

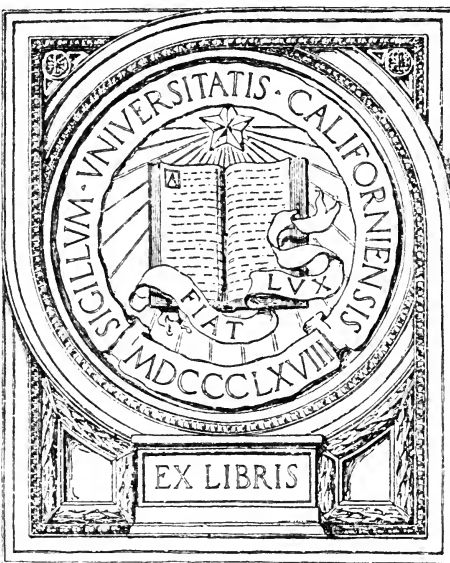
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EXCHANGE



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The Preparation, Properties, and Composition of Silundum

DISSERTATION

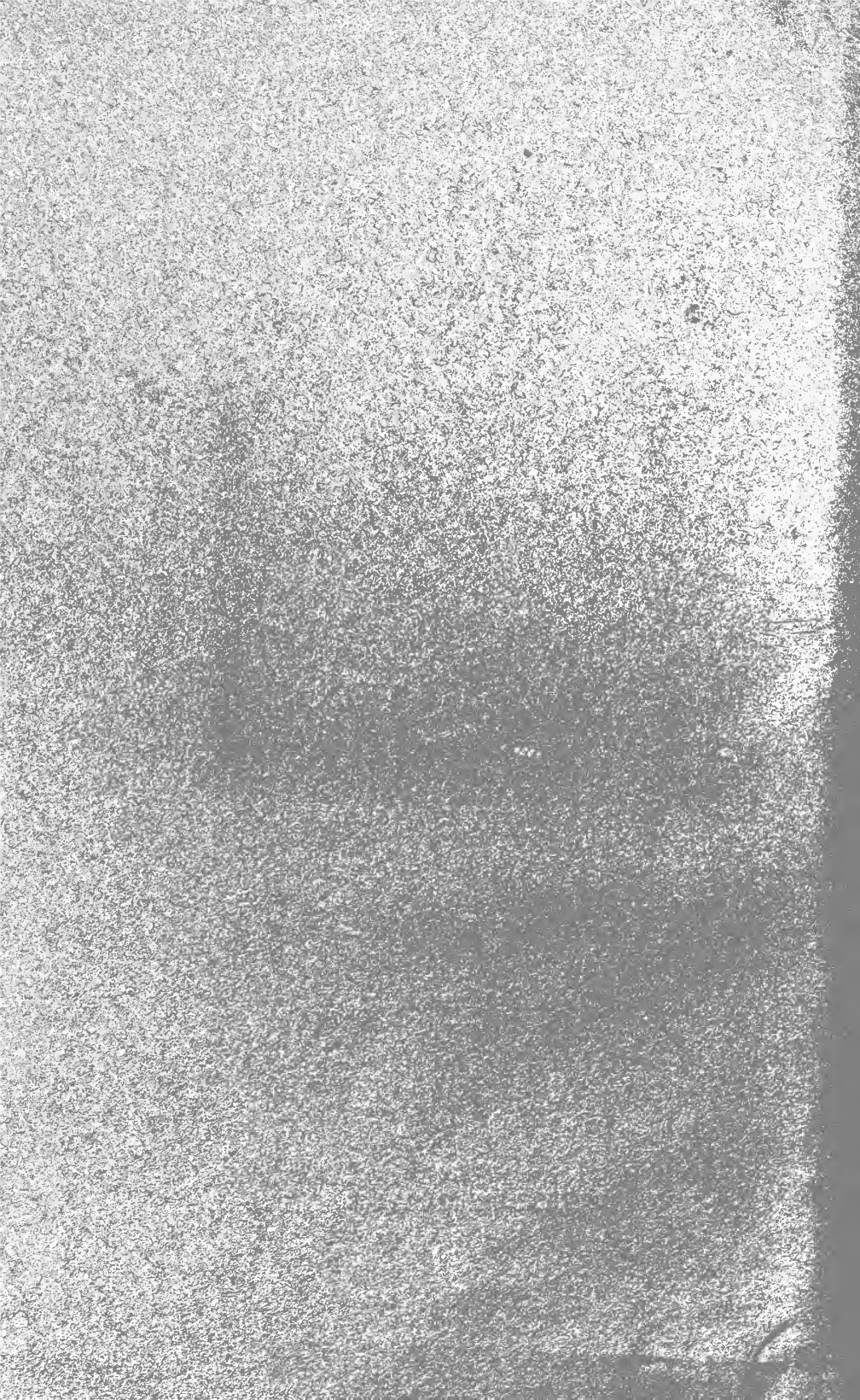
SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIRE-
MENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY,
IN THE FACULTY OF PURE SCIENCE, OF
COLUMBIA UNIVERSITY



BY
ALEXANDER LOWY, B.S., M.A.

NEW YORK CITY

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ALEXANDER LOWY

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April, 1915

EXCHANGE

THE PREPARATION, PROPERTIES AND COMPOSITION OF SILUNDUM

By ALEXANDER LOWY

Silundum is a product of the electric furnace, and was discovered by Bölling,¹ at Frankfort-on-the-Main, Germany. As early as 1900 he began the study of the use of the various silicon carbides as resistors, being led to this work by the fact that these carbides can be subjected to high temperatures without undergoing decomposition. His method was to mix the silicon carbide powder with various binders in order to hold the individual particles together. The mass is a non-conductor at low temperatures, but at about 700–800° C. it becomes conductive, thus being useless at a higher temperature.

