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Research of The Interaction of Graphite with Copper in Powder Composite Materials for EDM Tools During Sintering.

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ABSTRACT

The work researches the impact of copper on the structure of the colloid and thermal expanded graphite at the solid phase sintering with copper and also the physical and mechanical and operational properties of the EDM tools of the system "copper-graphite" during the electrosparking. Composite materials based on copper with various contents of carbon phases were manufactured using the method of powder metallurgy. The traces of the formation of graphite and sp^3 combinations intercalated by the copper that promoted the increase of the conductivity and capillary properties of the material were found by the methods of X-rays phase analysis and Raman spectroscopy in the graphite sintered with copper. When machining tool steel at roughing conditions, it was found out that erosion wear of EDM tools of the systems "copper-colloid graphite" and "copper-thermal expanded graphite" is 8-15 times less than the copper has, and the productivity is higher. The explanation of the wear resistance of the electrodes of the system "copper-graphite" was offered.

Keywords: electroerosive machining, EDM tool, composite material, intercalation, copper, graphite, erosion resistance.

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PREFACE

Wear resistance of EDM tools for electroerosive sparking impacts the accuracy of a part processing and the cost of the process. Development of the new technological processes of creation of erosion resistance materials, low cost and high wear resistant, is a very important problem and has a high economic significance because erosion wear of EDM tools manufactured from copper, brass, cast iron can be 10-100 times higher than the volume of the metal removed from a part and that decreases drastically the efficiency and sometimes even makes it pointless to use the electroerosive machining [1]. Now, the main materials used for the machining are copper and graphite despite the developed composite materials with the improved operation properties. Thus, the famous manufacturers of electroerosive equipment Mitsubishi Electric (Japan), EDM-Deutschland (Germany) manufacture brass, copper and "copper-tungsten carbide" pseudo-alloy electrodes; GF Agie Charamilles, Sarix S.A (Switzerland) and Tokai Carbon Europe (UK), European distributor of the Japan company Tokai Carbon, improve the quality of the machining due to the increase of dispersion of the graphite materials. Copper-graphite electrodes obtained by the methods of infiltration and solid phase sintering of powdered materials are used rather rarely despite they possess some advantages over graphite (increased wear resistance and resistance to mechanical treatment and operation) and over the copper materials (higher densities of current and machining accuracy) [1]. Manufacture of copper-graphite materials is considered to be a complex technological problem because the copper does not interact with graphite chemically and absorptionally [2]. Due to the existing variety of carbonic structures, there is a necessity to study their structures, properties and applications for manufacture of various functional materials.

The aim of the research was to study the formation of structure of carbonic phases – colloid and thermal expanded graphite at the sintering with copper and determination of the dependence of the relative wear of EDM tool during the electroerosive machining from its composition.

METHODS

The powders of electrolytic copper PEC-1 (GOST 49-60-75), dry colloid graphite brand C-1 (Technical Specifications 113-08-48-63-90) and thermal expanded graphite manufactured by JSC Novomet-Silur were used to manufacture the electrodes from composite materials.

Colloid graphite is obtained by grinding of natural or artificial flake graphite to the size of 4 microns and the following treatment in sulphuric or nitric acids to form the oxides or salts (biosulphates are the most wide-spread) of graphite, able to form the water solutions and organic liquid solutions [3]. During the chemical treatment, the intercalates of graphite are formed, containing the molecules and ions of acids between the graphene layers [3].

Thermal expanded graphite (TEG) is obtained by the processing of natural and artificial graphites in the sulphuric acid and forms the intercalated acid compound remains and the following shock heating up to 900-1200 °C, when the acid remains are deleted from the interlayer spaces together with the increase of the interplane distances up to 300-500 times and formation of "twisted" planes of graphite [3].

Copper powder PEC-1 was mixed with the powders S-1 or TEG, the samples were pressed from the mixtures, then the samples were tempered in the vacuum kiln for 2 hours at the temperature 1070±10 °C. To clarify the impact of the copper on the formation of "diamond" connections in graphite the graphite powders were pressed and sintered in vacuum at 1200 °C.

