in shape to an ellipsoid while the volume of the fusion zone increases and, as a result, the average concentration of lead decreases.

Further heating of the fusion region (experiment No. 5) removes all stresses and, as a result, local structures disappear. As a result, the fusion region becomes homogeneous with a uniform distribution of inclusions of a copper-lead alloy with a characteristic size of 1-2 mm (see Fig. 8). The depth of penetration of lead into copper, in this case, was 2.5 mm.

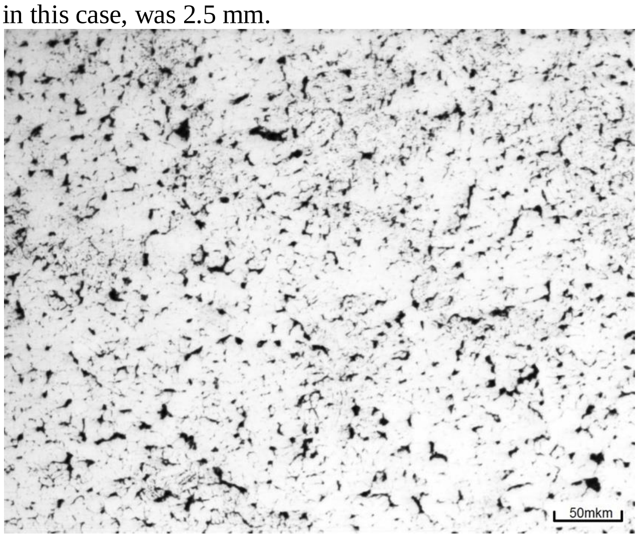

Fig 8: Microstructure of the fusion zone in experiment №5

It should be noted that the considered microstructural formations can be observed within the same experiment. It is possible to create conditions for all the above structures to present in the same fusion zone. That is determined by the characteristics of the electric pulse action and the conditions of heat removal from the interaction zone. When a high-energy electric current is applied, ASB regions occur in the Pb-Cu contact zone, extending to the entire fusion area (up to 2-3 mm). Due to this, the lead is evenly distributed throughout the entire fusion zone. The structures shown in Fig. 5 are observed near the boundary of the fusion zone. However, if the lead was in excess at the initial moment, the structure shown in Fig. 4 is realized near the contact point of copper and lead. If the electrical action continues in the Pb-Cu contact zone, a heatwave propagates through the fusion zone, heating the alloy to the temperature Tm. That leads to a change in the microstructure of the fusion zone, with the appearance of the structures shown in Fig. 7 and 8.

IV. CONCLUSIONS

The possibility of copper contact with lead with forming a composite in an alloy zone containing a given amount of an alloying component is demonstrated. Furthermore, it is shown that changing the duration of the current pulse (the amount of transmitted energy) and the specific amount of the alloying element makes it possible to control the doping depth in the range from 0.1 mm to 2-3 mm. At the same time, the content of the alloying component can vary widely.

To demonstrate the possibilities of applying the results of these studies, samples of composites with high tribological properties were obtained (composite 1 and 2, Table. 2) in the form of a copper plate with a size of 40x40x4 mm, containing an area of fusion with a size of 14x11 mm, the composition of which corresponded to the composition of CuPb30 grade bronze (see Table 2). The process of alloying the Composite 1 sample consisted of sequentially obtaining five rectangular fusion zones of 11x3mm on a copper plate. When obtaining each of these zones, an insulator with a thickness of L=0.4 mm was used, the pulse duration τ =0.04, the degree of filling of the cavity δ=0.

Table 2: Samples' tribological properties

Sample name	Content, wt%	K_t	K_t^*
Composite 1	Cu 68 Pl 32	0.23	0.45
Composite 2	Cu 68 Pl 32 Quenched	0.25	0.50
Bushing 1	Cu 75 Pl 25	0.25	0.60
Bushing 2	Cu 85 Pl 10 Sn5	0.45	0.80

The following sample (Composite 2) was obtained under the same conditions as Composite 1, but with subsequent annealing at a temperature of 500°C and quenching in water. These samples were tested on a TRB–SEE-0000 CSM Instruments tribometer. The sliding friction coefficient Kt was determined without lubrication at a load of 0.25 N (counter body - a steel ball with a diameter of 6 mm). The results are presented in Table 2. Here are the test results of samples made from standard industrial products that served as sliding bearings.

As can be seen from the table, for the Composite 1 and Composite 2 samples, the Kt value is close to the value corresponding to CuPb30 bronze and less than the corresponding values for industrial materials. The last column of Table 2 shows the values of Kt* obtained in experiments lasting 114 minutes at a load of 1.0 N. It can be seen that the prototypes are more stable in results than industrial bushings. Thus, the possibility of obtaining composite materials with high anti-friction properties was demonstrated.

