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## **SURFACE MODIFICATION OF SYNTHETIC GRINDING POWDERS DIAMOND WITH HEAT-RESISTANT OXIDES AND CHLORIDES LIQUID PHASE APPLICATION METHOD**

**Abstract.** *The restrictions to the selection of oxides, which may be interesting in the modification of forging heat-resistant oxides of the surface of diamond grinding powders, are defined. It is shown that the first group of the most efficient applied for modifying the surface of the diamond grinding powders includes the following oxides –  $B_2O_3$ ,  $TiO_2$ ,  $SiO_2$  and  $Al_2O_3$ . The second group, less effective –  $ZnO$ ,  $BaO$  and  $CaO$ . To achieve an additional positive effect from the modification it is possible to consider a double modification of surface of diamond grains with a mixture of oxides of the first group and chloride ( $CaCl_2$ ,  $NaCl$ ). The process of grain surface modification of synthetic diamond grinding powders by heat-resistant oxides and chlorides of metals and non-metals by liquid phase application has been studied. The structural characteristics of the external structure have been studied and the quantitative elemental composition of the surface of modified powders has been determined. It is established that to achieve a guaranteed increase in wear resistance of diamond wheels when grinding hard alloys at least 2 times it is recommended to modify the surface of diamond grains with a combination of oxides:  $B_2O_3$  grain surface modification (50 % grain) and  $Al_2O_3$  grain surface modification (50 %).*

**Keywords:** *modification; method of liquid-phase deposition, thermal stability; oxides; physical properties; modification of oxides; diamond grinding powders.*

### **Introduction**

Oxygen in cutting processes is an important factor in changing the tribotechnical characteristics of contact surfaces [1]. Oxide layers formed under the action of oxygen or its compounds on contact surfaces significantly reduce friction. And the higher the chemical activity of the metal to oxygen, the more friction is reduced. It is known that in all cases of friction, the presence of oxide film translates the tribosystem into the area of least dangerous oxidative wear.

The protective properties of the oxide film depend on its composition, thickness, hardness of the substrate, etc. [2].

The presence of such an effect is also important for the grinding processes of wheels made of superhard materials (SHM). In [1] the authors determined that to increase the efficiency of grinding processes with wheels with SHM it is possible to apply the following conditions for the delivery of oxygen to the treatment area:

- the bond of the working layer of the wheel must contain materials that are quite actively oxidized (Al, Si, Sn, Cu, Ti, etc.), and it is necessary to create conditions for their oxidation during processing;
- additionally, for example, plasma, impact on the working surface of the wheel should be such that oxide films are formed on the bond and on the grains of SHM;
- as supporting elements in the working layer of the circle can be effectively used oxide granular mineral concentrates, especially oxide rutile ( $\text{TiO}_2$ ) concentrates;
- abrasive materials in the form of counterfeit oxide ( $\text{Al}_2\text{O}_3$ ) tool ceramics can be effectively used in wheels when processing polymeric materials and cast irons.

Other options for introducing oxygen into the treatment area, as an example, are the use of 0.5% solution of hydrogen peroxide in water [3], i.e. the use of special lubricating and cooling process medium (LCPM). The participation of oxygen as a component of the external environment is the most significant in the lubricating effect of LCPM. The lubricating effect of moist air increases when it is sprayed. Mineral oil enhances the effect of oxygen, as it delivers oxygen to the treatment area, as some hydrocarbon compounds are able to dissolve oxygen in an amount of up to 50 %. When spraying oils, the processes of formation of their oxidation products are activated, which easily give atomic oxygen to the metal surface. The role of oxygen-containing compounds increases with increasing cutting speed. In the case of using oils as lubricants, three factors are important: the oxidative activity of the gaseous medium and its humidity, the oxidation of carbon compounds, the conditions of transfer of molecular oxygen to the friction zones.

Consider what we know from recent scientific publications in this area. Oxygen on the surface of diamonds can be caused by normal oxidation. In [4] it was shown that microcrystalline and nanocrystalline diamond layers behave differently during oxidation. In general, microcrystalline samples were more easily oxidized, and this may be due to the fact that in such a sample with larger diamond grains there is a certain ordering of the amorphous carbon phase, indicating the graphitization of  $\text{sp}^2/\text{sp}^3$ .

In [5] the morphological and structural evolution that occurs during the graphitization of microcrystals of synthetic diamond of cubic octahedral shape at a temperature of 1600 °C in the process of vacuum annealing is studied. It is established that graphitization begins with the vertices and edges of crystals. Octahedral faces {111} are more prone to graphitization than cubic ones {100}. The graphite structures formed during the complete graphitization of diamond microcrystals retained the shape of the original crystals.

The authors [6] investigated the graphitization of diamond under the additional presence of metal, namely titanium during its scribing with diamond.

The diamond graphitization wear is ascribed to the catalytic effect of titanium atoms on crystal structure transformation. When the temperature reached up to 1100 K, Raman shifts peak of graphite corresponding to  $1544\text{ cm}^{-1}$  was detected to illustrate the graphite transformation of diamond crystal structure, and the existence of  $\text{TiO}_2$  and C–O bond were confirmed to explain the oxidation wear of diamond grain at the atmosphere of air medium.

Let's pay attention to this C–O bond. The possibility of its use was proved by works [7, 8] through graphene oxide. In paper [7], a novel method with addition of graphene in diamond slurry is proposed to conduct CMP lapping of sapphire wafer. Two kinds of graphenes are added including graphene oxide (GO), reduced graphene oxide (RGO). Results indicate that addition of graphene in diamond slurry can significantly increase material removal rate (MRR) of sapphire wafer. MRR of sapphire wafer is proportional to graphene weight fraction. At higher weight fraction, GO/diamond slurry leads to higher MRR than RGO/diamond slurry does.

