Chemistry

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1965

SovietRxiv

Abstract

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The Role of Hydroxides and Carbonates of Alkali Metals in the Oxidative Dissolution of Diamond

Diamond crystals are oxidized when heated in air or in oxidizing media. Oxidation in air becomes noticeable at temperatures above 500–600° ([1,2]). Gradual oxidation (etching) of diamonds has been observed in melts of caustic and carbonic alkalis, saltpeter, and in melts of silicate rocks at temperatures up to 1100° ([1–5]). A. E. Fersman attached great importance to experiments on diamond etching, since they provide valuable information on the physicochemical properties of diamonds and their genesis. A considerable number of studies on the oxidative dissolution of diamond were devoted to the investigation of surface etch sculptures and to clarifying the role of dissolution processes in the formation of rounded crystal shapes ([3,6,7]). However, the very low physicochemical level of the experiments on diamond etching, characteristic both of older works and of some modern ones, is striking.

Table 1

Characteristics of the diamond crystals studied

Crystal No.	Initial weight, mg	Shape and other features	Luminescence in UV rays: color (visually)	Luminescence in UV rays: brightness (by LYuF-57, % of standard 2)
8	3.258	Yellowish fragment of an octahedron with small inclusions	Yellow	19

Crystal No.	Initial weight, mg	Shape and other features	Luminescence in UV rays: color (visually)	Luminescence in UV rays: brightness (by LYuF-57, % of standard 2)
16	2.300	Colorless flattened octahedron with a trigonal outgrowth and inclusions	Blue	49
22	1.657	Colorless doublet of octahedra of the spinel type, without inclusion	Bright blue	100
39	2.812	Yellowish flattened doublet of the spinel type with pitted striation on the faces	Greenish	58
42	2.490	Yellowish flattened doublet of the spinel type with blunting of edges by parallel striation	Green-blue with a blue spot inside	41

Crystal No.	Initial weight, mg	Shape and other features	Luminescence in UV rays: color (visually)	Luminescence in UV rays: brightness (by LYuF-57, % of standard 2)
43	3.423	Colorless flattened octahedron with rounded edges; there are inclusions of colorless and dark minerals	Yellow-green with a blue spot inside	32
71	5.666	Grayish fragment of an octahedron with small cracks and dark inclusions	Yellow-greenish	56
74	5.092	Slightly greenish flattened doublet of the spinel type	Indeterminate	14
78	4.240	Colorless intergrowth of two octahedra with pitted striation on the faces and small inclusions	Indeterminate	64

Crystal No.	Initial weight, mg	Shape and other features	Luminescence in UV rays: color (visually)	Luminescence in UV rays: brightness (by LYuF-57, % of standard 2)
95	4.324	Colorless rounded rhombododecahedron with small inclusions	Greenish	22

To determine the solubility of diamond, small whole crystals and fragments of crystals of Yakut diamonds were taken (see Table 1). The work was carried out in a specially designed quartz microapparatus with an indirect temperature-control system ([8]). To prevent contact of the diamonds and the alkaline melts with quartz, the apparatus had an inserted platinum reactor. The crystals under study were placed in a capsule made of platinum mesh. The melt was held in the capsule by the forces···

wetting. The flow of the gas phase through the apparatus was maintained at a constant rate of $\sim$ 600 ml/hour. The gas phases studied were: air; dry nitrogen purified of oxygen over copper heated to 600° and a pyrogallol solution; dry carbon dioxide purified of oxygen; superheated water vapor obtained from distilled deaerated water. NaOH, KOH, Na_2CO_3, and K_2CO_3 were used in chemically pure grade. In experiments combining carbonate with carbon dioxide, caustic alkalis were taken, which were then converted into carbonates under the action of CO_2.

The usual duration of an experiment was 2 hours. Experiments were carried out with individual crystals or with groups of 3-6 crystals. The same crystals were used successively in different series of experiments. After the experiments the alkaline melt was dissolved in water or dilute hydrochloric acid, and the crystals were washed with water and absolute ethyl alcohol.* The cleanliness of the crystal surface was checked under a microscope. Microphotography of the shape of the crystals and of the surface sculptures was performed with a MIN-4 polarizing microscope. The crystals were weighed before and after the experiments on MV-20 semimicrobalances. The weight loss of each crystal was determined as a percentage. From the data obtained and from the values of the geometrical surface area of the crystals, the rate of oxidative dissolution of diamond was calculated in $mg/mm^2 \cdot hour$. The experimental results are given in Table 2.