The X-rays phase analysis was carried out on diffractometer "XRD-6000 Shimadzu" in Cu Kα- radiation. The identification of the phase compound was carried out according to the card index of the International centre of diffractometric measurements. Raman spectra (spectra of the combination dispersion) of the samples were obtained on multifunctional dispersion spectrometer of the light combination dispersion "Senterra". The length of a wave of excitation laser was 532 nm. Electronic microscopic research was carried out on scanning electronic microscope "Tescan Vega 3 SEM". The density of the composite materials was determined according to the standard method (GOST 18898-89). Electric resistance was measured at the digital programmable milliohm meter GOM-802.

Tests of performance characteristics of electrodes were carried out during the electroerosion machining of the steel sheet H12F, thickness 5.5 mm with 58 HRC on the lathe Electronica Smart CNC at roughing conditions of the E81 mode (impulse length 100 microseconds, pause 32 microseconds, current strength 15 A) and E92 mode (impulse length 150 microseconds, pause 32 microseconds, current strength 20 A). EDM Oil – IPOL SEO 450 was used as working fluid.

Relative wear of electrode was determined according to the ratio of the depth of a machined hole in the steel sheet to the linear wear of electrode. Capacity was determined as a ratio of the operation time of the tool to the volume of the material processed, mm^3/min [1].

RESULTS AND DISCUSSION

The structure of the sintered materials of the systems "copper-carbon phases" consists of the copper base, pores and dispersed particles of the carbon phases. The microhardness of the copper base in the materials was 730 MPa. The particles of the carbon phases are well seen in the fractures of the sintered materials, Fig. 1. The particles of the flake colloid graphite are well seen in the materials containing graphite, Fig. 1a, and the particles of the thermal expansion graphite with well seen "twisted" grapheme planes, Fig. 1b.
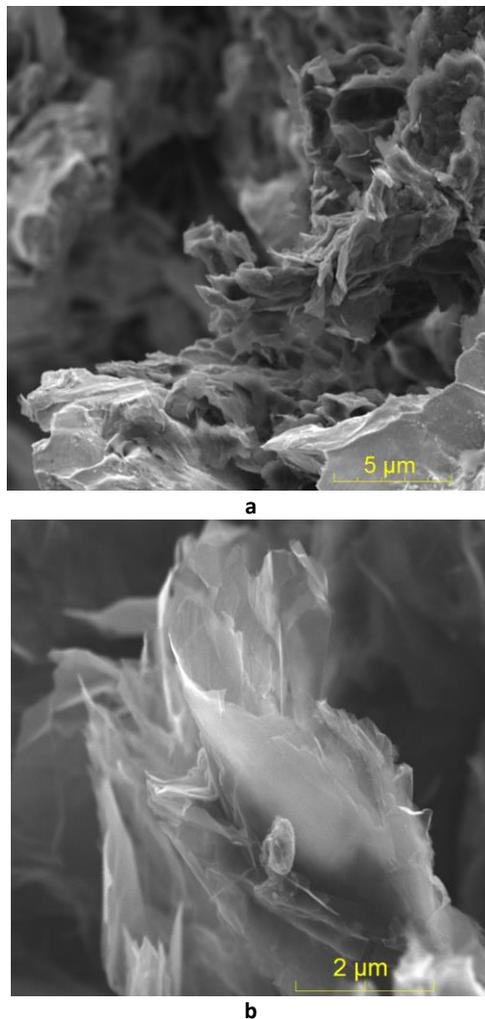

a

b

Fig. 1. Fracture of sintered materials, a – "copper-colloidal graphite", b – "copper-thermally expanded graphite"

The XRD pattern of the powder of colloid graphite C-1 contains reflexes referred to the graphite and silicon carbide that can be an admixture of the natural graphite, which is an original material for C-1, Table 1. The interplane distances along the axis *c* are 0.672 nm. Standard XRD pattern made in the radiation of Cu Kα in the scanning mode at the speed of 2 degree/minute, composition "Cu – 20 vol. % of colloid graphite C-1"

shows the availability, besides copper lines, of the more intensive graphite line (002). Also the light line from the angle is seen 2Θ =12.4° that can be identified as reflex (001) from the modified graphite grid.