By 1904 a process was worked out and patented by which it is possible to convert any piece of carbon, *e. g.*, a crucible, brick, rod, etc., into silicon carbide. By this method resistors without any binding material are obtained, which will stand temperatures as high as 1650–1700° C. Previous to 1904, silicon carbide had been known in two conditions only—amorphous and crystalline—and it was supposed to be formed by the interaction of sublimed carbon and sublimed silicon. Bölling, however, discovered that silicon penetrates carbon when both are in a highly heated condition, but at too low a temperature for the carbon to have any appreciable vapor tension. He claimed that silicon at about 1600° C. exists in the form of vapor. Carbon at this temperature has an extremely small vapor pressure. According to Bölling's definition, silundum is the product that is obtained when carbon is heated in an atmosphere of silicon vapor.

An electric furnace such as is used for the manufacture of carborundum was used for the preparation of silundum. Pieces of carbon pressed to the desired shape were introduced into a mixture of sand and

¹ F. Bölling, *Chem. Ztg.*, **32**, 1104; *Electrochem. and Met. Ind.*, **7**, 24

carbon, and this was heated by using as a resistor a granular core of coke. The sand was reduced and the silicon, volatilizing, penetrated the carbon objects and thus "silundumized" them.

Moyat¹ criticized Bölling's work, and claimed that silundum was not a new chemical individual, but merely a new variety of silicon carbide.

Acheson's patent² No. 895,531 is interesting, inasmuch as it deals with a similar product. In order to protect crucibles, tuyères, bricks, muffles, and other articles of carbon from destruction at high temperatures in the presence of oxygen, or when exposed to molten metals, Acheson proposes to cover them with a coating of a highly refractory siloxicon, or silicon oxycarbide. This prolongs their life and prevents disintegration. A portion of the carbon on the surface of the article itself is utilized in producing the siloxicon coating. After having been shaped to the form desired, the carbon or graphite article is embedded in a mixture of silica and carbon in the proportion of two parts of sand to five of carbon, and is exposed to the proper temperature at which silicon, oxygen, and carbon combine to form siloxicon.

The product obtained by this method resembles in appearance the lighter-colored silundum, which is to be discussed later in greater detail.

Tucker and his co-workers³ in 1909 made an experimental study of the formation of silundum. In their experiments the charge was made up according to the proportion $\text{SiO}_2 : 2\text{SiC}$. This charge was heated in a carborundum furnace, the core of which, instead of being of granular carbon, consisted of a number of small carbon plates, pressed together between two horizontal graphite electrodes. Around the core was placed a charge of sand and carborundum, in which were embedded, at varying distances from the core, the carbon articles to be silundumized. These workers also investigated the reactions between sand and carbon. Their experiments showed that silundum can be produced by either of the above reactions, *i. e.*, by the reaction of sand and carbon or of sand and carborundum. They also showed the relative difficulty of oxidizing silundum. Two plates, silundumized on the surface, were heated to a high temperature by means of an electric current. The

¹ Moyat. *Chem. Ztg.*, **32**, 1166.

² Acheson, U. S. Patent No. 895,531; *Electrochem. and Met. Ind.*, **6**, 379

³ Tucker, Kudlich and Heumann, *Trans. Am. Electrochem. Soc.*, **16**, 207.

graphite cores were completely oxidized, leaving only box-like shells of silundum.

Amberg-Bodio¹ also prepared silundum, and states that, "According to the temperature and the time, there is obtained a gray- to metallic-appearing silicon carbide, with a content of silicon greater or less than that which corresponds to the formula SiC. The process may be interrupted at any time and a coating of silundum of any desired thickness produced."

Within the past few years, F. J. Tone² has obtained four patents for the preparation and manufacture of dense, compacted silicon carbide. From his description, the term "dense compacted silicon carbide" is synonymous with the term "silundum."

Egly,³ early in 1913, patented a substance called "Silit" which is prepared by heating to a fairly high temperature silicon carbide, silicon, and a binder, until a homogeneous mass results. "Silit" is a good resistor and has many industrial applications.

F. J. Tone⁴ describes a silicidized carbon which he calls "Silfrax." In order to show the interior structure of the material, he gives microphotographs of it.

A survey of the literature and a careful preliminary examination of several samples of silundum, indicated to the writers that in all probability the material known as silundum exists in two modifications. The crudeness of the analytical methods used in determining the composition of these refractory materials made it impossible to draw any definite conclusion from the work already published. Moreover, little or no data are available on such important conditions for the preparation of silundum as temperature, proportions of reacting materials, and time of heating. It seemed, therefore, that by a careful investigation into the best conditions of temperature for preparing silundum, with an improved method of analysis and a careful examination of properties, considerable light might be thrown upon the question of the composition of silundum. With this purpose in mind the present investigation was undertaken.

Silundum, according to the conditions under which it is formed, exists in two modifications. One of these,

¹ Amberg-Bodio, *Z. Elektrochem.*, **15**, 725-727; *Chem. Abs.*, **4**, 149.

² Tone, U. S. Patents Nos. 913,324, 992,698, 1,013,700, 1,013,701.

³ Egly, *Elektrotechn. Zeit.*, **34**, 263-267; *Chem. Abs.*, **6**, 536; **7**, 1142, 2357.