The tribological properties of oxidized wood-derived nanocarbons (oWNCs), which have the same surface chemical composition as graphene oxide (GO), were investigated as additives in water-based lubricants [8]. WNCs were synthesized from four kinds of Japanese wood powder by metal-catalyzed carbonization, and were strongly oxidized by a modified Hummer's method. The four oWNCs have aggregated chain-like nanostructures and maintain graphitic layers. In particular, the aqueous dispersion of the oWNC derived from Japanese cedar (J. Cedar) wood powder showed a very low friction coefficient and formed a thick tribofilm on the plate surface.

Now let's look at how a diamond reacts to the presence of metals in contact with it. Electroless composite plating is a valuable way to prepare diamond magnetic abrasives [9]. Diamond magnetic abrasives were prepared by the electroless composite plating method using iron particles and micro diamond particles. The experimental results show the adsorption rate of microdiamond particles on iron powder substrate can be forecasted by the established formula.

The above, as well as data on titanium [6], indicate the importance of taking into account the reaction of diamonds with metals, as discussed in [10]. To explore the difficulty of diamond reacting with different kinds of metals and metal oxides, the activation energies of the reaction between diamond and metals, as well as between diamond and metal oxides, were obtained by first-principle calculation. For the transition metals in the fourth period of the Periodic Table of the Elements, when they react with diamond and form corresponding metal carbides, the order of activation energy from low to high is Mn, Fe, V, Ti, Cr, Co, Ni, Zn, and Cu. The calculated results are in accord with unpaired “*d*” electrons theory and previous studies. And when diamond reacts with  $\text{MnO}$ ,  $\text{FeO}$ ,  $\text{CoO}$ ,  $\text{NiO}$ , and  $\text{CuO}$  to form

metals and CO, the calculated activation energy in descending order is MnO, FeO, CoO, NiO, and CuO.

As we see, some attention is paid to oxides by researchers, so let's consider it more specifically. Let's start with CuO [11]. Surface morphologies showed that diamond coating can deposit on the substrate with CuO particles. However, CuO particles can lead to the formation of the amorphous carbons with high Raman bands.

In the work [12] W-containing coatings were deposited on the surface of diamond microcrystals by hot pressing using  $WO_3$  as a metal source. After treatment of the mixture at 850 °C for 15 min,  $WO_2$  and  $W_{18}O_{49}$  were found on the diamond surface. During the coating formation, the deposition selectivity with regard to the diamond facet was observed. The {100} facets of diamond were preferentially coated. The coating developed through the formation and coalescence of islands, which were of square shape on the {100} facets and of triangular shape on the {111} facets of diamond. In [13] filed the behavior of another refractory compound – V. During sintering, vanadium ions in the bond was enriched on the diamond surface and combined with the unsaturated carbon atom existed on the surface of diamond to form abrasive. Разом з тим, results showed that the refractoriness of the vitrified bond with 4 wt. %  $V_2O_5$  reached 555 °C, 17 °C lower than that of the vitrified bond without  $V_2O_5$ .

In the work [14] diamond was modified by coating  $SiO_2$  layer through isothermal hydrolysis method. Diamond abrasives with three different micro-nanoscale particle sizes were chosen to be modified. The results show that  $SiO_2$  thin film is uniformly grafted onto the diamond surface. The results of polishing tests show that the  $SiO_2$ -modified diamond abrasives exhibit higher material removal rate and better polishing quality than that of unmodified diamond abrasives.

Given a certain positive from the modification of  $SiO_2$  in a number of works [15–17] another heat-resistant oxide -  $Al_2O_3$  was considered.

In the work [15] diamond powders have been coated with thin layers of  $Al_2O_3$  by atomic layer deposition with the aim of prevent its thermal oxidation. it was found that the weight loss onset temperatures ( $T_{onset}$ ), that denotes the temperature at which decomposition diamond to  $CO_2$  begins, shifted towards higher temperatures (an increment of  $\approx 50$  K) as result of protective effect of the  $Al_2O_3$  layer.

Understanding and rationally controlling the interfacial electronic states of the  $Al_2O_3$ /diamond ( $Al_2O_3(001)/C(001)$ ) appears to be crucial in the next generation oxide-semiconductor devices on the basis of diamond. In the work [16] the density functional theory computations are used to systematically elucidate the effects of the different terminated planar of  $Al_2O_3$  and diamond on the electronic properties of the  $Al_2O_3$ /diamond interfaces.

Ще один приклад застосування  $\text{Al}_2\text{O}_3$  поданий в статті [17]. A Cu-Ni-Sn matrix reinforced by  $\text{Al}_2\text{O}_3$  particles (referred as CuNiSn/ $\text{Al}_2\text{O}_3$ ) has been developed as a potential substitute for cobalt to fabricate diamond-cutting tools. The new CuNiSn/ $\text{Al}_2\text{O}_3$  matrix is promising for fabricating diamond tools with low cost, high processing efficiency and long service life.

At the end of our review we will also pay attention to some exotic but interesting options for grain surface modification, such as boron - with the formation of  $\text{B}_2\text{O}_3$  on the grain surface [18], activation of NaCl [19] and diamond coating with hydrogen [20].

It was demonstrated that the properties of diamond can be improved by surface engineering [15]. It is also important to modify the surface of diamond grains with oxides [21], because it will allow to deliver oxygen to the treatment area.

In this setting, this problem is little studied, and the possibility of their implementation is discussed in this article. Synthetic diamond-polished grinding powders modified with heat-resistant oxides were used as abrasive powders in the working layer of the abrasive tool. This allowed to efficiently deliver the oxides directly to the area of treatment with diamond grains, i.e. directed oxides to the surface of diamond grains. The functions that must be performed by oxides in the treatment area are as follows: to calm the oxidation processes of diamond; to influence the facilitation of plastic deformation of the processed material; change the friction processes in the treatment area; reduce the temperature in the treatment area.

In the first stage, we determined which oxides can perform these functions. At one time, [22] investigated the loss of mass of diamond grains in a mixture with various metals or oxides when heated in air at  $900 \pm 10$  °C for 20 min. It was found that the investigated metals in the experimental conditions are oxidized to form oxides, and therefore the decisive influence on the heat resistance of diamonds are no longer the metals themselves, but their oxides.

