High Temperature Ionic Liquids Electrosynthesis of Mo$_2$C Protective Coatings on Diamond, Boron Nitride, Silicon and Boron Carbide

VICTOR MALYSHEV[1], ANGELINA GAB[2], DIMITRI SHAKHNIN[1], CRISTINA DONATH[3], ELENA IONELA NEACSU[3], ANA MARIA POPESCU[3,4], VIRGIL CONSTANTIN[3,4*]

[1]Vernadskii Institute of General and Inorganic Chemistry, Ukrainian Academy of Sciences, 32-34 Acad.Paladine Ave., 03680, Kyiv, Ukraine

[2]National Technical University of Ukraine Kyiv Polytechnical Institute, 37 Peremogy Ave., 03057, Kyiv, Ukraine

[3] Ilie Murgulescu Institute of Physical Chemistry of the Romanian Academy, Laboratory of Electrochemistry and Corrosion, 202 Splaiul Independentei, 006021, Bucharest, Romania

[4]Technology Transfer Center-ICF, 202 Splaiul Independentei, 006021, Bucharest, Romania

On the basis of the thermodynamic analysis of the reactions of dielectrics and semiconductors with ionic melts, the systems suitable for an electrochemical synthesis from high temperature ionic liquids of films consisting in molybdenum carbide on the surfaces of these materials were selected. Then, the study of their electrochemical behavior was performed.

Keywords: molybdenum carbide, coatings, electrodeposition, ionic liquids

Diamonds (natural and synthetic) and cubic boron nitride are high-resistance dielectrics (HRD), i.e., they hardly conduct current. According to reference data, the electrical resistivity of the majority of natural diamonds is 10^{10}-10^{14} $\Omega \times$cm in the 973-1173 K range [1, 2] and that of boron nitride is10^8-10^{13} $\Omega \cdot$cm [3]. Hence, the use of these dielectrics as a cathode material is impossible under usual conditions. Silicon and boron carbides fall into the category of semiconductors (SC). Their electrical resistivity is 10^1-10^3 and 10^{-4}-10^{-1} $\Omega \cdot$cm, respectively [2,3]. There are scarce published data on the galvanic treatment of HRD and SC in ionic melts.

We found that HRD crystals, upon the contact with ionic melts of a certain composition, acquire the property to conduct current [3], and the SC crystals, have the property to change their electrode potential in relation to the melt composition [4]. This is explained by the concepts of the generation of a stationary potential and surface conductivity as a result of redox processes occurring on the HRD-SC-melt interface [5]. In this case, when the current passes through the dielectric or semiconductor occurs the electrochemical precipitation of pure elements. Therefore a high-temperature electrochemical synthesis is possible on their surfaces. The use of ionic melts as an electrolyte makes it possible to carry out the high-temperature electrochemical synthesis (ES) of the compounds which cannot be precipitated from aqueous solutions (e.g., molybdenum carbide Mo$_2$C). The precipitation of molybdenum carbide on the grain surface of diamonds (C), boron nitride (BN), and silicon and boron carbides (SiC, SiB) is a powerful means for increasing their efficiency in applications. Due to the coating, operating characteristics of tools are considerably improved, and thus the specific consumption of HRD and SC is decreased [6].

The aim of the present work is the selection of the conditions for carrying out electrochemical synthesis on the surfaces of HRD and SC in high temperature ionic liquids (HTILs). The basis for this elaboration is the thermodynamic analysis of the reactions of C, BN, SiC and SiB with ionic melts, the study of their electrochemical behavior and the appraisal of the possibility for using ES in HTILs systems, which were realized on metal electrodes, as we reported earlier [7].