⁴ Tone, *Trans. Am. Electrochem. Soc.*, **26**, 181.

a steel-gray variety, is formed at a temperature of about 1900°C . and analyzes very closely to the formula SiC ; the other, a slate-green variety formed at about 1600°C ., is an oxycarbide of silicon of the formula $\text{Si}_4\text{C}_4\text{O}$. It has been determined that silundum does not decompose below 2200°C . At higher temperatures silicon distills off, leaving a graphite skeleton of the same form as the original silundum, which action would indicate that the graphite does not vaporize at the temperature of decomposition, and would show, further, that silundum is formed by the reaction of silicon vapor and solid carbon, the temperature of formation being lower than the temperature of decomposition.

The action which takes place in the process of silundumization may be summarized as follows: The silicon which is liberated from silica by the reducing action of coke- or sugar-carbon penetrates the solid carbon or graphite objects, and there reacts with the carbon, forming a steel-gray variety of silundum. This takes place above 1800°C . Below this temperature the slate-green variety is formed, most likely by the penetration of the carbon by the silicon vapor and carbon monoxide.

The stumbling block in the analysis of such refractory substances as silundum has been the difficulty of completely decomposing the material and burning all the carbon to carbon dioxide. The silicon may be determined easily by means of the well-known sodium carbonate and potassium nitrate fusion. In order, therefore, to overcome the difficulties hitherto encountered in the carbon determination, various fluxes and oxidizing agents were tried, with the object of replacing the inadequate sodium peroxide and magnesia method¹ previously used. After considerable experimentation litharge was found to be an excellent flux for decomposing the material and partially oxidizing it, complete oxidation being effected by means of a stream of oxygen. Using this method on carborundum crystals, results were obtained that were accurate within 0.3 per cent of theoretical. Considering the nature of the material treated, this was satisfactory. Analyses of silundum samples were made by this new method, and the results checked on duplicates. Therefore, we consider this to be a good method for the accurate determination of carbon in refractory carborundum-like substances.

¹ Fitzgerald, *Electrochem. Ind.*, **2**, 443.

DESCRIPTION OF EXPERIMENTS

PREPARATION OF SILUNDUM—In order to obtain sufficient amounts of the substance for the further study of its properties and composition, silundum was prepared in a coke resistance furnace (Experiments 1 to 7). Since this type of furnace does not lend itself to accurate temperature measurements, the temperatures of formation and decomposition were measured in a separate series of experiments (8 to 13) in the Arsem vacuum electric furnace.¹

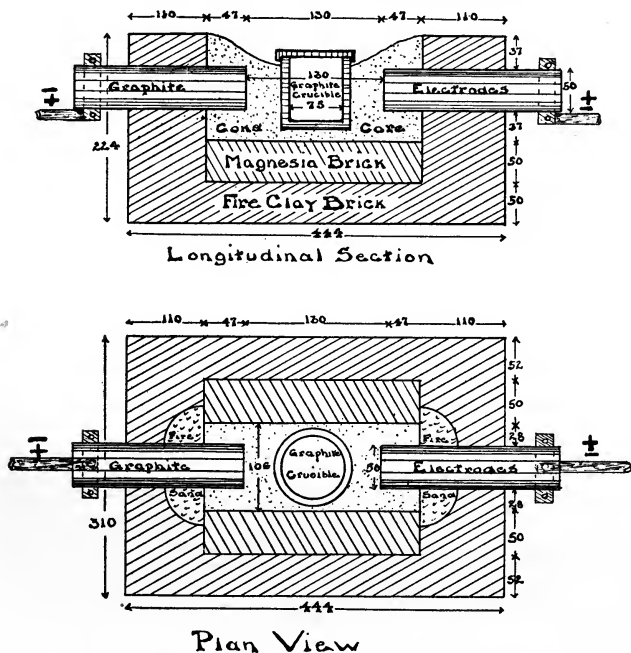


FIG. 1—RESISTANCE FURNACE (DIMENSIONS IN MMS.)

* The coke resistance furnace² was chosen because with it a range of temperatures up to about 2600° C. can be obtained by varying the amount of electrical energy. The furnace, diagrammatically represented in Fig. 1, consists essentially of a coke resistor enclosed by cemented fire-clay brick walls with magnesia lining. The graphite electrodes extend through the walls into the coke.

The graphite crucible containing the charge and the articles to be silundumized were embedded in the coke core. The energy was supplied by a 50

¹ Arsem, *Trans. Am. Electrochem. Soc.*, 9, 153.

² Tucker, *Ibid.*, 11, 307.

kw. A. C. generator. The measurements and the exact details of construction of the furnace are indicated in the diagram.

Carbon and graphite rods varying in diameter from $\frac{1}{8}$ to $\frac{3}{8}$ in., and 2 in. in length were used. In a few experiments carbon tubes were used. The charge consisted of clean sand and coke. For the samples that were to be analyzed, special charges, consisting of precipitated silica and sugar-carbon were used, in order to obtain a pure product. The objects to be silundumized in these cases were also made of graphite of the highest purity.

EXPERIMENTS IN COKE RESISTANCE FURNACE

Experiments 1 to 7 were conducted in order to find out how the variation of the different factors of time, energy consumption and composition of charge would affect the nature of the product formed. The readings taken during these experiments appear in Table I.