It has also been shown that the loss of diamond grains is the lowest in the presence of boric anhydride ( $\text{B}_2\text{O}_3$ ), tungsten or tungsten anhydride ( $\text{WO}_3$ ), and zinc oxide ( $\text{ZnO}$ ). Manganese and silicon dioxide ( $\text{SiO}_2$ ) almost do not change the weight loss of diamond grains, and cobalt, copper, nickel and their oxides  $\text{Co}_3\text{O}_4$ ,  $\text{CuO}$ ,  $\text{NiO}$  significantly impair the heat resistance of diamond. From [22] it can also be concluded that in order to achieve the quenching condition of the diamond oxidation process, it is desirable to have metals or oxides in contact with it with low melting points. In addition, since diamonds are compressed in the bond of the working layer of the wheel, it is desirable that the oxides do not have large values of coefficient of thermal expansion and specific heat.

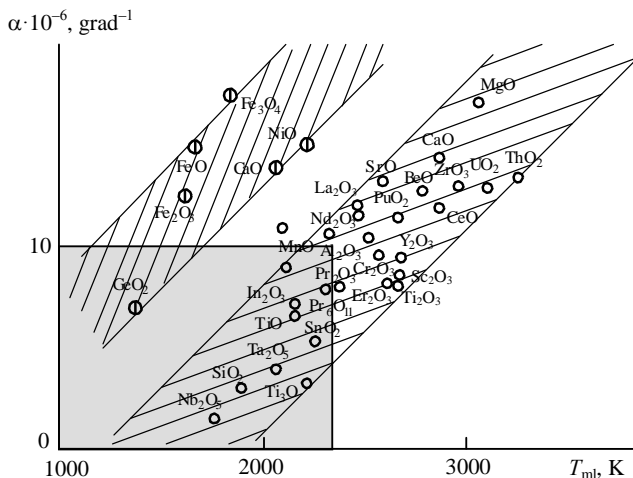


Figure 1 – Correlation between melting point and CLTE of oxides

We analyze the relationship between data on thermal expansion and other properties of oxides and carbides, given in [23, 24]. It is known [25] that thermal expansion is closely related to the parameters characterizing the state of a solid, and there are such dependences for metals, but the authors of this article did not find similar generalized data for oxides and carbides. It is known [26] that for metals the coefficient of linear thermal expansion (CLTE) is the lower, the higher the melting point of the metal. For oxides, as we found in the analysis of the data set [23, 24], there is an inverse relationship: with increasing melting point ( $T_{ml}$ ) of oxides, their CLTE increases (Fig. 1). In fig. 1 shows that the oxides of metals of group VIII – iron, cobalt and nickel, as well as germanium occupy a separate area parallel to the main.

A similar grouping is observed in the analysis of the relationship between CLTE and standard molar heat capacity of oxides (Fig. 2). Analysis of the relationship between density and heat capacity shows that with increasing oxide density, the standard heat capacity increases slightly (see Figure 2). Significant growth is observed for oxides containing  $Me_2O_3$ . In general, the above-described grouping by valence of the metal oxide is observed. Therefore, oxides have a number of characteristic features, the analysis of which can be useful, for example, in explaining the behavior of ceramics in heating or the choice of oxides for modification of oxides on the grain surface.

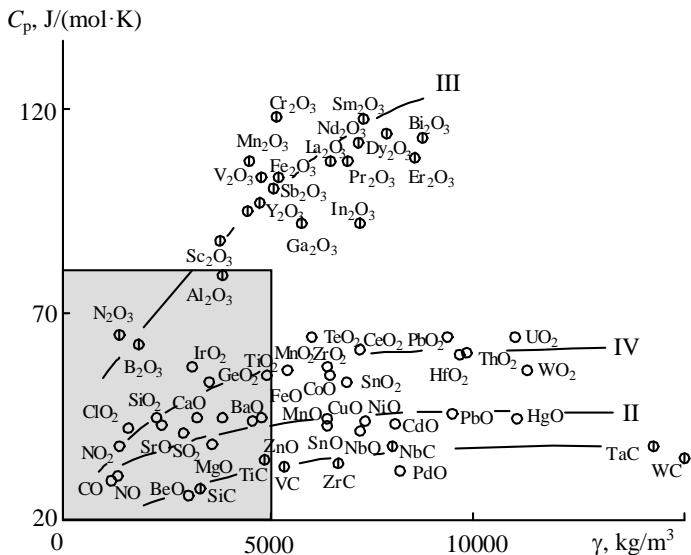


Figure 2 – Correlation between density and specific molar heat capacity of oxides and carbides; Roman numerals indicate the valence of oxide metals

Taking into account the experimental data obtained by the authors [1] on the introduction of oxides in the contact zone of the grinding wheel and the workpiece and the above correlations, it was determined that for the modification of grinding grains impractical. Other restrictions, according to the authors, are restrictions on the melting temperature of such oxides – no more than 2300 K (see Fig. 1), on the specific molar heat capacity – no more than 80 J/(mol·K) (see Fig. 2) and by the density of oxides - no more than  $5 \cdot 10^3$  kg/m<sup>3</sup> (see Fig. 2). Given the above limitations, the oxides that can be used in the modification of heat-resistant oxides of the surface of diamond grains include a significant part of the oxides of the group MeO<sub>2</sub> (TiO<sub>2</sub>, SiO<sub>2</sub>, GeO<sub>2</sub>, SnO<sub>2</sub>). Oxides of Me<sub>2</sub>O<sub>3</sub> (N<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>), as well as MeO (TiO, BaO, BeO, CaO) can be used to a lesser extent. According to the authors, the use of Me<sub>2</sub>O<sub>5</sub> oxides for modification is inexpedient. In addition, beryllium oxide (BeO) should be excluded, as it, like other beryllium compounds, is a carcinogen.