TABLE 1. Interplane distances in the powder of colloid graphite C-1, *d*, nm

C-1	Sintered powder material "Cu-C-1"	"Cu-C-1" [4]	Indices of plane (*hkl)*
n/a	0.713	0,7	001
$0.337_{100.00}$	0.3355	0.335	002
n/a	0.357	0,357	002
$0.213_{1.246}$			100
$0.203_{1.653}$			101
$0.168_{3.965}$			004
$0.155_{0.379}$			103
$0.116_{0.763}$			112
$0.112_{0.357}$			006

When surveying the points, pitch 0.02° and exposure 10 sec for a point, the weak reflexes were revealed corresponding to the line (001) of graphite, Fig. 2a, and also to the line 2Θ=25°, Fig. 2b, that together with the line 2Θ=26.5° correspond to the splitted line (002).

Additional reflexes revealed by the X-ray phase analysis of the sintered composite material "copper-colloid graphite" correspond to the reflexes described in the work [4], Table 1. The authors of the work [4] found out the formation of intercalated combinations of graphite and melted copper, the result of which is a corrugation of the graphene planes with the formation of sp^3 combinations (approx. 5%), Fig. 3, after the copper ions leave the interlayer spaces. The traces of the formation of diamond combinations is the appearance of additional reflexes on diffraction of the graphite with uneven *l* (001) and (003) and bifurcation of the existing reflexes (002), (004), (006). Taking into account the method of preliminary processing of graphite by acids and high copper vapour pressure, the formation of intercalated combinations with copper is quite possible at the pre-melting temperature. Besides, the traces of the formation of sp^3 combinations in the initial colloid graphite were not revealed using the method of X-ray phase analysis at low speed surveying, Table 1.

Other lines identified in the article [11] as reflexes of reflection from (003), (004) and (006), at the similar survey in the corresponding angle intervals: 40-43, 53-56 and 87.06-87.28 are not revealed, which can be explained by the low intensity of a composite with the volume ratio of graphite only 20% on a diffraction.

The decrease of intensity of graphite lines non-proportionally to the volume ratio but in a higher degree was revealed; the reason can be the highly reflected material of copper matrix that reflects the graphite particles laying in the layers at the depth of 0.1 mm, while it is possible to get the reflections in a thicker layer using the X-ray scanning of a pure graphite.

Nevertheless, the obtained data shown in Table 1 show a good match with the data of the work [4] and confirm the results qualitatively.

Intercalation of graphite by the copper is described also in other works, for example, in [5-6] at heating of cuprous chloride with graphite up to 1200 °C diffraction [5] shows the reflex in the angle area 2Θ, that corresponds to the interplane distance approx. 0.7 nm; however, the analysis of the result shown was not provided.

Explaining the results obtained, it can be added to the data [4] that the location of carbon atoms in the modified graphite shown in Fig. 4 to the right was revealed also in the graphite subjected to the high pressure [7].

Besides, if [4] presupposes that the deformed (corrugated) layers of the carbon atom network alternate with the non-deformed ones, the structure described in [7] consists of the layers, the directions of

deformation of which alternate. Mechanism of formation of such structures is a shift of graphene layers leading to the alternation of AB for AA and the deformation of these layers and formation of cavities.