TABLE I—READINGS TAKEN DURING EXPERIMENTS IN COKE RESISTANCE FURNACE

EXPERIMENT No. 1			EXPERIMENT No. 2			EXPERIMENT No. 3		
Time	Amperes	Volts	Time	Amperes	Volts	Time	Amperes	Volts
10.00	0	40	1.30	0	35	9.30	0	34
10.10	75	38	1.45	200	30	9.45	200	32
10.20	100	36	1.55	300	30	9.55	310	30
10.30	150	34	2.00	400	30	10.00	405	25
10.40	150	34	2.10	400	26	10.15	400	25
10.50	150	34	2.20	400	26	10.30	410	25
11.00	200	28	2.30	400	26	10.45	410	25
11.10	270	26	2.40	410	26	11.00	400	25
11.20	300	26	2.50	410	26	11.30	400	25
11.30	300	26	3.00	410	26	12.00	400	25
12.00	300	26				12.30	400	25
						1.00	400	25

EXPERIMENT NUMBER 5			EXPERIMENT No. 7					
Time	Amperes	Volts	Time	Amperes	Volts			
9.55	0	35	10.50	550	28	10.00	0	40
10.05	75	34	10.55	525	28	10.10	100	36
10.10	100	30	11.00	550	28	10.20	200	30
10.15	200	29	11.05	550	28	10.30	500	28
10.20	250	30	11.15	555	28	10.40	500	26
10.25	350	29	11.25	550	28	10.50	550	25
10.30	450	28	11.35	550	28	11.00	650	25
10.35	550	28	11.45	550	28	11.10	650	25
10.40	550	28	11.55	550	28	11.30	650	25
10.45	550	28	12.00	550	28	12.00	650	25
						12.30	650	25

EXPERIMENT I—A charge consisting of a mixture of 60 g. coke and 150 g. sand (the theoretical amount to produce silicon) was placed in a graphite crucible. Four carbon rods $\frac{1}{4}$ in. in diameter and 2 in. long were then embedded in the charge and the crucible tightly covered with a graphite cover. Crucible and contents were placed in the furnace within the coke resistor, and the electric current turned on. After two hours the furnace was allowed to cool, and examina-

tion of the contents of the crucible showed that the rods were not silundumized. The sand was fused around the graphite rods. This experiment indicated that a higher temperature was necessary for the accomplishment of the desired reaction.

EXPERIMENT 2 was conducted in order to study the effect of higher temperature on the reaction. The electrical energy consumption was increased, as indicated above, with the object of obtaining this desired higher temperature. The composition of the charge was the same as in Experiment 1. The graphite rods upon fracture were found to be silundumized half way through. The line of demarcation between the silundumized portion and the portion not acted upon was very sharp (see the microphotograph, Fig. 2). The color of this product was slate-green.

EXPERIMENT 3 was intended to produce silundum extending through the entire cross-section of the rods. The charge was made up exactly as in Experiment 1, and the temperature conditions were also duplicated as closely as possible. This experiment, however, was carried on two hours longer than Experiment 2. The rods were completely silundumized, and no graphite core was visible. The color of the rods was slate-green. They were conductors of electricity even at ordinary temperatures.

EXPERIMENT 4 was carried out in order to determine whether there is any difference in the nature of the product obtained when the rods are embedded in the charge and when they are exposed. The charge in this experiment consisted of 120 g. silica and 48 g. coke. The rod was placed in the charge with the upper half extending above the surface of the charge. The other conditions of the experiment were the same as in Experiment 2. The product was of a slate-green color. Fracture showed that the part embedded in the charge was silundumized about half way through, while the part exposed had only a superficial coating of silundum. This experiment shows that more complete silundumization takes place when the rods are embedded in the charge than when they are exposed.

EXPERIMENT 5 was intended to show the effect of still higher temperatures than were used in the previous experiments. A charge like that in Experiment 1 was used. The rods upon fracture were found to be silundumized about half way through. The color of the product was steel-gray, resembling carborundum. Clearly defined characteristic carborundum crystals

were found on the surfaces of the silundumized rods.

EXPERIMENT 6 was similar to Experiment 5 except that the heating was carried on for four hours. Subsequent examination of the rods showed that complete silundumization had taken place. The rods were steel-gray in color, and had small carborundum crys-

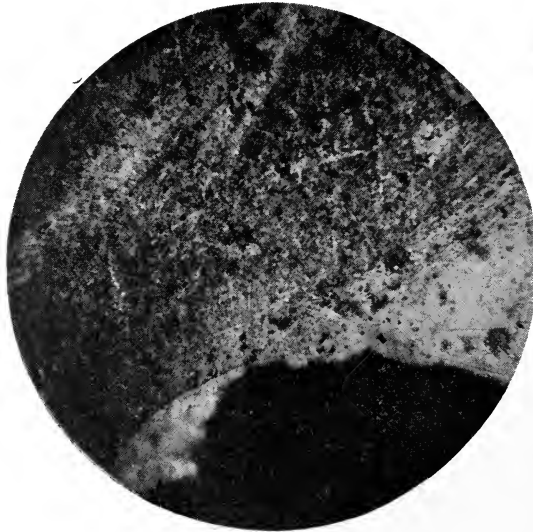


FIG. 2.

tals on the surface. They were conductors of electricity even at ordinary temperatures.

EXPERIMENT 7 was designed to study the effect of high temperatures. A rod of silundum of the steel-gray variety was placed in the graphite crucible and heated for two hours under electrical conditions as given in Table I. The silundum rod was found to have lost all its characteristic properties, and on further examination proved to be graphite.

Experiments were also carried out in order to determine what would be the effect of varying the composition of the charge used. It was found, however, that no appreciable difference in the nature of the product resulted from such variation. Some of the sand in the charge sinks to the bottom, and the coke, because of its lower specific gravity, remains at the top. There is never, therefore, any very intimate mixture of the ingredients. It is not surprising, in consequence, that small differences in the ratio of the components of the charge should produce no differences in the results.

