

The Interaction of Surface of Diamond and Diamond-like Dielectrics with Ionic Melts*

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Thermodynamic, corrosion, potentiometric, and voltammetric studies of the behaviour of dielectrics (namely, diamond and cubic BN) in halide, halide—oxide, and oxide melts have been carried out. It was found that electrochemical equilibrium and surface conductivity on dielectric—ionic melt interface appear as the result of redox processes on it.

Diamond and diamond-like substances (cubic BN (c-BN)) are high-resistance dielectrics (HD), *i.e.* practically do not conduct electric current. That is why the galvanic treatment of these materials under ordinary conditions in aqueous solutions is impossible. But the coating of HD by refractory metals and their compounds is of a great applied significance. It has been found [1] that the surface of natural and synthetic diamonds being in contact with melt based on a mixture of alkali tungstates, molybdates, and carbonates acquires electrical conductivity, which makes it possible to plate it with refractory metal carbides [2]. Behaviour of cubic BN crystals in ionic melts is similar to that of diamond ones. In order to explain mechanism of this phenomenon, the study of chemical and electrochemical reactions on the interface dielectric—ionic melt was carried out.

EXPERIMENTAL

Equipment. Two electrochemical methods of investigation, cyclic voltammetry and potentiometry were used. The potential and current functions were generated and controlled with the PI-50-1 potentiostat and the PR-8 programmer. The voltammograms (I — E curves) were recorded on the LKD-4-003 device. Electrode potential values were measured with high-resistance voltmeters SHCH-68003 and F-4800.

Electrodes and cells. The experiments were carried out in electric resistance furnace at 973—1173 K. The working electrode in the three-electrode cell was diamond or c-BN electrode which was a platinum net-made container filled with powder of AC-15 diamond (with 200—250 μm or 315—400 μm particles size) or cubic BN (with 115—160 μm or 160—200 μm particles size). The current was led to the container through

platinum wire. Platinum crucible was used as the container for melt and at the same time as the anode. In halide—oxide melts a lead electrode, $\text{Pb}|\text{NaCl}—\text{KCl}—\text{PbCl}_2$ [3], or a platinum wire ($d = 1$ mm, $s = 5$ cm^2) placed in the electrolyte under investigation was used as reference electrode. At designed positive CO_2 pressure, the Pt wire, as shown in [4], operates as a carbonate electrode. The platinum—oxygen reference electrode, $\text{Pt}, \text{O}_2|\text{Na}_2\text{WO}_4—0.2 \text{WO}_3$ (air atmosphere $p_{\text{partial}}(\text{O}_2) = 21.3$ Pa) was used in oxide melts [5].

The graphite electrode was a rod of 5 mm diameter made of spectral graphite. The upper part protruding from the melt was enclosed with a porcelain tube. The current was led to the electrode through a platinum wire.

Both in voltammetric and potentiometric investigations the mass and appearance of dielectrics under investigation were checked before and after each experiment.

Melt composition. The investigations were carried out in an ultra pure equimolar sodium chloride—potassium chloride melt and in an analytically pure sodium tungstate melt. The other reagents used were ultra pure, chemically pure or analytically pure.

Carbon dioxide was fed to a special cell after dehumidifying [6].

RESULTS AND DISCUSSION

Literature contains no information about electrochemical behaviour of HD in ionic melts. That is why a thermodynamic estimation of possible reactions between HD and oxygen-containing compounds of the IV and VI group elements (Tables 1 and 2) was carried out. For Gibbs energy calculations data on thermodynamic properties of compounds [7, 8] were used.

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Table 1. Temperature Dependence of the Gibbs Energy ($\Delta G^\circ/(\text{kJ mol}^{-1})$) of Interaction of Diamond with Oxygen-Containing Compounds of the Group IV and VI Elements