Experimental part

We used two electrochemical methods, namely the potentiometry and voltammetry with linear potential variation. The following electrochemical systems were studied: halide (1) and halide-oxide (2) systems at 1023 K and oxide (3) systems at 1173 K:

Pt, HRD(SC) | NaCl-KCl melt || NaCl-KCl-PbCl$_2$ melt| Pb liquid,   (1)

Pt, HRD(SC) | NaCl-KCl-Na$_2$MoO$_4$(Na$_2$CO$_3$) melt || NaCl-KCl-PbCl$_2$ melt| Pb liquid,   (2)

Pt, HRD(SC) | Na$_2$WO$_4$-MoO$_3$-Li$_2$CO$_3$ melt||Na$_2$WO$_4$-0.2WO$_3$ melt|O$_2$/Pt   (3)

Either the dielectric or semiconductor electrode is a container made of platinum gauze filled with the powder of the dielectric or semiconductor material. A platinum wire served as a current collector to the container. A platinum crucible was simultaneously the container for the melt and the anode. In systems (1) and (2) a lead electrode immersed in the NaCl-KCl (1:1)-2.5 mol% PbCl$_2$ melt was used as a reference electrode. In system (3) the electrode potential was measured relative to the Pt,O$_2$|Na$_2$WO$_4$-0.2WO$_3$ melt half-cell in an alundum test tube. The equimolar melt of potassium and sodium chlorides of special purity grade have served as supporting electrolyte. In the both potentiometric and voltammetric studies we controlled the mass and appearance of compounds. Also, the X-ray phase analysis of the surface of the material under study was made on a DRON-3.0 equipment, before and after each experiment.

Electrochemical studies were carried out with a TACUSSEL potentiostat PRT 20-10X connected to a PC computer for data acquisition and control. The electrochemical cell design was described previously [8].

To carry out the ES in HTILs in order to prepare films of molybdenum carbide on the grain surface of dielectrics and SCs, the grains were placed into a nickel container. A

*email: vconstan@chimfiz.icf.ro

graphite crucible (MPG-7 grade graphite) was simultaneously a container for the melt and anode. The coated grains were then separated from the electrolyte residue by boiling in distilled water.

Results and discussions

To estimate the possibility for the electrochemical synthesis of molybdenum carbide films on the surface of HRD and SC grains, we chosed the molybdate-and carbonate-containing systems: $NaCl-KCl-Na_2WO_4-MoO_3-Li_2CO_3$ and $NaCl-KCl-Na_2MoO_4-Na_2CO_3$ The data on the chemical behavior of diamonds and silicon and boron carbides in these melts are few in the literature [9,10]. Thus we carried out the thermodynamic analysis of the possible reactions of these melts with existing oxygen-containing compounds (Table 1). To find the standard Gibbs energies (DG) of the reactions we used the data on the thermodynamic properties of the compounds under consideration [11,12].

It follows from Table 1 that C (diamond) must be inert to the action of molten molybdates even up to 1200 K. Sodium carbonate melt does not react with diamond. Only in the melts containing molybdenum oxides the diamond will be susceptible to corrosion. The values of diamond corrosion in the individual NaCl-KCl and Na_2MoO_4 melts and in their mixtures were estimated. Diamond of ASK 400/315 grade practically does not corrode; at 1173 K in the $KCl-NaCl-Na_2MoO_4-Na_2CO_3$ melts its corrosion rate is 0.4-0.5 $g \cdot m^{-2} \cdot h^{-1}$. The introduction of Na_2CO_3 even at a context of 1 wt.% increases the corrosion by the factor 1.3-1.5. Thus, the thermodynamic analysis and the experimental studies of the diamond chemical behavior in oxide-containing melts gives a qualitatively equal result and show that redox processes proceed on the diamond surface upon its contact with a melt. These processes favor the appearance of a stationary potential on the diamond-melt surface.

Thermodynamic calculations (table 1) showed that the most energy favorable process for boron nitride is its oxidation to gaseous nitrogen and boron metaborate or oxide. A compound consisting in an element of group VI and carbon will be presumably chemically reduced to this element in the pure state or to its oxide of an intermediate oxidation state.

