

Review of the electrodeposition of molybdenum carbide on the surfaces of disperse dielectric and semiconductor materials

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Abstract: The systems suitable for a high-temperature electrochemical synthesis on the surfaces of diamond, boron nitride, and silicon and boron carbides were selected on the basis of thermodynamic analysis of the reactions of the dielectrics and semiconductors with ionic melts. The results obtained in the electrochemical study of these systems are reported. As example, the electrodeposition of molybdenum carbide on diamond, BN, SiC and boron carbide surfaces is discussed in detail.

Keywords: molten salts, electrodeposition, molybdenum carbide, coatings on dielectrics, coatings on semiconductors

Introduction

Natural and synthetic diamond and cubic boron nitride are high-resistance dielectrics (HRD). According to Novikov NV (1987), resistivity of majority of natural diamonds is in the range 10^{10} – 10^{14} $\Omega \cdot \text{cm}$ in the temperature interval 973–1173 K. Resistivity of boron nitride is ca 10^8 – 10^{13} $\Omega \cdot \text{cm}$ (Kosopalov TYa (1986)). Hence, the use of these dielectrics as cathode material is impossible under usual conditions. Silicon and boron carbides fall into the category of semiconductors (SC). Their resistivity is 10^1 – 10^3 and 10^{-4} – 10^{-1} $\Omega \cdot \text{cm}$, respectively (Kosopalov TYa (1986)). It has been found out (Malyshev VV, Novoselova IA, Gab AI, Sarychev SY (2003)) that HRD crystals, when they are in contact with ionic melts, certain composition, became conducting the electric current. On the other hand, SC crystals are changing their potential according to the melt composition (Novoselova IA, Malyshev VV, Gab AI, Shapoval VI (2001)). This behavior can be explained by redox processes occurring at the HRD (SC)/melt interface (Malyshev VV, Novoselova IA, Gab AI, Pisanenko AD, Shapoval VI (2000)). When the surface of grains of these material becomes electrically conducting, the electrochemical deposition of chemical compounds on their surface can be done. The use of ionic melts as an electrolyte makes it possible to carry out the high-temperature electrochemical synthesis (HTES) of the compounds which cannot be precipitated from

aqueous solutions. As example, we will discuss the synthesis (and electrodeposition) of molybdenum carbide Mo_2C . The precipitation of molybdenum carbide on the grains of diamonds, boron nitride or silicon and boron carbides is a powerful means for the change of their properties. Owing to this coating, the mechanical properties of industrial tools can be considerably improved (Naidich YuV, Lavrinenko IA, Volk GP (1983)).

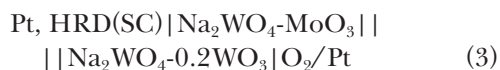
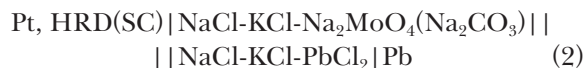
The aim of the present work is to determine the conditions enabling us to carry out the HTES on the surfaces of HRD and SC in ionic melts. These considerations are based on

- the thermodynamic analysis of the reactions of diamonds, boron nitride, and silicon and boron carbides with ionic melts,
- the experimental study of their electrochemical behavior,
- evaluation of the possibility of using HTES in the molten systems.

Item c) is the extension of the work carried out by Shapoval et al. (Shapoval VI, Malyshev VV, Novoselova, IA, Kushkhov KhB (1994)) on the metal electrodes.

Experimental

Two electrochemical methods were used: the potentiometry and the voltammetry with linear potential sweep. The following electrochemical systems were studied (halide and halide-oxide systems at 1023 K and oxide systems at 1173 K):



Platinum crucible was used as the container for the melt and it served also as the anode. The dielectric or semiconductor electrodes consisted of a platinum gauze container filled with the powder of the dielectric or semiconductor material. Platinum wire served as current supply to the container. For systems (1) and (2) the lead reference electrode with the melt of the composition NaCl-KCl (1:1) + 2.5 mol % of PbCl₂ was used.. The potential of system (3) was measured with respect to the Pt, O₂ | Na₂WO₄-0.2WO₃ half-cell. The equimolar melt of potassium and sodium chlorides of high purity

served as the electrolyte. Both in the potentiometric and voltammetric experiments, mass of the synthesized compounds were determined by weighing. Composition of the deposited layer was determined by the X-ray phase analysis (DRON-3.0).