Now let's look at the following. Aqueous solutions of LCPM based on alkali metal salts (electrolyte solutions) are often used in the process of diamond-abrasive grinding of hard alloys and tool steels and ceramics. High grinding temperatures do not exclude the possibility of simultaneous presence in the treatment area of both saturated saline solutions and alkali metal oxides. Sufficient oxygen, air, water and

thermal decomposition products of LCPM elements promote rapid oxidation of the metal surface. The growth of oxidation products is facilitated not only by high temperatures in the cutting zone by the grinding wheel, but also by the accumulation of electric discharges on the treated surface with a positive potential relative to the mass of the machine arising from abrasive grains on metal (thermoelectric effect). In this case, there are conditions for electrochemical reactions of anodic dissolution on the entire surface to be treated [27]. In the case of LCPM diamond treatment, impurities, often organic, containing chemically active elements: sulfur, chlorine, phosphorus, iodine, etc., which are released mainly in the contact zones during thermal decomposition of impurities, are introduced to increase the lubricating effect. The mechanism of lubricating action of impurities is based on their ability to form in the contact zones solid lubricating layers of the corresponding inorganic metal salts, thereby chemically modifying the surface. Combined impurities containing sulfur, chlorine and phosphorus are used simultaneously to expand the capabilities of LCPM [27]. Of these impurities can be considered salts of chlorides –  $\text{CaCl}_2$ ,  $\text{NaCl}$ ,  $\text{BaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{KCl}$ , of which the most environmentally friendly are  $\text{CaCl}_2$  and  $\text{NaCl}$ .

In general, this suggests that by analogy with the described action of LCPM can also be considered a double modification of the grain surface of diamond grinding powders with a mixture of oxides and chlorides, which can give an additional effect when modifying the surface of diamonds.

Therefore, the analysis of the above allowed us to draw the following conclusion. The first group, of most effectively used to modify the grain surface of diamond grinding powders, include the following oxides:  $\text{B}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , the second group, less effective -  $\text{ZnO}$ ,  $\text{BaO}$  and  $\text{CaO}$ . To achieve an additional positive effect from the modification, we can consider double modification of the surface of diamond grains with a mixture of oxides of the first group and chlorides ( $\text{CaCl}_2$ ,  $\text{NaCl}$ ).

Indirectly, our conclusions are confirmed by the data of [28], where it is shown that the addition of  $\text{ZnO}$  promotes the formation of oxygen polyhedra and at the same time a large amount of lean oxygen in the glass mesh, which leads to increased wettability of glazed bonds and the formation of  $-\text{C}=\text{O}$ ,  $-\text{O}-\text{H}$  and  $-\text{C}-\text{H}$  bond on the surface of diamond grains.

Now, in the second stage, we will understand the issues of surface modification of diamond grain grinding powders.

Our previous studies [21] found that it is promising to modify the grain surface of diamond grinding powders with heat-resistant inorganic non-metallic coatings (oxides and chlorides of metals and non-metals) by liquid-phase application. The most economically advantageous method is the liquid-phase application of the modifier - from aqueous solutions of oxides and chlorides of metals and non-metals.



## **Materials and methods of research**

For research, average samples of raw materials were selected: grinding powders of synthetic diamonds: AC6 125/100 and AC15 250/200, metallized Ni. The grain surface of the powders was modified by the isothermal method of liquid-phase application from saturated solutions of both heat-resistant oxides ( $B_2O_3$ ), chlorides ( $CaCl_2$ ,  $NaCl$ ,  $MgCl_2$ ,  $FeCl_3$ ) and their mixtures ( $B_2O_3 + CaCl_2$ ,  $B_2O_3 + NaCl$ ).

Determination of structural and morphological characteristics of the external structure and quantitative elemental composition of modified powders was performed using a scanning electron microscope (SEM) ZEISS EVO 50XVP, equipped with energy-dispersive X-ray spectrum analyzer INCA ENERGY 450.

**Modification of the surface of powder materials by the method of liquid-phase application** is the process of precipitation of the modifier substance released (crystallized) from the solution in the form of crystals or films on the surface of a solid (in our case, diamond grinding powder).

The fixation of the modifier on the grains of this powder is due to the process of physical adsorption, the phenomenon of absorption by some solids of gases, salts, etc. substances from solutions. The active centers that exist on the surface of synthetic diamond grains are the primary fixation centers of the modifier [13]. We point out the following features of physical adsorption: first, it is a weak type of interaction, because it is not caused by electronic transitions, but only by changing the nature of electron motion in adsorbent and adsorbate particles, and secondly, adsorbed particles retain their molecular nature. that is, they are chemically unchanged. Therefore, this interaction is considered molecular [29]. In our process of physical adsorption (modification) the adsorbent was synthetic diamond grinding powder, the adsorbate was a precipitated layer of the modifier substance ( $B_2O_3/NaCl/CaCl_2/ \dots$ ), the adsorbent was a saturated solution of the modifier substance.

In the liquid-phase method of forming a precipitated layer from a solution of heat-resistant compounds (for example,  $B_2O_3$ ,  $CaCl_2$ ,  $MgCl_2$ ,  $FeCl_3$ , etc.), when a substance is deposited on the grain surface of a powder material, its crystallization occurs. This is the case for a saturated solution and is positive because it helps to achieve a sufficient thickness of the precipitated layer. According to our research, even with a short duration of the modification process, the size of the crystals formed is much smaller (by one or two orders of magnitude) compared to the size of diamond grains.

## **Discussion of experimental results**

The investigated powder - synthetic diamond grinding powder (25 ct) was mixed with 10–15 ml of saturated solution of the modifier substance using a

magnetic stirrer for 10 minutes under normal conditions. Excess solution was drained and the remaining mixture was filtered. The obtained wet mass of powder was dried with stirring at a temperature of 120 °C to a dry homogeneous state. After coating by gravimetry, the relative amount of the modifier was determined, as well as the change in heat resistance of the modified powders. Heat treatment of both original and modified samples was carried out in air in a tubular furnace at a temperature of 800–900 °C for 30 minutes. The coefficient of heat resistance  $K_{ml}$  was determined by the loss of mass of the samples (Table 1).