The most energy favorable process for silicon and boron carbides will be their oxidation to a metasilicate (metaborate) or silicon (boron) oxide, respectively. A compound of an element of group VI and carbon will be also presumably reduced to the elements in the pure state or in the form of an intermediate oxide. In the $KCl-NaCl-Na_2MoO_4-Na_2CO_3$ melt, boron nitride with the 200/160 dispersity does not corrode. It was already found [9,10] that in the Na_2WO_4 melt at 1123 K its corrosion rate is 0.3 $g \cdot m^{-2} \cdot h^{-1}$. The introduction of stronger oxidating reagents (WO_3, MoO_3, and Na_2CO_3) into the Na_2WO_4 melt, even to the extent of 1 wt.%, essentially increases the corrosion rate of boron nitride: it attains 0.5, 1.7, and 2 $g \cdot m^{-2} \cdot h^{-1}$, respectively [10]. We did not observe corrosion and change in the appearance of the surface of silicon and boron carbides with the 400/315 dispersity at 1023 K in the $KCl-NaCl+10$ mol % Na_2WO_4 (Na_2MoO_4) melt. When stronger oxidating reagents (Na_2CO_3, Na_2WO_4, or Na_2MoO_4 to the extent of 10 mol %) are introduced into the melt, either SiC (B_4C) corrodes (in the case of Na_2CO_3, the corrosion rate is 1.67-1.99 $g \cdot m^{-2} \cdot h^{-1}$) or they interact and coat grains with a high-melting metal.

Thus, the thermodynamic analysis and the experimental studies of the chemical behavior of boron nitride, silicon and boron carbides in the melts lead to the conclusion that at 900-1200 K they must actively react with all the oxide compounds under consideration. It is likely that the difficulty in the experiments with them will consist in the selection of *soft* oxidating reagents, for which, on the one hand, redox processes must occur and, on the other, corrosion must not be too intensiv.

In order to evaluate the electrochemical behavior of dielectrics and semiconductors in ionic melts, we studied the stationary potentials of electrodes made from HRD and SC by measuring the electromotive forces of electrochemical cells (l)-(3). Simultaneously we recorded variations in the potential of the platinum container without HRD or SC to determine the acid-base properties of a melt. We found that C (diamond), BN, and SiC electrodes do not have their characteristic potentials in a purely chloride melt.

Reaction	$\Delta G°$ (kJ·mol⁻¹) at temperature, K			
	298	900	1100	1120
$C + Na_2MoO_4 = MoO_2 + CO + Na_2O$	302.9	-	-	-
$3C + 2Na_2WO_4 = 2W + 2Na_2CO_3 + CO_2$	350.6	222.2	207.1	182.4
$3C + 2Na_2MoO_4 = 2Mo + 2Na_2CO_3 + CO_2$	201.7	-	-	-
$2C + Na_2CO_3 = 2Na + 3CO$	635.5	294.1	239.7	129.7
$C + Na_2CO_3 = Na_2O + 2CO$	396.6	202.9	166.1	104.6
$C + Na_2W_2O_7 = WO_2 + Na_2WO_4 + CO$	110.4	-	-	-
$C + Na_2Mo_2O_7 = MoO_2 + Na_2MoO_4 + CO$	460	-	-	-
$C + MoO_3 = MoO_2 + CO$	-5.0	-105.4	-121.3	-153.6
$2BN + Na_2MoO_4 = 2NaBO_2 + Mo + N_2$	-77.4	-	-	-
$2BN + 3Na_2CO_3 = 2NaBO_2 + 2Na_2O + N_2 + 3CO$	-100.0	-186.2	-209.2	-231.8
$2BN + MoO_3 = B_2O_3 + Mo + N_2$	-73.2	-171.5	-187.9	-204.2
$SiC + 2CO_2 = SiO_2 + C + 2CO$	-269.9	-274.5	-275.3	-276.1
$SiC + 3CO_2 = SiO_2 + 4CO$	-659.8	-561.9	-546.0	-530.1
$SiC + Na_2CO_3 = Na_2SiO_3 + 2C$	-350.2	-326.8	-322.6	-318.0
$3SiC + 4Na_2MoO_4 = 3Na_2SiO_3 + 3CO_2 + 4Mo + Na_2O$	-336.8	-	-	-
$B_4C + 6CO_2 = 2B_2O_3 + C + 6CO$	-797.8	-802.1	-803.7	-809.2
$B_4C + 4Na_2CO_3 = 2B_2O_3 + 4C + CO_2 + 4Na_2O$	-63.1	-81.2	-82.0	-83.3
$B_4C + 3Na_2CO_3 = 2B_2O_3 + 4C + 3Na_2O$	-413.8	-271.1	-258.6	-235.1
$3B_4C + 8Na_2MoO_4 = 12NaBO_2 + 3CO_2 + 8Mo + 2Na_2O$	-2280.3	-	-	-