In the case of deposition of molybdenum carbide on the grains of dielectrics and semiconductors, a nickel container was used. In this case, graphite crucible (MPG-7 grade graphite) was used as a container for the melt. It served also as the anode. The coated grains were separated from the electrolyte residue by boiling in distilled water.

Results and Discussion

The deposition of molybdenum carbide on the surface of HRD and SC was carried out in the following melts: Na₂WO₄-MoO₃-Li₂CO₃ and KCl-NaCl-Na₂MoO₄-Na₂CO₃. The data on the chemical behavior of diamond and silicon and boron carbides

Tab. 1. Temperature dependence of the standard Gibbs energies ΔG° of the most probable reactions of diamond, boron nitride, and silicon and boron carbides with molybdenum, tungsten, and carbon oxygen-containing compounds.

Reaction	ΔG° (kJ · mol ⁻¹) at temperature (in K)			
	298	900	1100	1120
C + Na ₂ WO ₄ = WO ₂ + CO + Na ₂ O	376.1	281.6	269.9	248.1
3C + 2Na ₂ WO ₄ = 2W + 2Na ₂ CO ₃ + CO ₂	350.6	222.2	207.1	182.4
C + Na ₂ MoO ₄ = MoO ₂ + CO + Na ₂ O	302.9			
3C + 2Na ₂ MoO ₄ = 2Mo + 2Na ₂ CO ₃ + CO ₂	201.7			
2C + Na ₂ CO ₃ = 2Na + 3CO	635.5	294.1	239.7	129.7
C + Na ₂ CO ₃ = Na ₂ O + 2CO	396.6	202.9	166.1	104.6
C + Na ₂ W ₂ O ₇ = WO ₂ + Na ₂ WO ₄ + CO	110.4			
C + Na ₂ Mo ₂ O ₇ = MoO ₂ + Na ₂ MoO ₄ + CO	460			
C + WO ₃ = WO ₂ + CO	89.9	42.3	-19.2	-52.3
C + MoO ₃ = MoO ₂ + CO	-5.0	-105.4	-121.3	-153.6
2BN + Na ₂ WO ₄ = 2NaBO ₂ + W + N ₂	-2.5	-68.2	-79.9	-91.2
2BN + Na ₂ MoO ₄ = 2NaBO ₂ + Mo + N ₂	-77.4			
2BN + 3Na ₂ CO ₃ = 4NaBO ₂ + Na ₂ O + N ₂ + 3C	-100.0	-186.2	-209.2	-231.8
2BN + WO ₃ = B ₂ O ₃ + W + N ₂	23.8	-79.0	-95.8	-113.0
2BN + MoO ₃ = B ₂ O ₃ + Mo + N ₂	-73.2	-171.5	-187.9	-204.2
SiC + 2CO ₂ = SiO ₂ + C + CO	-269.9	-274.5	-275.3	-276.1
2SiC + 3CO ₂ = 2SiO ₂ + 3C + 3CO	-659.8	-561.9	-546.0	-530.1
SiC + Na ₂ CO ₃ = Na ₂ SiO ₃ + 2C	-350.2	-326.8	-322.6	-318.0
3SiC + 4Na ₂ WO ₄ = 3Na ₂ SiO ₃ + 3CO ₂ + 4W + Na ₂ O	-25.5	-311.3	-335.1	-362.3
3SiC + 4Na ₂ MoO ₄ = 3Na ₂ SiO ₃ + 3CO ₂ + 4Mo + Na ₂ O	-336.8			
B ₄ C + 6CO ₂ = 2B ₂ O ₃ + C + 6CO	-797.8	-802.1	-803.7	-809.2
B ₄ C + 4Na ₂ CO ₃ = 2B ₂ O ₃ + 4C + CO ₂ + 4Na ₂ O	-63.1	-81.2	-82.0	-83.3
B ₄ C + 3Na ₂ CO ₃ = 2B ₂ O ₃ + 4C + 3Na ₂ O	-413.8	-271.1	-258.6	-235.1
3B ₄ C + 8Na ₂ WO ₄ = 12NaBO ₂ + 3CO ₂ + 8W + 2Na ₂ O	-1681.9	-1736.4	-1740.5	-1740.5
3B ₄ C + 8Na ₂ MoO ₄ = 12NaBO ₂ + 3CO ₂ + 8Mo + 2Na ₂ O	-2280.3			