	Reactions	T/K				
		298	900	1000	1100	1200
1	$\text{Na}_2\text{WO}_4 + \text{C} = \text{WO}_2 + \text{CO} + \text{Na}_2\text{O}$	379.70	287.40	276.60	265.98	255.73
2	$2\text{Na}_2\text{WO}_4 + 3\text{C} = 2\text{W} + \text{CO}_2 + 2\text{Na}_2\text{CO}_3$	369.15	239.95	226.56	213.51	200.75
3	$\text{Na}_2\text{MoO}_4 + \text{C} = \text{MoO}_2 + \text{CO} + \text{Na}_2\text{O}$	305.77	206.15	190.00	174.01	161.71
4	$2\text{Na}_2\text{MoO}_4 + 3\text{C} = 2\text{Mo} + \text{CO}_2 + 2\text{Na}_2\text{CO}_3$	219.74	79.87	56.48	33.43	17.41
5	$\text{Na}_2\text{CO}_3 + 2\text{C} = 3\text{CO} + 2\text{Na}$	636.60	305.85	252.84	200.54	145.06
6	$\text{Na}_2\text{CO}_3 + \text{C} = 2\text{CO} + \text{Na}_2\text{O}$	394.63	203.01	172.51	142.30	112.51
7	$\text{Na}_2\text{SO}_4 + \text{C} = \text{SO}_2 + \text{CO} + \text{Na}_2\text{O}$	452.92	237.65	203.13	168.82	134.85
8	$2\text{Na}_2\text{SO}_4 + 3\text{C} = 2\text{S} + \text{CO}_2 + 2\text{Na}_2\text{CO}_3$	48.16	-116.65	-157.19	-197.65	-238.24
9	$2\text{Na}_2\text{CrO}_4 + 3\text{C} = \text{Cr}_2\text{O}_3 + 3\text{CO} + 2\text{Na}_2\text{O}$	242.96	-22.97	-68.07	-113.80	-152.05
10	$2\text{Na}_2\text{CrO}_4 + 3\text{C} = 2\text{Cr} + \text{CO}_2 + 2\text{Na}_2\text{CO}_3$	-18.91	-114.39	-132.76	-152.13	-164.72
11	$\text{Na}_2\text{O} + \text{C} = \text{CO} + 2\text{Na}$	241.96	102.84	80.33	58.24	32.55
12	$\text{Na}_2\text{W}_2\text{O}_7 + \text{C} = \text{WO}_2 + \text{CO} + \text{Na}_2\text{WO}_4$	128.66	21.88	6.61	-12.89	-24.14
13	$\text{Na}_2\text{Mo}_2\text{O}_7 + \text{C} = \text{MoO}_2 + \text{CO} + \text{Na}_2\text{MoO}_4$	33.26	-49.87	-65.10	-81.00	-97.11
14	$\text{WO}_3 + \text{C} = \text{WO}_2 + \text{CO}$	93.05	-5.94	-21.92	-37.74	-53.43
15	$\text{WO}_3 + 3\text{C} = \text{W} + 3\text{CO}$	352.63	36.15	-14.98	-65.69	-115.94
16	$\text{CO}_2 + \text{C} = 2\text{CO}$	120.08	13.01	-4.56	-22.05	-39.41
17	$\text{MoO}_3 + \text{C} = \text{MoO}_2 + \text{CO}$	-2.13	-99.58	-115.31	-130.88	-146.27
18	$\text{MoO}_3 + 3\text{C} = \text{Mo} + 3\text{CO}$	256.65	-56.27	-106.78	-156.86	-206.48
19	$\text{SO}_3 + \text{C} = \text{SO}_2 + \text{CO}$	-66.27	-160.46	-191.08	-212.92	-231.25

Table 2. Temperature Dependence of the Gibbs Energy ($\Delta G^\circ/(\text{kJ mol}^{-1})$) of Interaction of Boron Nitride with Oxygen-Containing Compounds of the Group IV and VI Elements