EXPERIMENTS IN ARSEM ELECTRIC VACUUM FURNACE

EXPERIMENTS 8 TO 13—As temperature determinations cannot be made with any degree of accuracy in the electric furnace used above, Experiments 8 to 13 were carried out in an Arsem electric vacuum furnace,¹ in order to determine the temperature of formation and decomposition of silundum. Details of the construction of this furnace, which is complex, are out of place in this article, and the reader is referred to the reference below. The temperature was measured with a Wanner optical pyrometer. As pyrometer readings are untrustworthy in the presence of fumes, blank runs were first made without any material in the furnace, noting at the same time the energy consumed and the temperature attained. These temperatures were then taken as the temperatures which would exist in the experiments made under the same conditions of time and energy consumed.

A graphite crucible, $\frac{3}{4}$ in. diameter and $2\frac{1}{2}$ in. high, was used. The carbon rod to be silundumized was placed in the center of this crucible and was surrounded with the charge, composed as usual of silica and coke. The energy consumption was recorded by a wattmeter. The results of these experiments are given in Table II.

TABLE II—RESULTS OF EXPERIMENTS IN ARSEM ELECTRIC VACUUM FURNACE

Exp. No.	Temp. ° C.	Ratio of SiO ₂ to C in charge	Color of product	Remarks
8.....	1300	30 : 12	No silundum formed
9.....	1606	30 : 12	Slate-green	Surface silundumization
10.....	1712	30 : 12	Slate-green	Surface silundumization
11.....	1845	30 : 12	Steel-gray	} Surface silundumization— most of charge volatilized
12.....	1900	30 : 12	Steel-gray	
13.....	Over 2200	30 : 12	Product decomposed	

Owing to the fact that a high vacuum was maintained as the temperature rose, some of the silicon distilled from the charge and the depth of silundumization was very small, but the surface layer was sufficiently characteristic to determine the nature of the product.

CONCLUSIONS FROM EXPERIMENTS

I—The temperature of formation of silundum is above 1300° C. (see Expts. 1 and 8).

II—Up to about 1800° C. the greenish slate-colored variety of silundum is formed (see Expts. 2, 3, 4, 9 and 10).

III—Above 1800° C. the steel-gray colored variety of silundum is formed (see Expts. 5, 6, 11 and 12).

¹ Arsem, *Trans. Am. Electrochem. Soc.*, 9, 153.

IV—Continued heating above 2200° C. results in decomposition of the silundum with formation of graphite (see Expts. 7 and 13).

V—The extent of penetration of silundumization depends upon the duration of heating (see Expts. 2, 3, 4, 5 and 6).

VI—More complete silundumization takes place when the object is embedded in the charge (see Expt. 4).

PROPERTIES OF SILUNDUM

According to Bölling,¹ silundum is a form of silicon carbide, and possesses properties similar to those of carborundum. It is capable of being maintained for a long time at temperatures up to 1600° C. without change, and may be heated for a short time to 1700° C. without deterioration. It is a conductor of electricity, its resistance being about six times that of carbon. At 1000° C. its resistance is one-half to two-thirds of that at room temperature. The electrical resistance is variable, and depends upon the variety and hardness of the carbon used in the preparation, that made from porous carbon having a higher resistance than that made from compact. Silundum cannot be melted; in this respect it resembles carbon. It may be nickel-plated, or covered with a layer of platinum. It is a refractory material, but it is attacked by molten metals at high temperatures. It may be heated to a white heat and plunged into cold water without cracking.

Briefly, the results of the present investigation of the physical and chemical properties of silundum may be summarized as follows:

1—Silundum is a good conductor of electricity, with a negative temperature coefficient for its resistance.

2—Silundum is a very hard substance—with a hardness on Mohr's scale of about 9.

3—The specific gravity of silundum is 2.9 to 3.

4—Silundum is not attacked by hydrogen, oxygen, or nitrogen even at 1100° C.

5—Silundum is attacked by some fused salts.

6—Silundum is not attacked by acids.

ELECTRICAL CONDUCTIVITY—The following is the method for determining the electrical conductivity of silundum: A cylindrical rod of uniform diameter was used. In order to diminish the contact resistance as much as possible the ends were copper-plated, thus: the rods were dipped into paraffine, the ends

¹ Bölling, *Loc. cit.*

craped clean, coated with a very thin layer of graphite, and then copper-plated electrolytically. Copper wires were soldered on, and the rods were cleaned. The resistance was determined at various temperatures with a very accurate Wheatstone bridge.¹

The rod of the slate-green variety was 1.871 cm. long and 0.635 cm. in diameter. The rod of the steel-gray variety was 2.078 cm. long and 0.348 cm. in diameter. Owing to the fusion of the solder, measurements could not be made above 225° C. The rods were heated in a small Hoskins electric furnace, and

TABLE III—RESISTANCES OF THE TWO VARIETIES OF SILUNDUM

Temp. ° C.	SLATE-GREEN VARIETY Rod 1.871 Cm. Long and 0.635 Cm. in Diameter		STEEL-GRAY VARIETY Rod 2.078 Cm. Long and 0.348 Cm. in Diameter	
	Measured resistance Ohms	Specific resistance Ohms per cc.	Measured resistance Ohms	Specific resistance Ohms per cc.
20	0.91450	0.1546	5.2250	0.2391
25	0.91270	0.1543	5.1886	0.2374
50	0.90000	0.1522	4.9786	0.2278
75	0.89092	0.1506	4.8186	0.2205
100	0.88192	0.1491	4.6291	0.2118
125	0.87212	0.1474	4.4191	0.2022
150	0.86202	0.1457	4.2791	0.1958
175	0.85392	0.1443	4.1541	0.1901
200	0.84522	0.1429	4.0441	0.1850
225	0.83530	0.1412	3.9541	0.1809

the temperature was read by means of an ordinary thermometer with its bulb in the heating chamber. Table III shows the measured resistances and the specific resistances in ohms at the various temperatures. The specific resistances are plotted against the temperatures in Fig. 3.