in the melts are not available in literature. Possible chemical reactions in this system can be estimated on the basis of thermodynamic data (see Table 1). (Naumov GV, Ryzhenko VN, Khodakovskii IL (1978), JANAF (1971)). It follows that diamond should not react with tungstate or molybdate up to 1200 K. Sodium carbonate also does not react with these materials. It seems that diamond will be susceptible to corrosion only in the melts containing molybdenum and tungsten oxides. Experiment proved that diamond of ASK 400/315 grade practically does not corrode at 1173 K in the KCl-NaCl- Na_2MoO_4 - Na_2CO_3 melt. In Na_2WO_4 melt, its corrosion rate was $0.4\text{--}0.5 \text{ g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$. The 1 wt. % addition of Na_2CO_3 increased the corrosion rate by the factor of 1.3–1.5.

From thermodynamic point of view, boron nitride can be oxidized under formation of gaseous nitrogen and boron metaborate or oxide. For silicon and boron carbides, the most energy favorable process of corrosion will be their oxidation to a metasilicate (metaborate) or silicon (boron) oxide. Compounds of any element of group VI and carbon will be preferably reduced to the elements in pure state or to intermediate oxides.

Boron nitride grains with dispersion 200/160 do not corrode in the KCl-NaCl- Na_2MoO_4 - Na_2CO_3 melt, while in Na_2WO_4 melt its corrosion is $0.3 \text{ g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ at 1123 K. The addition of 1 wt. % of stronger oxidizing agents (e.g. WO_3 , MoO_3 or Na_2CO_3) to Na_2WO_4 melt remarkably increases the corrosion rate of boron nitride up to $2 \text{ g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$.

Corrosion or changes of the surface of silicon and boron carbides having 400/315 dispersity, when they were immersed into the melt of composition KCl-NaCl-10 mol % Na_2WO_4 (Na_2MoO_4), were not observed. However, when stronger oxidizing agent (Na_2CO_3 , Na_2WO_4 , or Na_2MoO_4) up to 10 mol % was added, corrosion rate of SiC (or B_4C) reached $1.67\text{--}1.99 \text{ g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$

Electrochemical behaviour of dielectrics and semiconductors in ionic melts

Potentials of the electrodes made from HRD and SC have been studied in electrochemical cells described by schemes (1)–(3). Simultaneously, changes in the potential of platinum container unfilled with HRD or SC were measured in order to determine the acid-base properties of the melt. It was found that diamond, boron nitride or silicon carbide electrodes do not have their own well defined electrode potential in purely chloride melts. Their potentials coincide with that of the platinum gauze. Introduction of Na_2MoO_4 into the chloride melt (the change of the acid-base properties of the melt) had a little

effect on the potential of the platinum electrode but it substantially affected the potentials of the HRD and SC electrodes (Fig. 1).

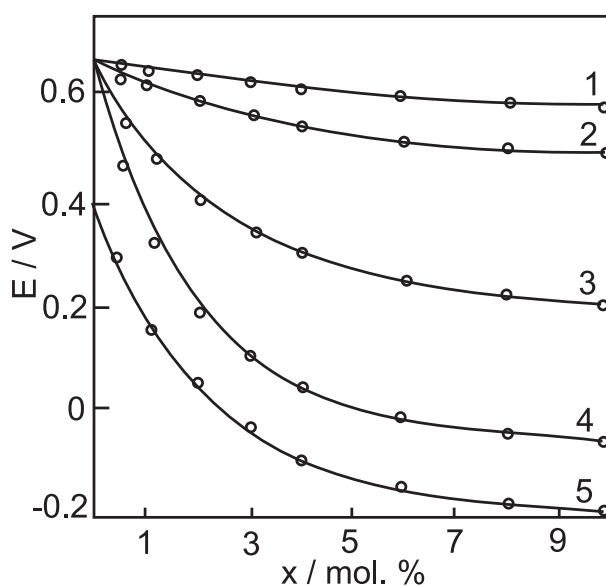


Fig. 1. Potentials of the different electrodes in the NaCl-KCl melt as functions of the Na_2MoO_4 concentration. $t = 1023 \text{ K}$, Pb/Pb^{2+} reference electrode. (1) platinum gauze, (2) diamond, (3) boron nitride, (4) silicon carbide, and (5) boron carbide electrodes. (Malyshev VV, Uskova NN (2000))