Table 1 – The results of modification of synthetic diamond grinding powders with saturated solutions of heat-resistant oxides and chlorides

№	Samples	Modifier	The amount of modifier, %	$K_{ml}$
1	AC6 125/100	CaCl <sub>2</sub> (*)	8.2	0.95
2	AC6 125/100	NaCl	9.7	0.98
3	AC6 125/100	B <sub>2</sub> O <sub>3</sub>	6.3	0.98
4	AC6 125/100	B <sub>2</sub> O <sub>3</sub> (тричі)	7.4	0.98
5	AC6 125/100	MgCl <sub>2</sub> (*)	6.0	0.92
6	AC6 125/100	FeCl <sub>3</sub> (*) (5 мл р-ну)	5.2	0.97
7	AC6 125/100	B <sub>2</sub> O <sub>3</sub> +CaCl <sub>2</sub> (*)	8.7	0.94
8	AC6 125/100	B <sub>2</sub> O <sub>3</sub> +NaCl	9.2	0.98
9	AC15 250/200 (Ni)	B <sub>2</sub> O <sub>3</sub>	5.9	0.95
10	AC6 125/100 output			0.91

\* *Hygroscopic powders*

The degree of coverage of diamond grains, for example, with boron oxide (B<sub>2</sub>O<sub>3</sub>) is on average 5.64% (B<sub>2</sub>O<sub>3</sub> density – 2.55 g/cm<sup>3</sup>, diamond density – 3.56 g/cm<sup>3</sup>).

From the data in Table 1, we pay attention to the fact that virtually all grinding powders with grains that have undergone surface modification have a coefficient of heat resistance higher than the original diamond powder. Moreover, the largest values of the coefficient are characteristic of the conditions of grain surface modification with boron oxide (B<sub>2</sub>O<sub>3</sub>).

In Figure 3 shows a sample of grinding powder of diamond AC6 125/100, three times modified with B<sub>2</sub>O<sub>3</sub> oxide – sample № 4 (see Table 1), and shows the areas in which the elemental composition of the grain surfaces of the sample was determined by local X-ray spectral (LRS) analysis.

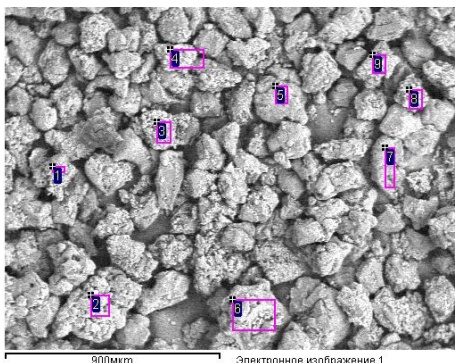


Figure 3 – Areas subjected to elemental analysis on the grain surface of sample № 4 and their quantitative elemental composition % wt.:

Spectrum	Researched elements		
	<i>B</i>	<i>C</i>	<i>O</i>
1	10.05	28.63	61.32
2	12.53	19.69	67.79
3	4.85	41.01	54.14
4	8.87	28.78	62.35
5	0.00	34.53	65.47
6	7.16	37.88	54.96
7	5.17	72.26	22.58
8	9.44	41.60	48.97
9	8.52	26.96	64.52

As you can see, the results of quantitative LRS analysis of sample № 4 (three times modified B<sub>2</sub>O<sub>3</sub>) show the content of carbon (diamond) from 72.26 to 19.69 %, boron from 0.0 to 12.53 %, oxygen from 22.58 to 67.79 %.

Thus, we have described above the features of surface modification of synthetic diamond grinding powders both separately with heat-resistant oxide (B<sub>2</sub>O<sub>3</sub>) and in combination with chlorides (NaCl, CaCl<sub>2</sub>).

In the future, we studied the performance characteristics of diamond wheels with grinding powders of synthetic diamond brand AC6 with the above surface modifications.

Heavily machined tungsten-titanium-cobalt hard alloy brand T15K6 with sample sizes 63x15x7 mm was selected for processing. Grinding modes: wheel rotation speed - 18 m/s, transverse feed – 0.05 mm/double stroke, longitudinal feed – 0.57 m/min (for processing productivity of 200 mm<sup>3</sup>/min) and 1.14 m/min (for processing productivity of 400 mm<sup>3</sup>/min). Grinding was carried out without

cooling, so as not to introduce additional disturbances in the processing process, as it is unknown at this time the possibility of possible interaction of chlorides with the components of the process fluid, which may be the subject of further research. The wear resistance of the grinding tool was evaluated according to the relative consumption of diamonds ( $q$ ) and the roughness of the treated surface according to ( $R_a$ ). The test results are given in table. 2.

Table 2 – Performance of diamond grinding wheels on a polymer bond B2-08 with a relative grain concentration of 100% with different options for surface modification of diamond grains brand AC6 125/100

Modification of a surface of diamond grains in a working layer of diamond wheels 12A2-45° 125x5x3x32	Processing productivity:			
	200 mm <sup>3</sup> /min		400 mm <sup>3</sup> /min	
	$q$ , mg/g	$R_a$ , mkm	$q$ , mg/g	$R_a$ , mkm
Modification of B <sub>2</sub> O <sub>3</sub> grain surface (50 % of grains) and modification of Al <sub>2</sub> O <sub>3</sub> grain surface (50 %)	7	0.37	17	0.43
Modification of CaCl <sub>2</sub> grain surface (100 %)	9	0.37	20	0.41
Modification of B <sub>2</sub> O <sub>3</sub> grain surface (50 % of grains) and modification of MgCl <sub>2</sub> of grain surface (50 %)	12	0.40	24	0.41
Modification of FeCl <sub>3</sub> grain surface (100 %)	15	0.48	26	0.43
<b>AC6 125/100 B2-08 100 without modifying the surface of the grains</b>	<b>17</b>	<b>0.31</b>	<b>37</b>	<b>0.52</b>
Modification of NaCl grain surface (100 %)	17	0.33	46	0.44
Modification of B <sub>2</sub> O <sub>3</sub> grain surface (100 %)	25	0.45	32	0.49
Modification of a mixture (B <sub>2</sub> O <sub>3</sub> + CaCl <sub>2</sub> ) of grain surface (100 %)	22	0.45	43	0.40
Modification of the mixture (B <sub>2</sub> O <sub>3</sub> + NaCl) of the grain surface (100 %)	343	0.36	–	–