Table 2

Oxidation of diamonds in air, carbon dioxide, and superheated water

vapor in gaseous and liquid media

Temperature, °C	Gas phase; flow rate	Liquid phase	Number of crystals in the experiment	Mean weight loss in 2 hours, %	Mean oxidation rate, mg/mm^2 · hour
867	N_2+21% O_2; 600 ml/hour	–	1	98.7 *	0.3190
884	CO_2; 550 ml/hour	–	3	3.16 **	0.0102
871	H_2O; 600 ml/hour	–	3	0.61 ***	0.0018
878	N_2+0.25% O_2; 600 ml/hour	NaOH	6	1.30	0.0040
880	N_2+0.25% O_2; without flow	NaOH	6	0.20	0.0005
878	N_2+0.25% O_2; without flow	Na_2CO_3	6	0.07	0.0002
880	N_2+0.25% O_2; 30 ml/hour	KOH	6	0.78	0.0018
879	N_2+0.25% O_2; 20 ml/hour	K_2CO_3****	6	0.34	0.0006
873	CO_2; 600 ml/hour	Na_2CO_3	6	0.46	0.0010
873	CO_2; 600 ml/hour	Na_2CO_3	6	0.47	0.0010
873	CO_2; 600 ml/hour	K_2CO_3****	6	2.80	0.0075
872	H_2O; 600 ml/hour	NaOH	6	6.60	0.0200

Temperature, °C	Gas phase; flow rate	Liquid phase	Number of crystals in the experiment	Mean weight loss in 2 hours, %	Mean oxidation rate, $mg/mm^2 \cdot$ hour
872	H_2O; 600 ml/hour	Na_2CO_3	6	6.14	0.0180
876	H_2O; 600 ml/hour	KOH	6	23.00	0.0480
871	H_2O; 600 ml/hour	KOH	6	23.95	0.0710
871	H_2O; 600 ml/hour	K_2CO_3****	6	30.70	0.0820

* Weight loss in 1 hour 32 min; an unburned part of the crystal weighing 0.020 mg remained.
** Mean values from 7 successive two-hour experiments.
*** Mean values from 14 successive two-hour experiments.
**** K_2CO_3 was in a partially molten state.

The strongest oxidizing agent proved to be the oxygen of air. The rate of combustion of diamond (crystal 22) in a current of air at 867° was 0.319 $mg/mm^2 \cdot$ hour, which is 30 times greater than the rate of destruction of diamond in a current of O_2 at 884° and 150 times greater than the rate of oxidation in superheated water vapor at 871° (see Table 2). From this it may be concluded that in a current of nitrogen containing 0.5-7.0% O_2, the rate of diamond combustion will be the same as in CO_2, and in nitrogen containing 0.1% O_2—the same as in water vapor. Consequently, in order to obtain accurate data on the dissolution of diamond in different media it is necessary to pay special attention to the complete removal—

* After some experiments, in which enhanced migration of platinum with redeposition of it on the diamond was observed, additional treatment of the diamonds in boiling aqua regia was carried out.

of the oxidizing action of free oxygen. Therefore, all experiments on the etching of diamond in which the condition of complete isolation from air was not fulfilled cannot be taken into account for assessing the actual solubility of diamond in different media or for explaining the mechanism of this process.

To verify the fact that diamonds are soluble in melts of alkali-metal hydroxides and carbonates, the following experiments were carried out. Diamond crystals

(16, 42, 43, 71, 78, and 96) were subjected to the action of a NaOH melt at 878° for 2 h in a stream of nitrogen purified by the method indicated above. Gas-chromatographic analysis showed the presence of 1.5% oxygen in the initial nitrogen and 0.23–0.27% in the purified nitrogen. The average rate of dissolution of diamond in this case proved to be 0.0040 $mg/mm^2 \cdot h$ (see Table 2). This is very close to the expected value if the decrease in weight is attributed to oxidation due to the admixture of oxygen in the nitrogen. Similar experiments with NaOH, KOH, Na_2CO_3, and K_2CO_3, but carried out in a very weak current of the same nitrogen or in a stagnant nitrogen atmosphere of the same degree of purification, confirm this explanation (see Table 2), since the average rate of dissolution of diamonds in these experiments decreased in accordance with the decrease in the volume of nitrogen that had contact with the reactor and the diamonds. Consequently, dissolution of diamond in melts of NaOH, KOH, Na_2CO_3, and K_2CO_3 themselves at 878–880° does not occur.