	Reactions	T/K				
		298	900	1000	1100	1200
1	$2\text{BN} + 3\text{Na}_2\text{WO}_4 = 2\text{NaBO}_2 + 2\text{Na}_2\text{O} + \text{N}_2 + 3\text{WO}_2$	497.60	464.93	466.60	468.90	471.58
2	$2\text{BN} + \text{Na}_2\text{WO}_4 = 2\text{NaBO}_2 + \text{N}_2 + \text{W}$	-2.51	-68.16	-79.96	-91.46	-102.34
3	$2\text{BN} + \text{Na}_2\text{MoO}_4 = 2\text{NaBO}_2 + \text{N}_2 + \text{Mo}$	-77.40	-148.16	-164.98	-181.33	-194.01
4	$2\text{BN} + 3\text{Na}_2\text{MoO}_4 = 2\text{NaBO}_2 + 2\text{Na}_2\text{O} + \text{N}_2 + 3\text{MoO}_2$	276.35	220.87	206.52	192.72	189.66
5	$2\text{BN} + 3\text{Na}_2\text{CO}_3 = 2\text{NaBO}_2 + 2\text{Na}_2\text{O} + \text{N}_2 + 3\text{CO}$	542.58	211.58	154.26	97.61	45.86
6	$4\text{BN} + 3\text{Na}_2\text{CO}_3 = 4\text{NaBO}_2 + \text{Na}_2\text{O} + 2\text{N}_2 + 3\text{C}$	-99.62	-186.23	-209.33	-231.79	-253.51
7	$2\text{BN} + 2\text{Na}_2\text{CrO}_4 = 2\text{NaBO}_2 + \text{Na}_2\text{O} + \text{N}_2 + \text{Cr}_2\text{O}_3$	-408.36	-420.58	-431.50	-443.17	-447.56
8	$2\text{BN} + \text{Na}_2\text{CrO}_4 = 2\text{NaBO}_2 + \text{N}_2 + \text{Cr}$	-202.25	-245.31	-259.58	-274.14	-285.06
9	$2\text{BN} + 3\text{Na}_2\text{SO}_4 = 2\text{NaBO}_2 + 2\text{Na}_2\text{O} + \text{N}_2 + 3\text{SO}_2$	717.47	315.68	246.14	177.28	109.04
10	$2\text{BN} + \text{Na}_2\text{SO}_4 = 2\text{NaBO}_2 + \text{N}_2 + \text{S}$	-163.13	-238.15	-261.29	-284.01	-321.83
11	$2\text{BN} + 3\text{Na}_2\text{Mo}_2\text{O}_7 = \text{B}_2\text{O}_3 + 3\text{Na}_2\text{MoO}_4 + \text{N}_2 + 3\text{MoO}_2$	-182.76	-265.10	-276.52	-290.45	-305.43
12	$2\text{BN} + \text{Na}_2\text{Mo}_2\text{O}_7 = \text{B}_2\text{O}_3 + \text{Na}_2\text{MoO}_4 + \text{N}_2 + \text{Mo}$	-80.58	-122.05	-137.82	-154.47	-171.46
13	$2\text{BN} + 3\text{Na}_2\text{W}_2\text{O}_7 = \text{B}_2\text{O}_3 + 3\text{Na}_2\text{WO}_4 + \text{N}_2 + 3\text{WO}_2$	10.71	-49.75	-61.38	-73.64	-86.53
14	$2\text{BN} + \text{Na}_2\text{W}_2\text{O}_7 = \text{B}_2\text{O}_3 + \text{Na}_2\text{WO}_4 + \text{N}_2 + \text{W}$	43.43	-51.51	-67.66	-84.10	-100.79
15	$2\text{BN} + 3\text{WO}_3 = \text{B}_2\text{O}_3 + 3\text{WO}_2 + \text{N}_2$	-48.16	-133.30	-147.11	-160.83	-174.43
16	$2\text{BN} + \text{WO}_3 = \text{B}_2\text{O}_3 + \text{W} + \text{N}_2$	23.68	-79.41	-96.27	-113.18	-130.08
17	$2\text{BN} + 3\text{MoO}_3 = \text{B}_2\text{O}_3 + 3\text{MoO}_2 + \text{N}_2$	-334.97	-414.47	-427.40	-440.37	-452.92
18	$2\text{BN} + \text{MoO}_3 = \text{B}_2\text{O}_3 + \text{Mo} + \text{N}_2$	-73.18	-171.88	-188.15	-204.47	-220.62
19	$2\text{BN} + 3\text{CO}_2 = \text{B}_2\text{O}_3 + 3\text{CO} + \text{N}_2$	30.50	-76.48	-94.98	-113.93	-132.34
20	$2\text{BN} + 3\text{SO}_3 = \text{B}_2\text{O}_3 + 3\text{SO}_2 + \text{N}_2$	-528.52	-597.27	-667.47	-687.85	-707.93

For reactions between HD and Na_2WO_4 , Na_2MoO_4 , Na_2CrO_4 , $\text{Na}_2\text{W}_2\text{O}_7$, and $\text{Na}_2\text{Mo}_2\text{O}_7$ calculations using Ulich's approximations [9] and thermodynamic properties data [10] were carried out. As follows from Tables 1 and 2, chemical resistance of diamond is higher than that of cubic BN. Calculations show that the diamond must be inert to action of Na_2WO_4 , Na_2MoO_4 , and Na_2CO_3 melts up to 1200 K and cubic BN must rapidly react with these melts.