Let's analyze the results of table. 2. First in terms of wear resistance of the diamond tool. At once we will pay attention that 100% modification of a surface of diamond grains by pure oxide B<sub>2</sub>O<sub>3</sub> and its mix with chlorides of CaCl<sub>2</sub> or NaCl on productivity of processing of 200 mm<sup>3</sup>/min only increases the wear of the wheel. Note that the modification of the grain surface exclusively NaCl does not actually

affect the wear of the wheel, but such modification in a mixture with  $B_2O_3$  is unacceptable, because it immediately translates the wear of the wheel in the area of catastrophic wear, which does not allow research on such a wheel min. (see Table 2).

And what modification allows to increase wear resistance of a diamond wheel?

First, it is pure chlorides of  $CaCl_2$  and  $FeCl_3$ .

Second, combined modification, when 50 % of the grains are modified with  $B_2O_3$  oxide and the other 50 % of the grains are modified with  $MgCl_2$ , chloride or  $Al_2O_3$  oxide. We place the specified modification in a row as wear resistance increases:

*No modification –  $FeCl_3 – B_2O_3/MgCl_2 – CaCl_2 – B_2O_3/Al_2O_3$ .*

The difference in wear resistance for the first (without modification) and the last (for  $B_2O_3/Al_2O_3$ ) link of this series is 2.43, i.e. the wear resistance of the diamond wheel when modified with a combination of  $B_2O_3/Al_2O_3$  increases by 2.43 times. This range for a productivity of 200  $mm^3/min$ .

And what will happen with a 2-fold increase in productivity? In fact, the location of this series has not changed, but it included modifying the surface of the grains with  $B_2O_3$  oxide, and here this series looks like this:

*No modification –  $B_2O_3 – FeCl_3 – B_2O_3/MgCl_2 – CaCl_2 – B_2O_3/Al_2O_3$ .*

For higher processing productivity of 400  $mm^3/min$  the difference in wear resistance for the first (without modification) and the last (for  $B_2O_3/Al_2O_3$ ) link of this series is already 2.18, i.e. the wear resistance of the diamond wheel when modified with a combination of  $B_2O_3/Al_2O_3$  increases by 2.18 times. That is, modification of the surface of diamond grains with a combination of  $B_2O_3/Al_2O_3$  is guaranteed to double the wear resistance of diamond wheels, both at low and high processing productivity.

An indirect conclusion from the above is that at low processing productivity chlorides occur in the above series three times, and  $B_2O_3$  oxide – twice. With increasing productivity of processing chlorides and the specified oxide already occur equally - three times. In both cases of productive processing, it is best to modify the surface of diamond grains with a combination of  $B_2O_3/Al_2O_3$ .

From the table 2 also shows that the modification of the diamond surface with  $NaCl$  chloride, both alone and in a mixture with  $B_2O_3$ , is negative and the use of these two modifications for diamond powders is unacceptable. Note also that the modification of the mixture ( $B_2O_3 + CaCl_2$ ) of the grain surface also does not give a positive effect.

Now, before considering the impact of grain surface modification on the roughness of the treated surface, let's pay attention to the state of the cutting layer

of diamond wheels in different modifications, because this is what determines the roughness.

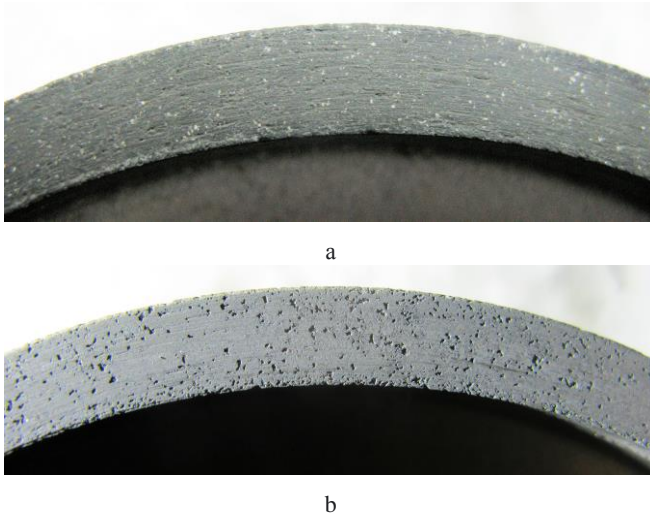


Figure 3 – Condition of the cutting surface of a circle with diamond grains with modification of their surface with a mixture of – ( $B_2O_3 + CaCl_2$ ): a – in the initial state, b – after grinding a hard alloy with a capacity of  $400 \text{ mm}^3/\text{min}$

In the case of modification of the surface of diamond grains with the use of chlorides, certain disturbances occur on the cutting surface. Thus, if we compare the cutting surface of the circle, for example, when modifying the surface of diamond grains with a mixture ( $B_2O_3 + CaCl_2$ ) in the initial state (Fig. 3, a) and after grinding hard alloy T15K6 (Fig. 3, b), we see that many wells appear on the cutting surface, probably from torn diamond grains, i.e. the diamond content here is deteriorating. Similar surfaces are formed when modified with the participation of other chlorides: NaCl,  $FeCl_3$  and mixtures – ( $B_2O_3 + CaCl_2$ ) and ( $B_2O_3 + NaCl$ ). The reason for this effect of chlorides on the cutting surface of the wheel is unclear and requires further research. Perhaps the peculiarities of diamond content of chloride-modified diamond grains contribute here.