Table 1
TEMPERATURE DEPENDENCE OF THE STANDARD GIBBS ENERGIES $\Delta G°$ OF THE MOST FAVORABLE REACTIONS OF DIAMOND, BORON NITRIDE, SILICON AND BORON CARBIDES WITH MOLYBDENUM AND CARBON OXYGEN-CONTAINING COMPOUNDS

Their potentials coincide with that of the platinum gauze. The introduction of Na_2MoO_4 into a chloride melt (due the variation in the acid-base properties of a melt) has little effect on the potential of the platinum electrode but substantially affects the potentials of HRD and SC electrodes (fig. 1).
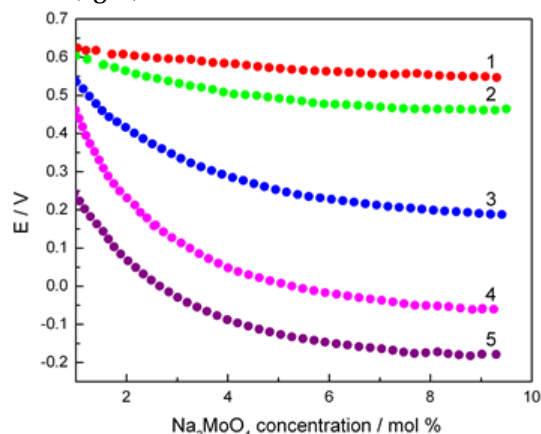

Fig. 1. Values of stationary potentials E using: (1) platinum gauze, (2) diamond, (3) boron nitride, (4) silicon carbide, and (5) boron carbide electrodes in the NaCl-KCl melt as functions of the Na_2MoO_4 concentration at 1023 K; Pb/Pb^{2+} reference electrode.

The stationary potential of the diamond electrode in the Na_2WO_4 melt is -1.35...-1.41 V, and it corresponds to the variation in the acid-base properties of the melt (by MoO_3 introduction) (fig. 2, curve 1). The resulting potential of the diamond electrode is practically equal to the stationary potential -1.32 ...-1.38 V of graphite electrode, which was measured earlier [13].

The boron nitride electrode acquires its own potential in the Na_2WO_4 melt, but the potential responds to the variation in the acid-base properties of the melt (fig. 2, curve 4).

Silicon carbide and boron carbide electrodes in the Na_2WO_4 melt containing MoO_3 take the potentials of the molybdenum electrode (fig. 2, curves 2 and 3) with the Nernst concentration dependences characteristic of the latter [14].
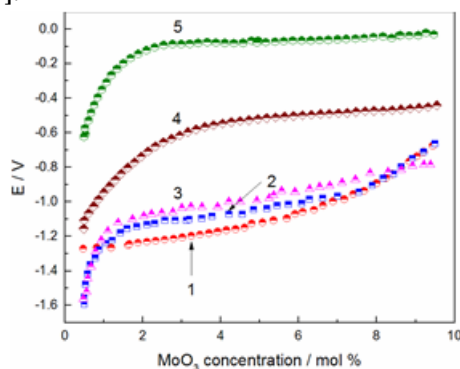

Fig. 2. Values of stationary potentials E using (1) diamond, (2) silicon carbide, (3) boron carbide, (4) boron nitride, and (5) platinum gauze electrodes in the Na_2WO_4 melt as functions of the MoO_3 concentration; T=1023 K; $Pt,O_2|Na_2WO_4-0.2WO_3$ reference electrode.