A distinguishing feature of the thermal expanded graphite is an increased distance along the axis *c* (0.3572 nm), Table 2.
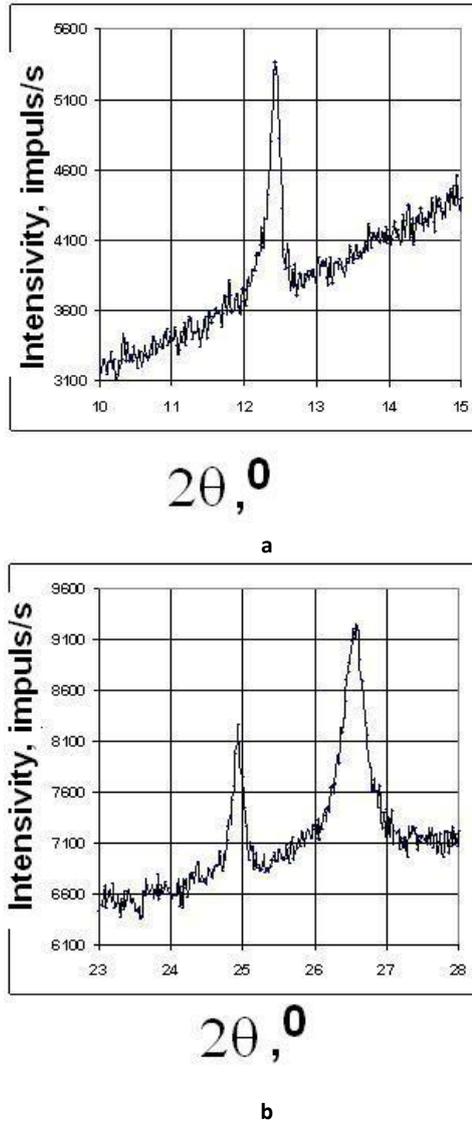

a

b

Fig. 2. The X-ray diffraction of sintered material "copper-20 vol. % of colloidal graphite" at intervals 2Θ (Cu Kα), a – 10-15°, b – 23-28°
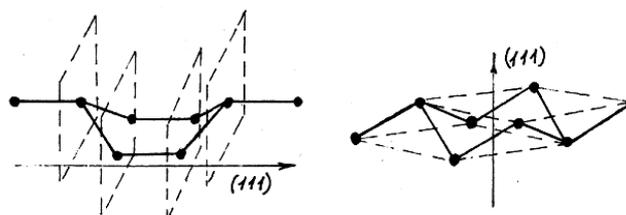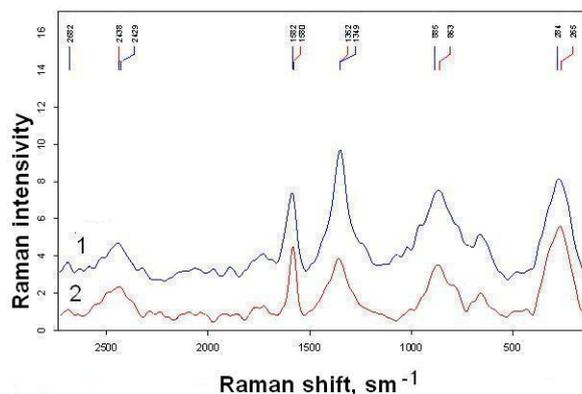

Fig. 3. Possible "goffered" (001) plane of intercalated graphite [4]

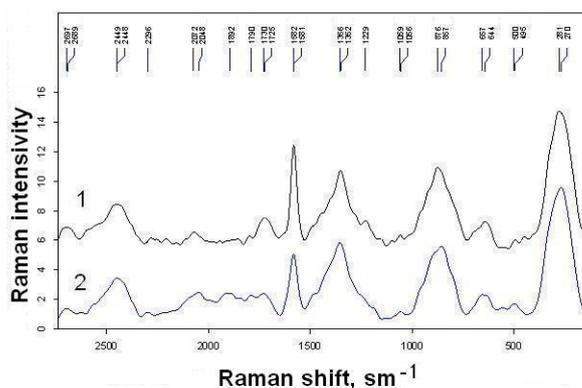**TABLE 2. Interplane distances of the powder of thermal expanded graphite and sintered composite material, *d*, nm**