Of course, such changes in the cutting surface can not but affect the roughness of the treated surface, which we will consider below. Note that the productivity of grinding has a significant impact. If at low productivity in  $200 \text{ mm}^3/\text{min}$  grinding wheel with diamond grains without surface modification gives the lowest value of the roughness of the treated surface according to the parameter  $R_a$  (Table 3), then at a much higher productivity of  $400 \text{ mm}^3/\text{min}$  the same wheel

already gives the largest values of roughness on the parameter  $R_a$  (Table 4). In this case, in the first case, close to the original wheel (within 20 % deviation) indicators for the parameter  $R_a$  (see Table 3) have wheels with subsequent surface modifications of diamond grains (in a row as the parameter  $R_a$  increases):

*No modification – NaCl – B<sub>2</sub>O<sub>3</sub>/NaCl – (CaCl<sub>2</sub> – B<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>).*

In turn, for productivity of 400 mm<sup>3</sup>/min roughness indices differ less (see table. 4) and those that differ the least, it is possible to arrange in a row as the parameter  $R_a$ :

*No modification – (CaCl<sub>2</sub> – B<sub>2</sub>O<sub>3</sub>/MgCl<sub>2</sub>) – (FeCl<sub>3</sub> – B<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>) – NaCl.*

We also pay attention to how the fullness of the rough surface differs according to such a parameter of the support surface curve as  $t50$ . The larger the value of  $t50$ , the better the roughness of the rough surface.

Table 3 – Roughness of the treated surface of the hard alloy T15K6 diamond grinding wheels on a polymer bond B2-08 with a relative grain concentration of 100 % with different options for modification of the surface of diamond grains brand AC6 125/100 (with a productivity of 200 mm<sup>3</sup>/min)

Modification of a surface of diamond grains in a working layer of diamond wheels 12A2-45° 125x5x3x32	Roughness indicators:			
	$R_a$ , mkm	$R_{max}$ , mkm	$S_m$ , mkm	$t50$ , %
<b>AC6 125/100 B2-08 100 without modifying the surface of the grains</b>	<b>0.31</b>	<b>2.27</b>	<b>72</b>	<b>48.92</b>
Modification of NaCl grain surface (100 %)	0.33	2.51	56	67.17
Modification of the mixture (B <sub>2</sub> O <sub>3</sub> + NaCl) of the grain surface (100 %)	0.36	2.78	47	48.56
Modification of B <sub>2</sub> O <sub>3</sub> grain surface (50 % of grains) and modification of Al <sub>2</sub> O <sub>3</sub> grain surface (50 %)	0.37	1.94	50	57.08
Modification of CaCl <sub>2</sub> grain surface (100 %)	0.37	2.28	53	43.82
Modification of B <sub>2</sub> O <sub>3</sub> grain surface (50 % of grains) and modification of MgCl <sub>2</sub> of grain surface (50 %)	0.40	2.16	175	68.13
Modification of B <sub>2</sub> O <sub>3</sub> grain surface (100 %)	0.45	3.26	63	57.26
Modification of a mixture (B <sub>2</sub> O <sub>3</sub> + CaCl <sub>2</sub> ) of grain surface (100 %)	0.45	2.89	64	50.36
Modification of FeCl <sub>3</sub> grain surface (100 %)	0.48	4.09	75	56.48

Table 4 – Roughness of the treated surface of the hard alloy T15K6 diamond grinding wheels on a polymer bond B2-08 with a relative grain concentration of 100 % with different options for modification of the surface of diamond grains brand AC6 125/100 (with a productivity of 400 mm<sup>3</sup>/min)

Modification of a surface of diamond grains in a working layer of diamond wheels 12A2-45° 125x5x3x32	Roughness indicators:			
	$R_a$ , mkm	$R_{max}$ , mkm	$S_m$ , mkm	$t50$ , %
Modification of a mixture (B <sub>2</sub> O <sub>3</sub> + CaCl <sub>2</sub> ) of grain surface (100 %)	0.40	3.47	53	69.33
Modification of B <sub>2</sub> O <sub>3</sub> grain surface (50 % of grains) and modification of MgCl <sub>2</sub> of grain surface (50 %)	0.41	3.03	68	57.38
Modification of CaCl <sub>2</sub> grain surface (100 %)	0.41	3.00	95	50.00
Modification of B <sub>2</sub> O <sub>3</sub> grain surface (50 % of grains) and modification of Al <sub>2</sub> O <sub>3</sub> grain surface (50 %)	0.43	4.73	96	90.14
Modification of FeCl <sub>3</sub> grain surface (100 %)	0.43	3.65	61	51.14
Modification of NaCl grain surface (100 %)	0.44	3.37	69	27.79
Modification of B <sub>2</sub> O <sub>3</sub> grain surface (100 %)	0.49	3.45	63	45.50
<b>AC6 125/100 B2-08 100 without modifying the surface of the grains</b>	<b>0.52</b>	<b>3.67</b>	<b>72</b>	<b>64.23</b>

For processing productivity of 200 mm<sup>3</sup>/min this figure varies within 25 % (see table. 3), and for 400 mm<sup>3</sup>/min this difference is already 63 % (see Table 4).

In more detail, the features of the supporting surfaces of the rough surface are presented in Fig. 4. That is, if necessary, changing the surface modifier of diamond grains from CaCl<sub>2</sub> to NaCl can not affect the bearing capacity of the rough surface obtained by grinding, in this case to increase it by the parameter  $t50$  from 43 % to 70 %.