ACKNOWLEDGMENT

This work was performed within the framework of the initial research "CeramicsSynthesis" and using the equipment of the Shared Science and Training Center for Collective Use RTU MIREA and supported by the Ministry of Science and Higher Education of the Russian Federation, and equipment of the Centre of Collective Usage “High Technology in Engineering” of Moscow Polytech (Number for publications: 0699-2017-0005). The authors express their gratitude to Dmitry V. Volgin for his help in designing the drawings.

REFERENCES

[1] E. Ma, Alloys created between immiscible elements, Progress in materials science, vol. 50(4) (2005) 413-509.

[2] K. Kaur, R. Anant, and O. P. Pandey, Tribological behavior of SiC particle reinforced Al-Si alloy, Tribology Letters, 44(1) (2011) 41-58.

[3] M. Xie, S. Zhou, S. Zhao, J. Jin, D. Chen, and L.-C. Zhang, In-situ Fe2P reinforced bulk Cu–Fe immiscible alloy with nanotwinned Cu produced by selective laser melting, Journal of Alloys and Compounds, 838 (2020) 155592.

[4] H. Zuo, W. Wei, X. Li, Z. Yang, Q. Liao, Y. Xian, and G. Wu, Enhanced wetting and properties of Carbon/Copper composites by Cu-Fe alloying, Composite Interfaces, (2021) 1-10.

[5] S. Srivastava, S. Mohan, Y. Srivastava, and A. J. Shukla, Study of the wear and friction behavior of immiscible as cast-Al-Sn/Graphite composite, Int J of Mod Eng Res, 2(2) (2012) 25-42.

[6] Yu. S. Avraamov, and A. D. Shlyapin, Splavy na osnove sistem s ogranichennoj rastvorimost'yu v zhidkom sostoyanii, Moskva, Russia: Interkontakt Nauka, (2002).

[7] Yu. S. Avraamov, V. I. Koshkin, V. E. Panin, I. B. Rudenko, and A. D. Shlyapin, Vliyanie elektroimpul'snoj obrabotki na mikrostrukturnye prevrashcheniya v zone kontakta raznorodnyh metallicheskih veshchestv,” Perspektivnye materialy, 6(2006) 10–14.

[8] V. E. Panin, A. V. Panin, D. D. Moiseenko, A. D. Shlyapin, Yu. S. Avraamov, and V. I. Koshkin, “Fizicheskaya mezomekhanika deformiruemogo tverdogo tela kak mnogourovnevoj sistemy. Yavlenie vzaimnogo pronikaniya chasticz raznorodny`x tverdy`x tel bez narusheniya sploshnosti pod vozdejstviem koncentrirovanny`x potokov e`nergii,” Fizicheskaya mezomekhanika, 4(2006) 5–13.

[9] Yu. S. Avraamov, V. I. Koshkin, V. A. Nizhnik, I. B. Rudenko, and A. D. Shlyapin, Poluchenie antifrikcionny`x metallicheskix kompozicionny`x materialov s pomoshh`yu e`lektroimpul`snoj obrabotki, Izvestiya MGIU, 1(2006) 2-7.

[10] I. B. Rudenko, Elektroimpul'snoe legirovanie zheleza tyazhelymi legkoplavkimi elementami, Mashinostroenie i inzhenernoe obrazovanie, 2(2010) 25-29.

[11] V. I. Koshkin, A. N. Kravchenkov, V. A. Nizhnik, I. B. Rudenko, V. V. Rybal'chenko, and A. D. Shlyapin, Strukturnye prevrashcheniya v zone kontakta metallov Al I Pb, Fe I Pb pri elektroimpul'snom vozdejstvii, Mashinostroenie i inzhenernoe obrazovanie, 1(2012) 3-27.

[12] S. G. Ponomarev, and V. V. Rybal'chenko, Scenarii razvitiya elektroimpul'snogo splavleniya v sisteme med' – svinec, Mashinostroenie i inzhenernoe obrazovanie, 1(2014) 16-20.

[13] N. Ranc, Laurent Tavarella, Vincent Pina, and Philippe Hervé, Temperature field measurement in titanium alloy during high strain rate loading—adiabatic shear bands phenomenon,” Mechanics of Materials, 40(4-5) (2008) 255-270.

[14] V. M. Nikonorov, and V. V. Nikonorov, Mathematical model of solid municipal waste management, IOP Conference Series: Earth and Environmental Science, 666(4) (2021) 042090.