The voltammetric study of the electroreduction of various anions on platinum electrode and on HRD and SC electrodes showed that electrochemical processes occur on the grain surfaces of dielectrics and semiconductors. Thus, a noticeable increase in the reduction current on the diamond grains electrode is observed during the CO_2 electrolytic reduction, as compared with the empty platinum container (fig. 3). The currents of the CO_2 reduction were determined on a diamond surface by subtracting the current on the platinum gauze from the total current of the
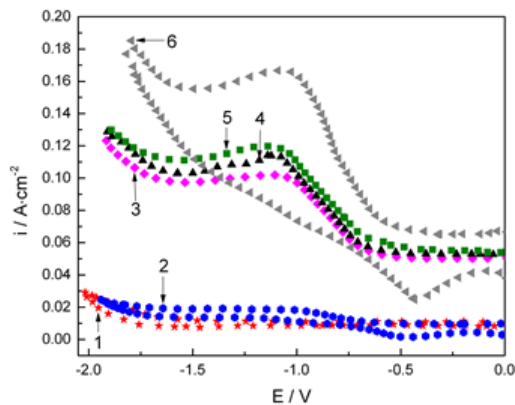

Fig. 3. Voltammograms of the NaCl-KCl melt using Pt in a normal atmosphere (1) and under the excess CO_2 pressure of $1.52 \cdot 10^3$ kPa (2) and using diamond electrodes (3-6); scan rate 0.1 $V \cdot s^{-1}$, temperature 1023 K; time of CO_2 action on diamond electrode (h) was: 1 (3), 1.5 (4), 2 (5), and 2.5 (6).

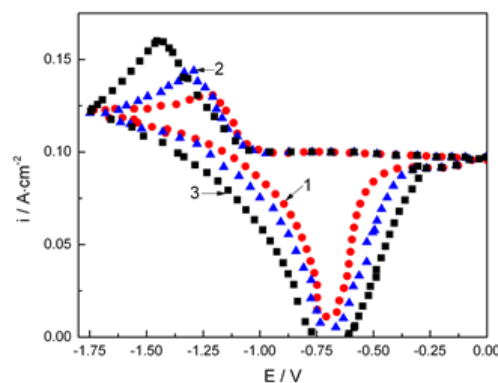Fig. 4. Cyclic voltammograms of the NaCl-KCl melt containing $5 \cdot 10^{-5}$ $mol \cdot cm^{-3}$ Na_2MoO_4 and $6.2 \cdot 10^{-3}$ $mol \cdot cm^{-3}$ $MgCl_2$, respectively, on the platinum gauze (1) and silicon carbide electrodes(2,3); scan rate 0.1 $V \cdot s^{-1}$ temperature 1023 K; (reference electrode Pt/O^{2-}; the SiC mass (g) was: 0.025 (2) and 0.050 (3)

platinum-filled with diamond grains electrode. Using the reported data [15] ($i(CO_2)=4.5$ $mA \cdot cm^{-2}$ at $p(CO_2)=1.52 \cdot 10^3$ kPa, and 0.1 $V \cdot s^{-1}$ scan rate), we calculated the working surface area of the diamonds, which was 25 cm^2. This value agrees well with the surface area calculated from the reference data for the diamonds with the specified dispersity. A similar effect of the increasing current density is also observed for the boron nitride electrode.
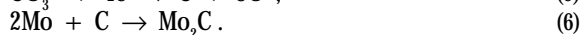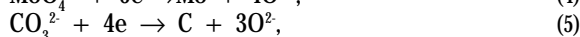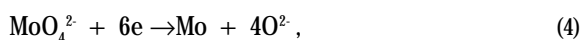
We also studied the electroreduction of the MoO_4^{2-} anions in the NaCl-KCl melt in the presence of the Mg^{2+} cations on the platinum gauze and silicon-carbide electrodes (fig. 4).