Experiments with melts of caustic and carbonated alkalis, with carbon dioxide and water vapor passed through as oxidants, showed a greater solubility of diamond. In the medium of carbonates, the rate of dissolution of diamond in carbon dioxide is lower than under the direct action of the gas phase. Conversely, under the action of water vapor on diamond in the medium of caustic and carbonated alkalis, the solubility is greater than under the direct action of the vapor phase (see Table 2). Specific differences are also observed in the solubility of diamond in the carbonate or hydroxide of sodium and potassium.

All this indicates the catalytic role of caustic and carbonated alkalis in the oxidative dissolution of diamond when O_2, CO_2, and H_2O act as oxidants. From the data in Table 2 it is seen that catalytic activity in the processes of diamond oxidation is associated with sodium and potassium ions and depends little on the anion.

During oxidation of diamond by water, melts of sodium and potassium hydroxides gradually turn into the corresponding carbonates. Therefore it may be considered that one of the products of the oxidation of diamond by water is CO_2, formed by the reaction

$$C_{\text{diamond}} + 2H_2O = CO_2 + 2H_2. \tag{1}$$

The process

$$C_{\text{diamond}} + H_2O = CO + H_2 \tag{2}$$

is also possible.

Process (1) should be favored by an excess of water, as well as by the binding of the CO_2 formed into carbonate, which, as was shown above, is not an oxidizing agent with respect to diamond. Under various conditions of diamond oxidation by water, apparently, different ratios between reactions (1) and (2) are possible.

Under the catalytic action of alkali-metal ions, the mechanism of oxidation of diamond by water in the medium of hydroxides and carbonates is apparently the same, since there are no differences in the rates of the oxidation process. The catalytic action of potassium and sodium ions in diamond oxidation apparently amounts to facilitating the formation of surface carboxyl groups upon rupture of the aliphatic C–C bonds of diamond. Convincing evidence in favor of this assumption is the 10-fold increase in the rate of oxidation of diamond by water in the case of Na^+ ions and the 40-fold increase in the case of K^+ ions, as compared with its direct action.

The rate of oxidation of diamond by carbon dioxide in potassium carbonate is 7–8 times higher than in sodium carbonate, i.e., the K^+ ion in this process also exhibits greater catalytic activity than the Na^+ ion. However, attention is drawn to the fact that, compared with the rate of direct oxidation of diamond in carbon dioxide, the rate of oxidation in a sodium carbonate medium is 10 times lower, and in a potassium carbonate medium 1.3 times lower. Consequently, in the presence of Na^+ and K^+ ions in the melt, there is a retardation of the process of diamond oxidation by carbon dioxide and an acceleration of the process of oxidation by water vapor.

Oxidation of diamond under the action of CO_2 can proceed only by the route

$$C_{\text{diamond}} + CO_2 = 2CO. \tag{3}$$

The retarding effect of alkali-metal ions in this process is apparently associated with the formation and stabilization of surface carboxyl groups with hydrogen replaced by a metal. The mechanism of action of alkali-metal ions here is evidently the same as in the case of oxidation by water, but the result is directly opposite because of differences in the nature of the oxidizing agent.

Microscopic observation of the structures obtained during etching of the diamond surface in oxidation processes shows that the results of surface etching differ depending on the nature of the oxidizing agent and on the presence or absence of a liquid medium. On the surface of a diamond crystal, during rapid combustion in air, coarse sculptural elements in the form of large steps are formed. During oxidation of diamond by carbon dioxide without a melt, matting of the surface occurs with the formation of directly oriented triangular pits with stepped walls. During oxidation of diamond by water, the surface of the crystals becomes covered with a multitude of directly oriented triangular pits. In this case the latter have the form of negative pyramids, either untruncated or truncated, with smooth faces and a smooth bottom. During oxidation of diamond by carbon dioxide and water in a medium of molten sodium or potassium hydroxides and carbonates, more perfect etching sculptures are formed than under their direct action. After etching by water in melts, the crystals retain the luster of the surface even with an overall decrease in their weight by 50–80%.

Apart from the formation of elements of trigonal-trioctahedral faces replacing octahedron edges in the form of perpendicularly striated bands, observed during dissolution of crystals Nos. 16 and 71, we did not note any substantial changes in the habit of the crystals even after a 50-80% decrease in their weight. The formation of rounded forms—if one does not count round cavities and disk-shaped sculptures formed on some crystals (for example, No. 42)—was not observed by us. On crystal No. 43, the formation of dissolution cracks along the direction of cleavage planes was noted; these gradually cut out part of the crystal.

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Received
16 III 1965

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Note: Figure translations are in progress. See original paper for figures.