According to the data of diamond behaviour in ionic melts (Table 1) all the compounds listed should be arranged by the order of their increasing oxidative strength into the following row of oxidants at 1000 K: Na_2CO_3 , Na_2O , Na_2WO_4 , Na_2MoO_4 , $\text{Na}_2\text{W}_2\text{O}_7$, CO_2 , WO_3 , Na_2CrO_4 , Na_2SO_4 , $\text{Na}_2\text{Mo}_2\text{O}_7$, MoO_3 , SO_3 . This row does not remain the same for BN (Table 2).

The corrosion rate of HD in Na_2WO_4 melt and

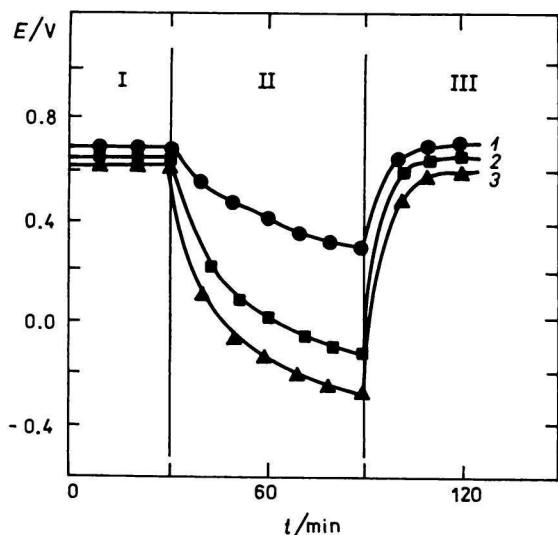
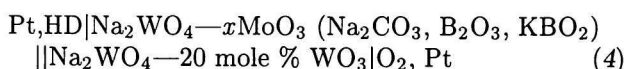
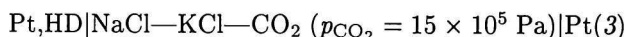
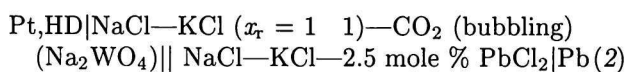
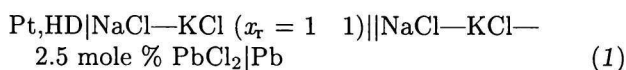


Fig. 1. Time dependence of stationary platinum (1), diamond (2), and cubic boron nitride (3) electrode potential variation in the NaCl—KCl melt in air (zones I, III) and when passing CO₂ over the melt (zone II). *T* = 1023 K.

mixtures based on this salt was estimated. In Na₂WO₄ melt at 1073 K the corrosion rate for c-BN and diamond is 0.3 g/(m² h) and 0.4–0.5 g/(m² h), respectively. Addition of as small amount as 1.0 mass % of oxidants (carbonate, sulfate, refractory metal oxides) to the Na₂WO₄ melt increases the corrosion rate by a factor 1.3–2.0 in the initial period.

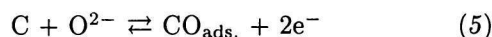
Thermodynamic analysis and corrosion measurements lead to the same conclusion. Redox processes occurring on dielectric surface contacting with ionic melts must lead to spatial charge separation on the interface dielectric—ionic melt and to an appearance of the electrochemical potential. That is why the potential of HD electrode was studied by e.m.f. measurement in the following halide—oxide systems



It is stated by potentiometric method that diamond and BN have not their own potential in halide—oxide melts. Values of these potentials are equal to that of the potential of platinum. The difference between potentials of Pt and HD electrodes appears when Na₂WO₄ is added or CO₂ is passed over the NaCl—KCl melt. For diamond this difference reaches