To take into consideration the cathode working surface of SC grains, we also obtained the I-E curves for the empty and filled containers. The voltammogram of the reduction of the MoO_4^{2-} ions on the empty gauze electrode is similar to that for their reduction on a needle platinum electrode [16]. The current of the MoO_4^{2-} reduction on this electrode is constant in time (fig. 4, curve 1). In the case of filled container with SiC grains the considerable increase reduction currents during electrolysis (fig. 4, curves 2 and 3) points out an increase in the surface area of the working electrode in the surface area of the working electrode.

The difference observed in the currents on the Pt and carbide electrodes allows us to determine the partial currents of the MoO_4^{2-} reduction on the surface of the SiC grains. Using the reported data [17], [$i(MoO_4^{2-}) = 9.5$ $mA \cdot cm^{-2}$ at $5 \cdot 10^{-5}$ $mol \cdot cm^{-3}$ and 0.1 $V \cdot s^{-1}$ scan rate], we calculated the working surface area of SiC as 21 and 47

cm² at the masses 0.025 and 0.050 g, respectively. These values agree well with the reference data for surface area of the grains with the specified dispersity. A similar effect is also observed for the boron carbide electrode and for SC electrodes in the pure Na_2WO_4-MoO_3 oxide melt.

The above electrochemical studies showed that the grains of C(diamond), BN, SiB and SiC in contact with the melt can be used as a cathode material for the HTIL-ES of molybdenum carbide. To electrochemically coat the HRD and SC grains, the grains were held in the melts of the following compositions: (1) Na_2WO_4-5 mol% of MoO_3-10 mol% Li_2CO_3 or (2) NaCl-KCl (1:1)-5 mol% of Na_2MoO_4-7.5 mol% of Na_2CO_3; the temperature was 1073-1173 K and the cathode current densities were 10-100 A·m⁻². Under such conditions the HRD and SC surfaces become conductive and play the role of an active support for the HTIL-ES of molybdenum carbide. The obtaining of Mo_2C coating consists of the co-precipitation of molybdenum and carbon with the simultaneous reduction of the molybdate and carbonate ions, which are present in the melts. Mo^{6+} and CO_3^{2-} ions and have close discharge potentials, and the following reaction yielding the product in the form of a compact precipitate may be described:

$$MoO_4^{2-} + 6e \rightarrow Mo + 4O^{2-}, \quad (4)$$
$$CO_3^{2-} + 4e \rightarrow C + 3O^{2-}, \quad (5)$$
$$2Mo + C \rightarrow Mo_2C. \quad (6)$$

At temperatures below 1073 K the adherent coating does not proceed, because powder-like precipitates are formed. We determined the cathode current density from the surface area of the HRD and SC grains. The coverage degree of coating was determined as the difference in the masses of the uncoated and coated grains. The quality of molybdenum carbide coatings was estimated by their appearance and physical and mechanical properties [17]. The deposit is presented as a light green thin-crystal compact precipitate. Its uniformity is pronounced on chips. The intense lines of molybdenum carbide were present in the X-ray diffraction patterns of the surface layer of coated grains. The growth rate of coating the diamond grains with Mo_2C substantially depends on both temperature and cathode current density (fig. 5). As these parameters increase, the rate of deposition increases at the equal testing duration. ASK 125/100 diamonds were tested on a *Tornado* installation of L'viv Polygraphic Institute (Lviv, Ukraine). The coefficient P of breaking load was determined as the ratio P_c/P_{st} of the breaking loads of coated and starting grains. Molybdenum carbide coatings deposited under certain operation conditions allow the initial breaking load of the diamond to be elevated by the
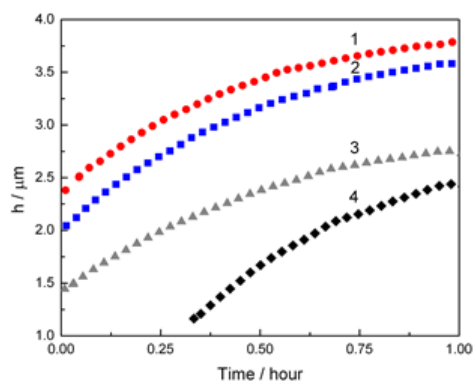
factor 1.3-1.9, depending on the electrolysis mode.