TEG	Copper- 20 vol. % of TEG	Indices of plane *(hkl)*
undetected	0.7_1	001
0.3572_{100}	$0.3380_{20,1}$ 0.3360_{10}	002
$0.21094_{9,3}$	$0.20963_{36,6}$	100
$0.16798_{4,71}$	1.68_6 0.16132_6	004
$0.112_{1,98}$	undetected	006

Diffraction of sintered material "copper-5 vol. % TEG" is quite similar to the diffraction of the material with colloid graphite due to the similarity of their structures and the methods of obtaining, Table 2, however the technology of obtaining TEG provides more breaches in the crystal structure of the graphite, and many reflexes were not detected or shifted. Besides, the technology of obtaining TEG provides the oxidation of graphite (formation of functional groups) and interaction of the introduced substances with the functional groups; however, intercalated combinations of the oxidated graphite are unstable and can be easily removed from the interlayer space [8].

The peaks typical for the carbon phases *G, D*1*, 288, 860 and 2450 cm*$^{-1}$ [9-10], Fig. 4, Table 3 were revealed in Raman spectra (RS) of all carbon containing materials. The spectra of the samples of colloid graphite C-1 (original and sintered with copper) include the strong lines *G* and *D*1 identifying the sp^2 combinations and a very weak peak *2D* showing the misalignment along the graphite axis *c* [9].

a

b

Fig. 4. Raman spectra, a – the sintered material "copper-20 vol. % of colloidal graphite C-1" (1) and graphite powder C-1 (2), b – expanded graphite powder (1), and sintered material "copper-20 vol.% of expanded graphite" (2)

In both cases, a peak 2*D* is not directly asymmetrical and has a low intensity; consequently, there is a structure order, in both spectra there are weak peaks *D*3 typical for nanocarbon and indicating the availability of interlayer defects [9].

In the graphite structure sintered with copper, the peaks *G* and *D*1 become wider, and this indicates the presence of the misalignment of the graphite. On the peak *G*, there is a "shoulder" *D2* – it is the so called "shoulder of defects" that together with the peak *D*1 indicates the appearing defects on the edges and inside the graphene planes. Besides, there is a weak peak *D4* that indicates the availability of sp^3 combinations. Low intensity of the reflexes is connected with the low concentration of graphite in copper and probably with the small number of corrugated planes. The ratio of peak intensities *D*1/*G* in graphite after sintering with copper is increasing and we can conclude on the decrease of the crystal size. The spectra TEG and TEG sintered with copper do not differ much, Table 3.

TABLE 3. Raman spectra of the powders of carbon forms and sintered composite materials "copper-carbon"

Material	Raman shift, cm^{-1}						
	G	*2D*	*D1*	*D2*	*D4*	*D3*	*LA*
	1582	*2700*	*1332*	*1620*	*1212*	*1510*	*453*
Graphite C-1 Initial Sintered	1580	2682	1352	no	no	1510	no
	1580	2678	1352	1620	no	no	no
"copper-20 vol. % of graphite C-1" sintered	1582	2682	1349	1620	1233	1510	no
TEG Initial Sintered	1576	2691	1351	no	1212	1510	no
	1578	2677	1352	1620	1218		no
Copper- 20 vol. % of TEG" Sintered	1582	2700	1360	1620	1218	1516	496

In the spectrum of initial TEG, the peaks of the "shoulder of defects" are absent, and this indicates the absence of misalignment inside the graphene planes, and there is a reflex *D4,* indicating the availability of sp^3 combinations stipulated by the technology of obtaining TEG (oxidation by the functional groups) [5, 15], peak of the amorphous carbon is absent. The spectrum TEG sintered with copper shows the misalignment in the graphene planes and a weak peak of amorphous carbon intensity of the line *D*1 become higher than the intensity of the line *G.* Reflex *D4* remains, and this indicates the availability of sp^3 combinations and corrugation of the planes. In comparison with Raman spectra (RS) of colloid graphite, the reflexes TEG (pure form and sintered with copper) are more degraded, probably, due to the breach of crystallinity. The necessary role of copper in formation of the diamond combinations in the graphite can be explained by the absence of typical peaks in the graphite powders sintered without copper in vacuum at 1200 °C.