280 mV (Fig. 1, curve 2), for c-BN 320 mV (Fig. 1, curve 3) when CO₂ is passed and 350 mV and 400 mV, respectively, when Na₂WO₄ is added. Potentials of the diamond and c-BN electrodes in the Na₂WO₄ melt and in the mixtures based on it (system (4)) were measured. The potential of the diamond electrode in the Na₂WO₄ melt took the values between –1.35 V and –1.40 V and the difference between diamond and Pt electrodes potentials reached 850 mV. The potential of the c-BN electrode in this melt was equal to –1.1 V and the difference between c-BN and Pt electrodes potentials reached 500 mV. HD electrodes potentials were responsive to changes in the acid-base properties of the melt. For instance, the addition of acidic additives (WO₃, MoO₃) makes the HD electrode potential more positive, the addition of basic additives (Na₂CO₃) makes it more negative.

The reaction proceeding on the diamond electrode can be written as

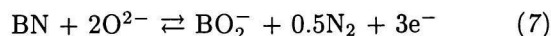


Potential of the diamond electrode may be calculated from the following equation

$$E = E^{\circ} + \frac{RT}{nF} \ln \frac{[\text{CO}]}{[\text{O}^{2-}]} = E_{*}^{\circ} + \frac{2.3RT}{2F} p\text{O}^{2-} \quad (6)$$

E° is the standard potential of diamond electrode, E_{*}° the reduced standard potential of diamond electrode.

The reaction for BN can be introduced as



The equation of BN electrode potential can be written as follows

$$E = E^{\circ} + \frac{RT}{3F} \ln \left\{ \frac{[\text{BO}_2^-][\text{N}_2]^{1/2}}{[\text{BN}][\text{O}^{2-}]^2} \right\} \quad (8)$$

Eqns (6) and (8) properly explain experimental dependences of changes in acid-base properties of the melt.

Voltammetric study of the CO₂ electroreduction under its excess pressure in the NaCl—KCl ($x_{\tau} = 1 \text{—} 1$) melt on diamond and BN electrodes was carried out. At first we registered *I*—*E* curves of the CO₂ reduction on an empty Pt container for measuring cathodic surface of the Pt net. Then the Pt container filled with HD was used. A noticeable increase in reduction current on the diamond electrode against platinum container and rise of the current in the initial period were observed (Fig. 2, curves 3, 4). This experimental fact can be explained by an increase of the working electrode surface which becomes possible as the result of conductivity appearance on the HD surface. An increase of working electrode area due to conductivity appearance in diamond and nitride phases was ob-

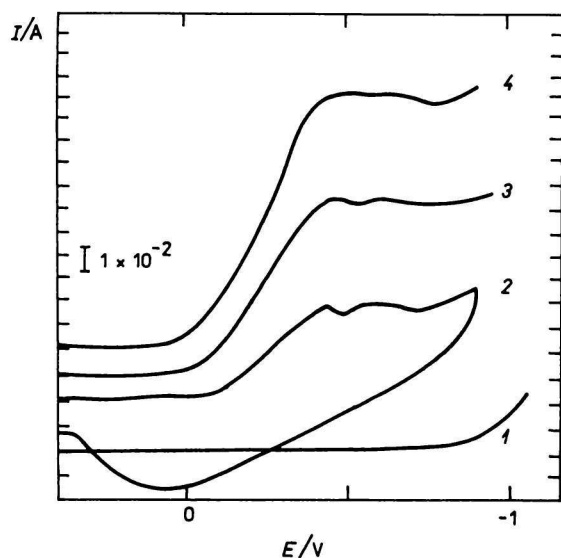


Fig. 2. Voltammograms for the NaCl—KCl melt (1) under a positive CO_2 pressure of 1.225×10^3 kPa (2—4) on the platinum net electrode (1, 2), on the boron nitride electrode (3), and on the diamond electrode (4). Time of exposure of the HD electrodes to CO_2 (h): (3) 0.5, (4) 1. Polarization rate: 0.1 V/s.

served under voltammetric study of the $\text{W}_2\text{O}_7^{2-}$ electroreduction in the Na_2WO_4 — WO_3 melt.

Results and conclusions made in this work can be explained by the concept of surface conductivity appearance in HD crystals due to redox processes un-

dergone on the dielectric—ionic melt interface. This phenomenon allows the application of surface conductivity to galvanic treatment of HD in ionic melts.

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