AS-32 500/400 diamonds were tested in accordance with GOST 9206-80 on the breaking machine IMASh-20-75 equipped with a UVT microscope and a reversing gear for the creation of a compressing stress. The diamond grains were crushed between polished plates of ASPK poly-crystal diamond. The MO_2C coating on AS-32 500/400 diamonds enhances the breaking load by a factor of 1.1-1.3 when is compared with annealing process (table 2). In this case, the load increases as either the mass or thickness of the coating increases.

Pilot lots of tools made from diamond electroplated with

Table 2
BREAKING LOAD OF COATED AS-32 500/400 DIAMONDS

Mass increase, wt.%	Coating thickness, μm	Load, N	
		after coating	after annealing*
-	-	46	31
3.2	0.9	50	41
6.0	1.9	52	38
7.5	2.5	52	37
10.0	3.2	54	34
12.0	3.9	57	35

Annealing in air at 1073 K for 1 h.

molybdenum carbide at high temperature were tested in coarse polishing of optical glass. The severability of tools was increased by the factor 1.5-2.0. Similar results were also obtained in the case of molybdenum carbide deposition on the boron nitride grains.

Mo_2C coatings were deposited on the silicon carbide grains with the 400/320 granularity the boron carbide grains with the 160/125 granularity at the same temperature, 1173 K. The cathode current densities were 50-200 A·m⁻² and the electrolysis time were 15-90 min. We established that the coating degree substantially depends on both cathode current density and the electrolysis duration: the deposition rate increases, as these parameters increase (fig. 6).

The grains of boron carbide and silicon carbide were tested for breaking in accordance with the State Standard 9206-81 (Ukraine) on a DA-2 installation. The capillarity characterizing the wettability of abrasives was determined by the lift of water level in glass tubes filled with either uncoated or coated grains [18]. Upon coating with molybdenum carbide, the coefficient of the breaking load of the grains of both boron and silicon carbides was 1.5-
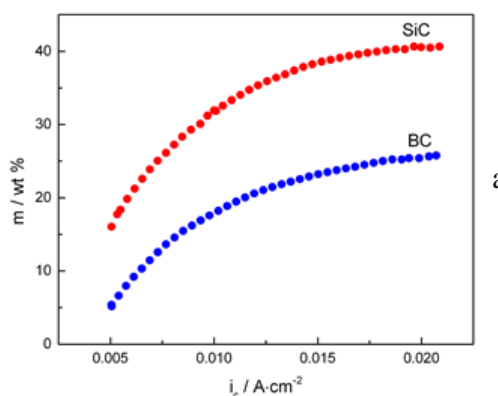

Fig. 5. Dependence of the thickness, h, of MO_2C coating on diamond grains on the duration/time in various electrolysis conditions: (1) 1173 K, 200 A×m⁻²; (2) 1173 K, 100 A×m⁻²; (3) 1123 K, 200 A×m⁻²; (4) 1123 K, 100 A×m⁻²

Fig. 6. Dependences of the degree m (wt.%) of coating for the grains of SiC and BC with molybdenum carbide versus: (a) cathodic current density i_c 1 h electrolysis duration
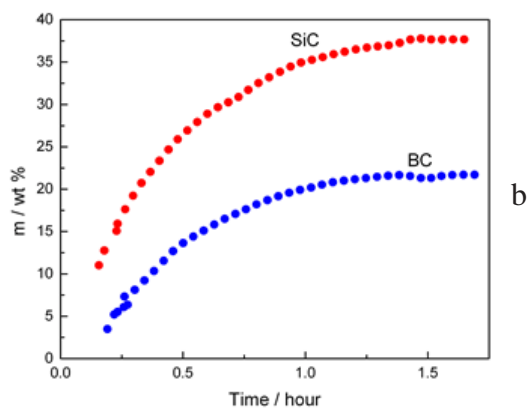
Fig. 6. Dependences of the degree m (wt.%) of coating for the grains of SiC and BC with molybdenum carbide versus: (b) the electrolysis time when the cathodic current density is kept constant at $i_c = 100$ A·m⁻²

2.5; this means that the capillarity of the grains of silicon and boron carbides increased by the factors of 3.4-4.0 and 2.3-2.5, respectively.