Attempts were made to spray the ends of the rods according to the Schoop² method, but when they were heated, the brass contacts became loosened from the ends of the rods.

It is evident from the above results that the resistance is practically a linear function of the temperature. The temperature coefficient of resistance is negative. The specific resistance is much less than that for carborundum, being, at 25°, 0.1543 ohm per cubic centimeter for the slate-green variety, and 0.2374 ohm per cubic centimeter for the steel-gray variety, while that of carborundum is 50 ohms per cubic centimeter at 25°.³

It was attempted to measure the ohmic resistance of the above rods at higher temperatures by clamping them between platinum plates. The resistance varied

¹ This was done in the Electrical Testing Laboratory of Columbia University.

² *Met. Ind.*, 1914, p. 457. *THIS JOURNAL*, 4, 853; 5, 776; 7, 72.

³ Pamphlet, "Chemical and Physical Properties of Carborundum," published by The Carborundum Co., Niagara Falls, N. Y., 1913.

from 75 ohms to a fraction of an ohm, depending upon the pressure exerted upon the platinum plates, so that measurements of the same order of accuracy as those determined above with plated ends could not be made above 225° C.

HARDNESS and specific gravity measurements are given in Table IV for the two varieties of silundum and for Tone's and Bölling's products.

SPECIFIC GRAVITY was determined by means of a specific gravity bottle, care being taken to expel all air bubbles by careful heating and subsequent cooling.

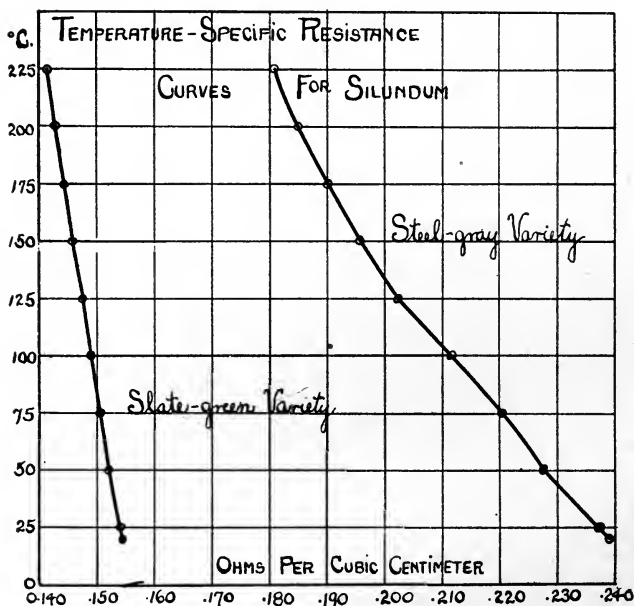


FIG. 3

TABLE IV—HARDNESS AND SPECIFIC GRAVITY OF SILUNDUM

	Specific gravity	Hardness (Mohr's scale)
Tone's "Silifrax".....	2.96	9 plus
Bölling's silundum.....	2.97	9
Greenish variety silundum.....	2.92	8 to 9
Steel-gray variety silundum.....	2.94	9 minus

PROPERTIES OF BOTH VARIETIES OF SILUNDUM

ACTION OF GASES—Oxygen, nitrogen, and hydrogen have no action on silundum heated to temperatures up to 1100° C. An attempt was made to oxidize silundum in a bomb calorimeter under a pressure of 25 atmospheres of oxygen, in a gelatine capsule containing a mixture of benzoic acid and silundum. The gelatine and the benzoic acid were completely oxidized, but the silundum was unattacked.

ACTION OF FUSED SALTS, ETC.—Silundum is not decomposed by the following fused salts: sodium silicate, borax, a mixture of potassium chlorate and potassium nitrate, potassium acid sulfate, cryolite, potassium dichromate.

Silundum is decomposed by fused sodium carbonate, sodium hydroxide, and potassium hydroxide in presence of air, yielding the corresponding silicates and carbon dioxide.

ACTION OF ACIDS—Silundum is not acted upon by hydrochloric, nitric, or sulfuric acids, nor by a mixture of hydrochloric and nitric acids, a mixture of chromic and sulfuric acids, nor by fused boric acid. Commercial silundum, however, is slightly attacked by hydrofluoric acid and by a mixture of nitric and hydrofluoric acids, because of the presence of free silicon and silicon dioxide; but pure samples of silundum are not attacked by these acids.

ACTION OF OTHER SUBSTANCES—Molten sulfur has no action on silundum. Sodium peroxide oxidizes it to sodium silicate plus sodium carbonate. Lead oxide also oxidizes it, producing metallic lead and carbon dioxide (pp. 566 and 570). Fused sodium in presence of air decomposes silundum, yielding sodium silicate and sodium carbonate. The action in this case is most likely due to the presence of sodium peroxide formed from the sodium.