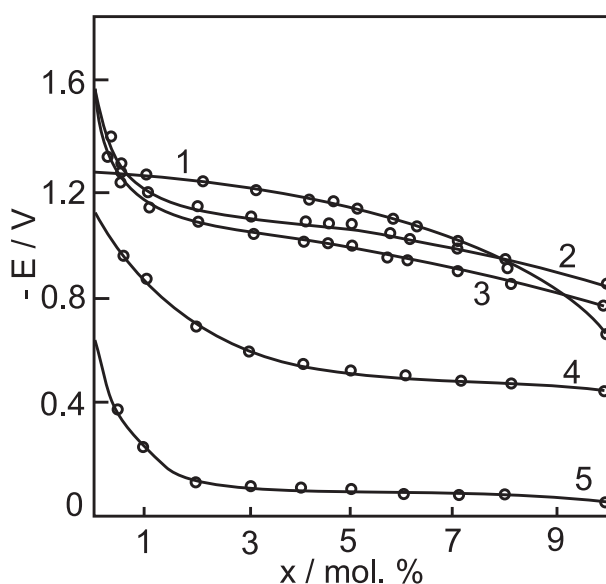


Fig. 2. Potentials of the different electrodes in the Na_2WO_4 melt as function of the MoO_3 concentration. $t = 1023 \text{ K}$, $\text{Pt}, \text{O}_2 | \text{Na}_2\text{WO}_4\text{--}0.2 \text{ WO}_3$ ref. electrode. (1) diamond, (2) silicon carbide, (3) boron carbide, (4) boron nitride, and (5) platinum gauze electrodes. (Malyshev VV, Uskova NN (2000))

The potential of diamond electrode in pure Na_2WO_4 melt changed from -1.35 V to -1.41 V. When MoO_3 was added to the melt, the potential change of diamond electrode can be seen from (Fig. 2, curve 1). The resulting potential of the diamond electrode equals to the stationary potential of graphite electrode (-1.32 V to -1.38 V) which have been measured earlier (Kushkhov KhB, Shapoval VL, Novoselova IA (1987)).

The boron nitride electrode acquires its own potential in the Na_2WO_4 melt and it corresponds to the changes in the acid-base properties of the melt (Fig. 2, curve 4).

Silicon carbide and boron carbide electrodes immersed in the Na_2WO_4 melt containing MoO_3 have potential of the molybdenum electrode (Fig. 2, curves 2 and 3) (Malyshev VV (2007)).

The presented results suggest that the HRD and SC, when immersed into the above mentioned melt, became suitable for the construction of electrodes. The voltammetric study of electroreduction of various anions on the platinum or HRD and SC electrodes showed that the electrochemical processes occur on the grain surfaces of dielectrics and semiconductors when they became electrically conductive. Noticeable increase in the reduction current on the diamond electrode was observed during CO_2 electrolytic reduction in comparison with the platinum container (Fig. 3). The currents corresponding to CO_2 reduction were determined on diamond surface by subtracting the current obtained on platinum gauze from the total current of the platinum-diamond electrode. Using the data from Kushkhov KhB, Shapoval VL, Novoselova IA (1987) ($i(\text{CO}_2) = 4.5 \text{ mA} \cdot \text{cm}^{-2}$ at $p(\text{CO}_2) = 1.52 \cdot 10^3 \text{ kPa}$, and $V = 0.1 \text{ V} \cdot \text{s}^{-1}$), we could calculate the working surface area of the diamond electrode, which was 25 cm^2 . This value agrees well with the surface area calculated from the data of the reference book by Novikov NV (1987) for diamond powder with the same specified dispersity. A similar effect of the increase of current density was observed for the boron nitride electrode.