Conclusions

Electroplating of the grains of dielectrics and semiconductors with molybdenum carbide favors the increase in their breaking load and wettability and in the efficiency of tools.

References
1. MAY, P.W., Phil. Trans. R. Soc. Lond. A, **358**, 2000, p. 473.
2. STARYGA, E., BAK, S.W., Diam. Relat. Mater., **14**, no. 1, 2005, p. 23.
3. BERNARD, S., SALAMEL, C., MIELE, P., Dalton Trans., **45**, 2016, p. 861.
4. MALYSHEV, V.V., NOVOSELOVA, I.A., GAB, A.I., SARYCHEV, S.Y., Green Industrial Applications of Ionic Liquids., R.D. ROGERS et al., Eds., Kluwer Academic Publishers, Netherlands, 2003, p. 517.
5. NOVOSELOVA, I.A., MALYSHEV, V.V., GAB, A.I., SHAPOVAL, V.I., Sverkhtverd. Mater., no. 3, 2001, p. 3.
6. XIANG, D., YIN., L.W., LIU, K.G., JIA, L.Q., Adv. Mater. Res., **79-82**, 2009, p. 699.
7. MALYSHEV, V.V., GAB, A.I., GAUNE-ESCARD, M., Mater. Manuf. Processes., **23**, no. 8, 2008, p. 748.
8. MALYSHEV, V.V., SHAHNIN, D., GAB, A.I., ASTRELIN, I., MOLOTOVSKA, L., SOARE, V., DONATH, C., NEACSU, E.I., CONSTANTIN, V., POPESCU, A.M., Rev. Chim.(Bucharest), **67**, no. 12, 2016, p. 2490.
9. MALYSHEV, V.V., GAB, A.I., SHAKHNIN, D.B., PISANENKO, A.D., AMBROVA, M., DANIELIK, V., FELLNER, P., Acta Chim. Slov., **5**, no. 2, 2012, p. 139.
10. MALYSHEV, V.V., GAB, A.I., PISANENKO, A.D., SOLOVIEV, V., CERNENKO, L.A., Mater. Sci. & Eng. Technol., **45**, no. 1, 2014, p. 51.
11. RUSCIC, B., REINHARDT, E., von LASZEWSKI, G., KODEBOYINA, D., BURCAT, A., LEAHY, D., MONTOYA, D., WAGNERA, A.F., J. Phys. Conf. Ser., **16**, 2005, p. 561.
12. NIST-JANAF Thermochemical Tables, 2013.
13. MALYSHEV, V.V., GAB, A.I., GAUNE-ESCARD, M., J. Appl. Electrochem., **38**, 2008, p. 315.
14. MALYSHEV, V.V., Teor. Osnovy Khim. Tekhnol., **41**, no. 3, 2007, p. 302.
15. ONISCHENKO, V.A., SOLOVIEV, V.V., CHERNENKO, L.A., MALYSHEV, V.V., Mater. Sci. & Eng.Technol., **45**, no. 11, 2015, p. 1030.
16. MALYSHEV, V.V., Poverkhnost'. Fizika, Khimiya, Mekhanika, no. 5/6, 1999, p. 153.
17. MALYSHEV, V.V., USKOVA, N.N., Sverkhtverd. Mater., no. 3, 2000, p. 73.
18. SOLOVIEV, V.V., MALYSHEV, V.V., GAB, A.I., Rentgenovskiye, Sinkhrotronnye i Neytronnye Issledovaniya, no. 9, 2005, p. 72.