COMPOSITION OF SILUNDUM

In order to obtain silundum as pure as possible for analysis, graphite rods were silundumized according to the previously described methods, in a charge consisting of sugar-carbon and precipitated silica. The resulting silundum was broken up into small pieces in a steel mortar, and subsequently ground to a very fine powder in an agate mortar. The powder was then purified. Depending upon the conditions of preparation, the product obtained was either silicon carbide or silicon oxycarbide, with probable impurities either from the charge or from the reaction, or from the mortar in which the material was ground. The impurities may be silicon, silica, carbon, and iron. Silicon was removed with boiling potassium hydroxide solution, any remaining silica by means of hydrofluoric acid, and the uncombined carbon by long oxidation with a strong blast lamp. Finally, in order to assure complete oxidation the material was boiled with chromic and sulfuric acids, and then with hydro-

chloric acid in order to remove any particles of iron which may have been abraded from the mortar. The material was then thoroughly washed, and when dried was ready for analysis.

For the silicon determination 0.3 to 0.4 g. of the above purified substance was weighed into a platinum crucible. To this were added 4 g. of chemically pure sodium carbonate and a small crystal of potassium nitrate. The contents were then well mixed and the covered crucible heated, great caution being used to avoid spattering. The heating was continued until a quiet fusion resulted, then strongly increased until all the carbon particles were oxidized, leaving a clear melt. This upon cooling gave a clear, white mass, which was dissolved in hydrochloric acid and evaporated to dryness, dehydrated three times, and the determination of silica made as in rock analysis. The silica was weighed by difference after repeated evaporation with hydrofluoric acid. Duplicate analyses checked within 0.15 per cent. From the amount of silica obtained the percentage of silicon was calculated. The results are given in Table V.

TABLE V—ANALYSES OF SILUNDUM FOR SILICON

PER CENT Steel-gray silundum	SILICON FOUND Slate-gray silundum	THEORETICAL PER CENT in silicon carbide	PER CENT SILICON in Si ₂ C ₃ O
69.46	63.16	70.22	63.88
69.59	63.28

The method¹ formerly employed for the determination of combined carbon in carborundum-like substances was to fuse about 0.3 g. of the substance with 3 g. of calcined magnesium oxide and 6 g. of sodium peroxide in a nickel crucible. A blank test had to be run at each set of experiments to determine the amount of carbon dioxide present in the magnesia and sodium peroxide. Furthermore, it was necessary to heat the crucible with a hydrogen flame until a vigorous reaction occurred, and the crucible while still hot was transferred to a desiccator charged with soda-lime and allowed to cool. The carbon dioxide was then determined by any suitable method.

This scheme is subject to grave error, owing to the appreciable amounts of carbon dioxide present in the magnesia and sodium peroxide. The carbon dioxide content of the sodium peroxide continually increases, and therefore, even with the blank corrections, the results are subject to error. The reaction is generally so violent that spattering is almost unavoidable.

¹ Fitzgerald, *Loc. cit.*

Moreover, the process is long, and involves too many operations to yield absolutely quantitative results under the conditions given.

The method worked out in this paper avoids these difficulties.

After preliminary experiments with various oxides, such as pure cupric oxide, ferric oxide, and manganese dioxide, as oxidizing agents, it was found that only molten litharge gave good results on carbon determinations in carborundum-like substances. Molten litharge disintegrates the particles of silundum, and at the same time oxidizes the carbon to carbon dioxide. The reactions may be written as follows:

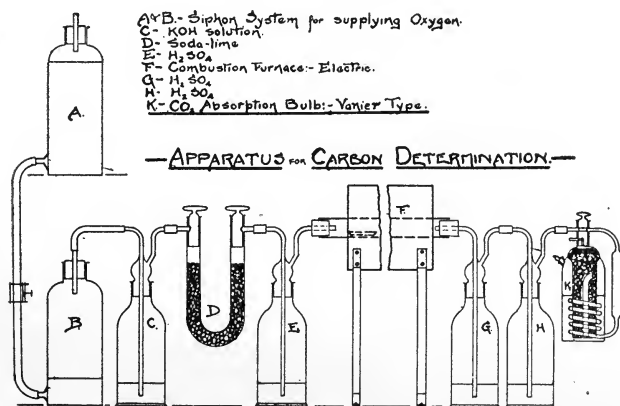
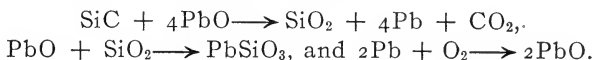


FIG. 4

PROCEDURE—0.20 to 0.25 g. of the sample was weighed out in a watch glass. This was thoroughly mixed with 5 g. of litharge whose carbon dioxide content had been determined in a blank test carried out under the same conditions as the analysis. The mixture of litharge and sample was placed in a C. M. Johnson combustion boat made of vitrified clay, 120 mm. long and 15 mm. wide.¹ Experiments were also made with combustion boats of porcelain, alundum, nickel, iron, and copper, but all except the vitrified clay were attacked and fused by the molten litharge.

The boat with its charge was placed in the silica tube of an electric combustion furnace, and the air in the furnace displaced by oxygen that had been thoroughly dried in a drying train. The current was

¹ Eimer and Amend, New York

turned on and the temperature raised slowly enough to avoid too rapid decomposition, which, if it occurred, would blow the charge out of the combustion boat. A gentle stream of oxygen was passed through the apparatus throughout the determination, and the course of the reaction was followed by observing the rate at which the bubbles of gas passed through the absorption apparatus. As soon as the evolution of carbon dioxide tended to become rapid, the electric current and the flow of oxygen were turned off until the reaction subsided, and no more bubbles of gas passed through the absorption apparatus. Then the current was turned on again, and a slow stream of oxygen passed through. The temperature inside the furnace was kept at about 600° C. for about 45 minutes, and then gradually raised to about 1000°. This was done to eliminate any possibility of carbon dioxide remaining in the molten mass. The carbon monoxide that may be given off at this temperature is converted into carbon dioxide by passing over a heated coil of cupric oxide. The carbon dioxide evolved was absorbed in a Vanier KOH absorption apparatus.