The electroreduction of the MoO_4^{2-} oxoanions in NaCl-KCl-MgCl_2 melt on the platinum gauze or silicon-carbide electrode is demonstrated by cyclic voltammogram (see Fig. 4). Taking into account the working surface of SC grains, we obtained $I - E$ curves for empty and filled containers. Pattern of the reduction of MoO_4^{2-} ions obtained with empty gauze electrode is similar to that on needle platinum electrode (Malyshev VV (1999)). Current of the MoO_4^{2-} reduction on this electrode is constant with time (Fig. 4, curve 1). Considerable increase in the reduction current in the case of filled container (Fig. 4, curves 2 and 3) points to the increase in the

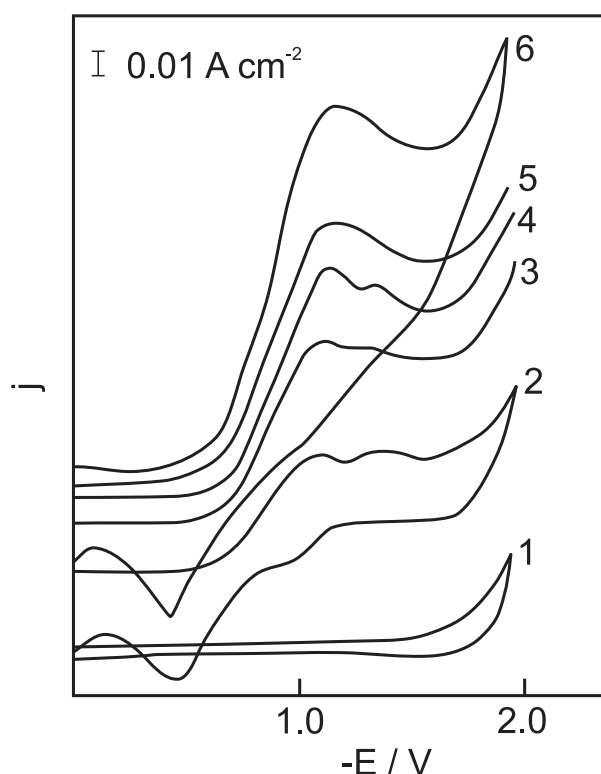


Fig. 3. Voltammograms of the NaCl-KCl melt (1) under the excess CO_2 pressure of $1.52 \cdot 10^3 \text{ kPa}$ on the (2) platinum gauze and on (3–6) diamond electrodes. Sweep rate $0.1 \text{ V} \cdot \text{s}^{-1}$.

Time of CO_2 electrolysis on the diamond electrode (h): (3) 1, (4) 15, (5) 2, and (6) 2.5.

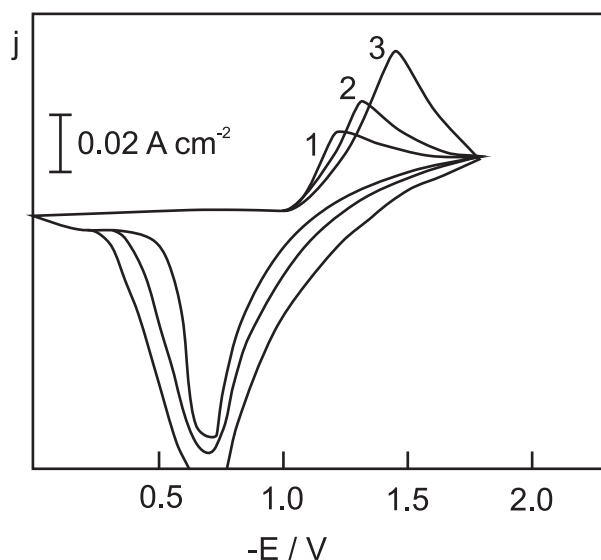


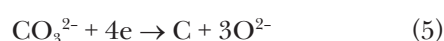
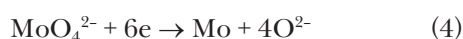
Fig. 4. Cyclic voltammograms of the NaCl-KCl melt, containing $5 \cdot 10^{-5}$ and $6.2 \cdot 10^{-3} \text{ mol} \cdot \text{cm}^{-3}$ of Na_2MoO_4 and MgCl_2 , respectively. (1) platinum gauze; (2 and 3) silicon carbide electrodes.

$t = 1023 \text{ K}$, reference electrode Pt/O^{2-} , polarization rate $0.1 \text{ V} \cdot \text{s}^{-1}$.
SiC mass (g): (2) 0.025 and (3) 0.050.

surface area of the working electrode. The difference in currents observed on platinum and carbide electrodes allows us to determine the partial currents for MoO_4^{2-} reduction on the surface of SiC grains. Using the data presented in Malyshev VV, Uskova NN (2000) ($i(\text{MoO}_4^{2-}) = 9.5 \text{ mA} \cdot \text{cm}^{-2}$ at $C = 5 \cdot 10^{-5} \text{ mol} \cdot \text{cm}^{-3}$ and $V = 0.1 \text{ V} \cdot \text{s}^{-1}$), we obtained following surface of silicon carbide: 21 and 47 cm^2 for the mass of 0.025 and 0.050 g SiC. These values agree well with the surface area of the grains with the specified dispersity calculated on the basis of data by Kosopalov TYa (1986). A similar effect is also observed for the boron carbide electrode.