Thus, the traces of the graphite combinations intercalated by copper were detected in colloid graphite after sintering with a copper. The possibility of copper ions interfering, without copper melting, into the interlayer space of graphite is explained by the preliminary chemical treatment of graphite and mechanism of formation of intercalates can be shown by the following: the ions of acid remains separate the grapheme layers and are removed in a vapour phase at heating, copper ions possessing high vapour pressure get into increased interlayer spaces of graphite and form the intermediate complexes or come into chemical combination with acid residue and are restored by carbon, migrate; in case when metal ions leave couple of rings in the graphite plane, the released electrons of carbon form "diamond" combinations that deform the graphene planes in the places where the metal ion was located instead of weak interlayer electrons. Mechanism of intercalation is similar to the mechanism of catalytic synthesis of a diamond with formation of special electronic configurations between the ions of metal-catalyst and graphite, corrugation and shift of the layer. However, until now it was supposed that pure copper can not be a catalyst for the diamond synthesis [11-12]. The role of acid residues is to increase the interlayer space of graphite, because only metal can lead to the strong delocalization of graphite electrons (they are also catalysts of the diamond synthesis), and, perhaps, as anionic "traps" for metal cations. Deformation of graphene layers during intercalation and after processing of diamond combinations is confirmed by RS responsible for the defects inside and on the edges of the graphene planes.

Metal ions that did not leave the interlayer spaces of the graphite after sintering influence on the conducting properties of the composite material "copper-graphite": Even at rather high residual porosity, the conductivity of the copper-graphite material is not decreasing or decreasing slightly in comparison with the pure pore-free copper.

The misaligned structure of the thermal expanded graphite does not allow to reveal the intercalation as definitely as in the colloid graphite C-1, however, the similarity of the structure and the method of obtaining of these two brands of graphite can stipulate the general regularity of the formation of intercalations and "diamond" combinations revealed by researches.

Addition of graphite to the copper improved or slightly decreased the conductivity of composite materials in comparison with the table value of a pure copper, that is stipulated by the low conductivity of the graphite and, may be graphite with copper, Fig. 5.

We observed the slight increase of conductivity when increasing the volume of colloid graphite up to 20%, which is possibly connected to the formation of additional porosity when decreasing the metal contact at sintering that deteriorates the properties of conductivity in comparison with a pure copper. The well-known improved conducting properties of intercalated carbon structures are already used for the development of the electrotechnical materials [13]. The relative wear of the electrodes made from the pure copper at the machining at the E81 and E92 modes was 5.6 and 6.9% correspondingly. The relative wear of all electrodes made from composite materials was lower (Fig. 6a, 6b).

In the systems "copper – carbon phases", the improvement of the performance characteristics was achieved due to the low conductivity of the composite materials even with a rather high porosity (up to 13%). Besides, the improvement of the properties is stipulated by the formation of three-dimensional network from the refractory phase with the smaller cell size (capillary) at the expense of a higher dispersion of particles of the refractory phase – graphite.
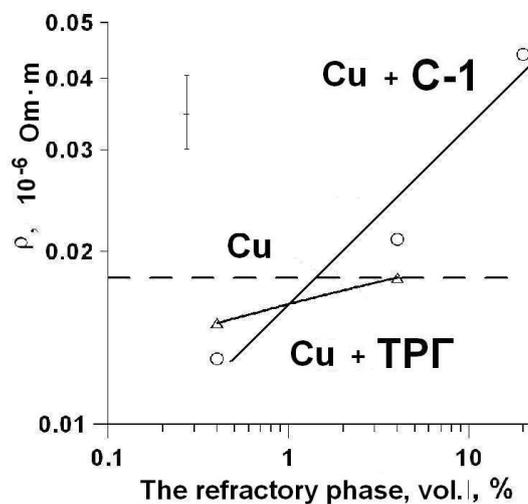