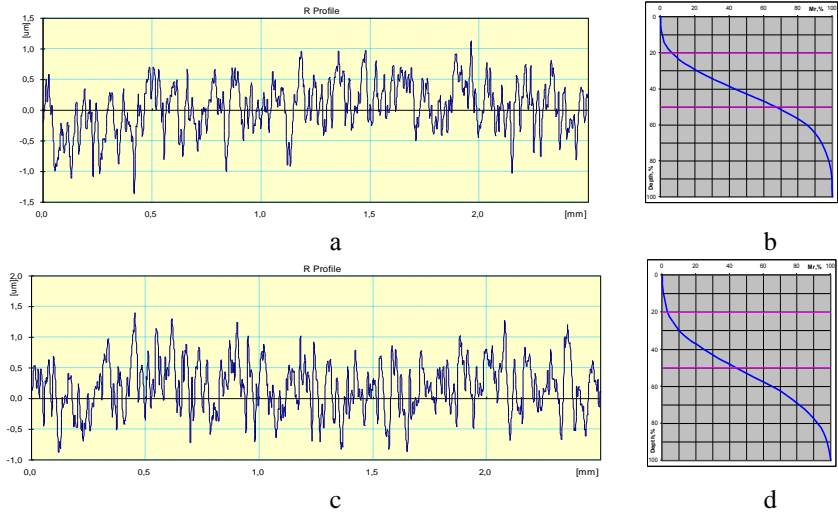


Figure 4 – Profilograms (a, c) and curves of the relative reference length of the profile (b, d) of the surface treated with a wheel with modified surface of NaCl grains (a, b) and a wheel with modified surface of CaCl<sub>2</sub> grains (c, d) when grinding hard alloy with a productivity of 200 mm<sup>3</sup>/min

## Conclusions

1. The possibility of directed modification of the surface of diamond grinding powders with heat-resistant oxides and chlorides of metals and non-metals is shown.

2. Modification of the surface of diamond grains with oxides and chlorides increases the heat resistance of synthetic diamond grinding powders. The best result was obtained by modifying the surface of diamond grains with boric anhydride (B<sub>2</sub>O<sub>3</sub>).

3. It is established that to achieve a guaranteed increase in wear resistance of diamond wheels when grinding hard alloys at least 2 times it is recommended to modify the surface of diamond grains with a combination of oxides: B<sub>2</sub>O<sub>3</sub> grain surface modification (50 % grain) and Al<sub>2</sub>O<sub>3</sub> grain surface modification (50 %). Modification of the surface of diamond grains with CaCl<sub>2</sub> chloride increases the wear resistance of diamond wheels by a maximum of 1.8 times. A third acceptable option is grain surface modification by a combination of oxide and chloride: grain surface B<sub>2</sub>O<sub>3</sub> modification (50 % grain) and grain surface MgCl<sub>2</sub> modification (50 %). This modification makes it possible to increase the wear resistance of the wheels by 1.4-1.5 times.

4. It was found that diamond grains modified with sodium chloride or modified with a mixture ( $B_2O_3 + NaCl$ ) should be used to achieve the minimum roughness during finishing grinding operations. As grinding productivity increases, this relationship disappears and it is recommended to use diamond grains modified with calcium chloride or modified with a mixture ( $B_2O_3 + CaCl_2$ ).

5. It was found that if we have the condition to achieve a rough surface with the highest bearing capacity, then the use of diamond grains with chloride modification is unacceptable, and it is necessary to use diamond grains in wheels with surface modification combination  $B_2O_3/Al_2O_3$ .

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## **МОДИФІКАЦІЯ ПОВЕРХНІ СИНТЕТИЧНИХ АЛМАЗНИХ ШЛІФПОРОШКІВ ЖАРОСТІЙКИМИ ОКСИДАМИ І ХЛОРИДАМИ РІДКОФАЗНИМ МЕТОДОМ НАНЕСЕННЯ**

**Анотація.** *Визначено обмеження на вибір оксидів, які можуть становити інтерес при модифікуванні штампувальними жаростійкими оксидами поверхні алмазних шліфпорошків. Досліджено процес модифікації поверхні зерен синтетичних алмазних шліфпорошків термостійкими оксидами та хлоридами металів та неметалів методом рідкофазного нанесення. Досліджено структурні характеристики зовнішньої структури та визначено кількісний елементний склад поверхні модифікованих порошків. Показано можливість спрямованого модифікування поверхні алмазних шліфпорошків термостійкими оксидами та хлоридами металів та неметалів. Модифікація поверхні алмазних зерен оксидами та хлоридами підвищує термостійкість синтетичних алмазних шліфпорошків. Встановлено, що для досягнення гарантованого підвищення зносостійкості алмазних кругів при шліфуванні твердих сплавів не менше ніж у 2 рази рекомендується модифікувати поверхню алмазних зерен комбінацією оксидів:  $B_2O_3$  (50% зерна) та  $Al_2O_3$  (50 %). Модифікація поверхні алмазних зерен хлоридом  $CaCl_2$  підвищує зносостійкість алмазних кругів максимум в 1,8 рази. Третім прийнятним варіантом є модифікація поверхні зерна комбінацією оксиду та хлориду: модифікація поверхні зерна  $B_2O_3$  (50% зерна) та модифікація поверхні зерна  $MgCl_2$  (50%). Дана модифікація дозволяє підвищити зносостійкість кругів у 1,4-1,5 рази. Встановлено, що для досягнення мінімальної шорсткості при чистовому шліфуванні слід використовувати алмазні зерна, модифіковані хлоридом натрію або сумішшю ( $B_2O_3 + NaCl$ ). Зі збільшенням продуктивності шліфування ця залежність зникає і рекомендується використовувати алмазні зерна, модифіковані хлоридом кальцію або сумішшю ( $B_2O_3 + CaCl_2$ ). Встановлено, що якщо є умова отримання шорсткої поверхні з найбільшою несучою здатністю, використання алмазних зерен з хлоридною модифікацією неприпустимо, і необхідно використовувати алмазні зерна в кругах з комбінацією модифікації поверхні  $B_2O_3/Al_2O_3$ .*

**Ключові слова:** *модифікація; метод рідкофазного осадження; термічна стабільність; оксиди; фізичні властивості; модифікація оксидів; алмазні шліфувальні порошки.*