Electrochemical synthesis of molybdenum carbide on the grains of semiconductors and dielectrics

The electrochemical studies discussed above showed that the grains of diamond, boron nitride, and silicon and boron carbides, when being in contact with suitable melt, can be used as cathode material for deposition of molybdenum carbide. In this work we treated the diamond powder with the melts of following compositions: Na_2WO_4 – 5 mol % of MoO_3 – 10 mol % of Li_2CO_3 or KCl-NaCl (1:1) – 5 mol % of Na_2MoO_4 – 7.5 mol % of Na_2CO_3 . The temperature was in the range 1073–1173 K and the cathode current densities were in the range (10–100) $\text{A} \cdot \text{m}^{-2}$. Under such conditions the HTD and SC surfaces become electrically conducting. Potentials of reduction of molybdenate and carbonate are close. Underpotential corresponding to the formation of Mo_2C contributes also to the synthesis of this substance. The partial electrode reactions can be written as follows:



At the temperatures lower than 1073 K, homogeneous coating deposits could not be prepared. Only powder deposits of Mo_2C were obtained. At higher temperatures, diamond grains were covered with a homogeneous, light green Mo_2C layer. The degree of coverage was determined as the difference in mass of starting material and coated grains. The quality of molybdenum carbide coatings was estimated by their appearance. Physical and mechanical properties of this material were described by Malyshev VV, Uskova NN (2000). It was found out that mechanical properties of coated particles were superior (1.5–4) times with respect to the original powders

Mo_2C coatings were deposited also on silicon carbide grains with the 400/320 granularity and on the

boron carbide grains with the 160/125 granularity. Temperature of the bath was 1173 K and the cathode current densities were in the range (50–200) $\text{A} \cdot \text{m}^{-2}$. Time of deposition varied from 15 min to 90 min. It was found that the coating degree substantially depends on the cathode current density and duration of the electrolysis (Fig. 5, 6).

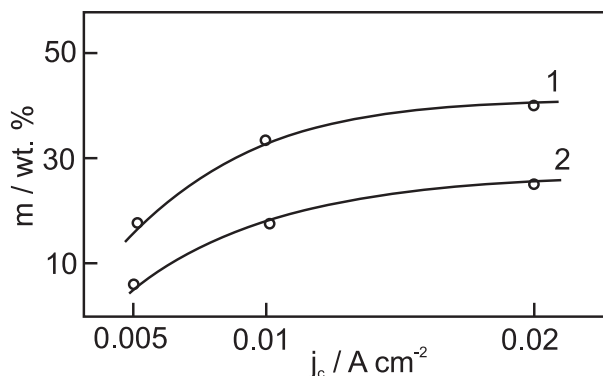


Fig. 5. Dependence of the degree of coating the grains of (1, 3) silicon and (2, 4) boron carbides with molybdenum carbide on cathodic current density ($\tau = 1 \text{ h}$)

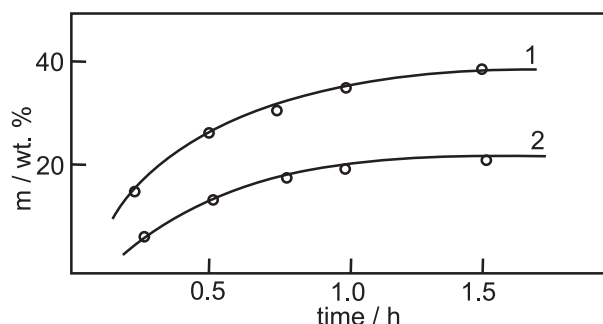


Fig. 6. Dependence of the degree of coating grains of (1, 3) silicon and (2, 4) boron carbides with molybdenum carbide on the electrolysis duration ($i_c = 100 \text{ A} \cdot \text{m}^{-2}$).

Acknowledgement

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