The arrangement of the apparatus as set up is indicated in Fig. 4. Analyses made by this method are given in Table VI.

TABLE VI—CARBON IN CARBORUNDUM AND SILUNDUM
Correction for CO₂ in PbO = 0.0175 Gram

SAMPLE	Weight Sample Grams	Grams CO ₂ evolved	Weight CO ₂ corrected	Per cent C in sample	Theoretical Per cent Carbon
Large carborundum crystals..	{ 0.2004	0.2330	0.2155	29.33	in SiC
	{ 0.2142	0.2488	0.2313	29.45	29.78
Steel-gray silundum.....	{ 0.2509	0.2925	0.2750	29.89	in
	{ 0.2214	0.2609	0.2434	29.95	SiC
	{ 0.2187	0.2586	0.2393	29.84	29.78
Slate-green silundum.....	{ 0.2082	0.2308	0.2133	27.94	in
	{ 0.2413	0.2633	0.2458	27.76	Si ₂ C ₃ O
	{ 0.2265	0.2488	0.2313	27.85	27.09

From the examination of the data in Tables V and VI as summarized in Table VII, it is evident that the percentage of carbon and the percentage of silicon in the steel-gray variety of silundum add up nearly to 100 per cent, indicating that the accepted formula SiC is correct for this modification or variety. On the other hand the silicon and carbon in the slate-green variety of silundum add up to only 91.07 per cent. This variety evidently does not correspond to the formula SiC.

It may be assumed from the careful method of preparation, in which only pure silica, sugar-carbon, and graphite were used, that the compound can con-

tain only silicon, carbon, and oxygen. Since a temperature of approximately 1600° C. must be attained for the reaction to begin, practically all the air is expelled from the covered crucible; and further, since carbon monoxide gas is formed by the reaction and sweeps out the last traces of air, the reaction product can consist only of carbon, silicon, and oxygen, and their compounds. The remaining 8.93 per cent may legiti-

TABLE VII—SUMMARY OF ANALYSES

	Carbo- rundum	Steel-gray silundum	Slate-green silundum
PER CENT FOUND { Si.....		69.53	63.22
{ C.....	29.39	29.89	27.85
TOTAL.....		99.42	91.07
		Silicon carbide	Si ₄ C ₄ O
PER CENT THEORETICAL { Si.....		70.22	63.88
{ C.....	29.78	29.78	27.09
TOTAL.....		100.00	90.97

mately be assumed to be oxygen. The percentage of oxygen corresponding to the formula Si₄C₄O is 9.03 per cent; oxygen by difference is 8.93 per cent, which is good agreement.

Attempts were made to determine the oxygen content of the slate-green variety directly. The sample was placed with a pure metal, such as lead, steel, or copper in a vitrified clay boat in a combustion tube of a platinum-wound electric furnace, in which a temperature of 1300° C. can be easily attained. The air in the apparatus was displaced by extremely carefully purified nitrogen, prepared from ammonium nitrite. The idea in view was that the molten metal would dissolve the substance and carbon monoxide or carbon dioxide might be liberated. Arrangement was made for the monoxide to be oxidized to dioxide by passing through a hot tube containing cupric oxide. Owing to the fact that the sample in each case floated on the surface of the molten metal, no reaction occurred, as evidenced by the fact that the KOH absorption apparatus did not gain in weight.

As regards the relationship of silundum to carborundum, results obtained in this paper indicate that the steel-gray variety is a form of carborundum. The following facts may be mentioned:

- 1—Silundum has the same chemical composition as carborundum.
- 2—Their chemical properties are similar.
- 3—The temperatures of formation and decomposition are practically the same.

4—Some of the physical properties measured vary from those given in the literature.¹ This difference most likely is due to the fact that the other workers used different methods for their measurements.

SUMMARY

I—Two distinct varieties of silundum were prepared.

1—The slate-green variety: formula $\text{Si}_4\text{C}_4\text{O}$.

2—The steel-gray variety: formula SiC .

II—Experiments were made to determine the effect of varying the temperature, duration of heating, and composition of charge.

III—The temperatures of formation and decomposition of the two varieties of silundum were determined.

IV—The physical and chemical properties of both forms of silundum were investigated.

V—Results obtained in this investigation tend to show that the steel-gray variety of silundum is a variety of carborundum.

VI—A quantitative method for carbon determination in carborundum-like substances has been devised.

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¹ Pamphlet, "Chemical and Physical Properties of Carborundum," published by The Carborundum Co., Niagara Falls, N. Y., 1913.

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Alexander Lowy was born on March 31, 1889. He received his early education in the New York City public schools. He attended the College of the City of New York from 1905 to 1910. He received the degree of B.S. from Columbia University in 1911. During the year 1911-1912 he pursued graduate work in Chemistry there, and received the degree of M.A. in 1912; the thesis for the M.A. degree was in organic chemistry. In the same year he was awarded a University Scholarship in organic chemistry. In 1912 he was appointed laboratory assistant in Electrochemistry. During the summer of 1913 and 1914 he was chemist for the City of New York. From 1911 to the present time he has studied under the Faculty of Pure Science of Columbia University for the degree of Doctor of Philosophy.



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