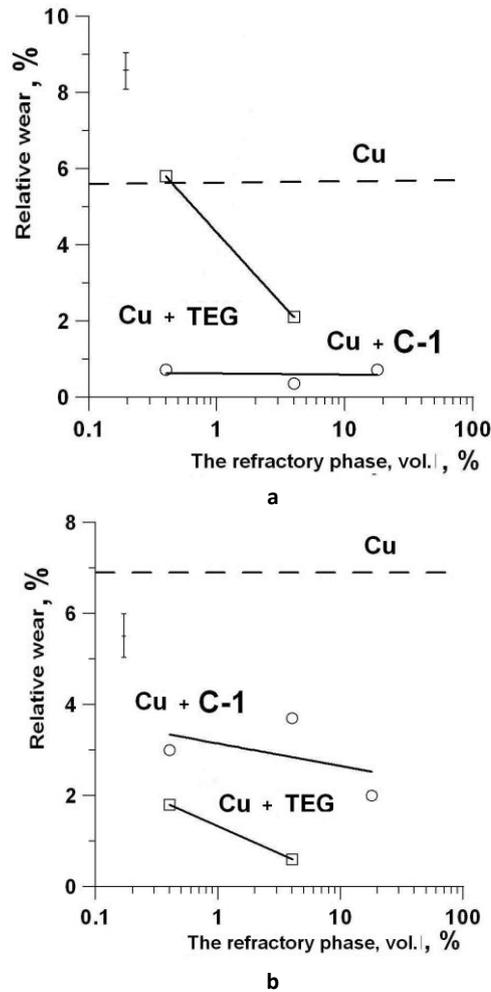**Fig. 5. The electrical conductivity of the sintered composite materials "copper-graphite" ТРГ - TEG**

**Fig. 6. Relative wear of electrodes made of composite
materials "copper-graphite C-1", "copper-thermally
expanded graphite", with EDM of steel, a – at the E81 mode,
b – at E92 Mode**

The capillary effect in carbon structures at the absence of moistening in the systems with copper is stipulated, probably, by intercalation. The relative wear of EDM tool made from sintered powder of pure copper was 15 times higher than in the composite materials "copper-graphite", Fig. 6a and 6b.

The distinguished mechanisms of impact of the structure of composite materials reveal the new possibilities for the creation of materials for EDM tools with the improved properties by the method of powder metallurgy.

The capacity of electrodes containing graphite was higher than in electrodes made of pure copper – with TEG at 40%, Table 4.

TABLE 4. Capacity of electrodes on the base of copper when machining the steel H12F

Graphite quantity, vol. %	Capacity, mm³/min	
	E81 mode	E92 mode
0.4 C-1	46.9	52.8
4.0 C-1	44.22	49.7
20.0 C-1	46.9	46.9
0.4 TEG	57,8	86
4.0 TEG	66	89
Copper M1	*34.7*	*49.7*

CONCLUSION

In this study, we found out the traces of formation of graphite intercalated by the copper and sp^3 combinations in graphite sintered with copper using the methods of X-ray phase analysis and Raman spectroscopy.

Sintered materials "copper-carbon phases" do not possess the conductivity higher than the copper, presumably due to the formation of intercalated structures.

During EDM tool machining at roughing conditions, it was found out that the erosion wear of EDM tools of the system "copper-colloid graphite" is 8-15 times lower than the copper has at the capacity exceeding the capacity of the pure copper up to 40%.

We offered a mechanism explaining the increase of wear resistance of EDM tools "copper-carbon phases" based upon the high conductivity and capillary properties of the intercalated structures.

Further research can be connected to the optimization of the graphite intercalation in powder systems "copper-graphite" to improve the conductivity and performance characteristics of EDM tools.

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