

CLASSICS OF SCIENCE: Moissan's Artificial Diamonds

Chemistry

In view of the recent controversy as to whether the crystals Moissan made in his electric furnace were really diamonds, it is interesting to read the original account of Moissan's experiments. If you have the equipment, perhaps you can make some of these minute hard crystals and try your hand at analyzing them. Science Service would appreciate samples of any crystals made by Moissan's method.

The Diamond

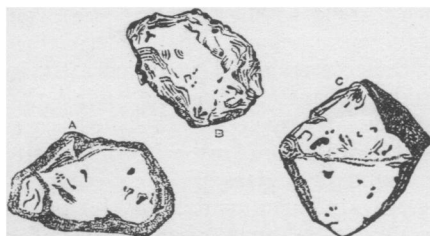
The diamond can be defined as follows: A simple body, having the greatest hardness, a specific gravity of 3.5, burning in oxygen above 700° and of which 1 gram by its combustion in oxygen gives 3.666 grams of carbon dioxide.

The three important factors are: The hardness, density, and combustion in oxygen. Heretofore the ordinary clear diamond scratched all other bodies and was scratched by none. We have demonstrated that this great hardness, which was believed to be a peculiar characteristic of the diamond, is also found in some of the new compounds that we have prepared in our electric furnace. The carbon boride slowly cuts the diamond and the titanium silico-carbide has a hardness which is almost equal to that of the diamond. On the contrary, certain varieties of *bort* of indistinct crystallization well known to jewelers, and the black diamond, possess greater hardness than the new compounds.

The electric furnace has increased the number of bodies which are hard enough to scratch the ruby. Among these may be mentioned silicon carbide, and many carbides, borides, nitrides, silicides, and silico-carbides of the metals. . . . It is necessary, then, in order to be considered diamond, that it must possess the three properties: Hardness, density, and the property of burning in oxygen, forming 3.666 grams carbon dioxide for one gram of substance burned. Each experiment, which rests on but one of these three properties, is insufficient and can lead to a false conclusion.

Combustion in Oxygen

In order to determine the combustion point, we used the electric pyrometer of Le Chatelier, which was placed in a porcelain tube that was glazed inside and outside. The alloy was placed on a small platinum support which contained the diamond to be burned. This apparatus, closed at each end by glass stoppers, cemented to the porcelain tube, permitted the combustion of the diamond in oxygen to be observed.*



ARTIFICIAL DIAMONDS prepared by Moissan. The originals of these magnified drawings were about 1/80th the size of the pictures

Two small drops of baryta water were placed in the apparatus, the one after the oxygen in order to insure its purity, the other after the porcelain tube, to determine when the combustion began. When the temperature was raised the combustion of the diamond, recognized by the action of the carbonic acid on the baryta water, proceeded slowly at first and without apparent production of light, but when the temperature was raised 40° to 50° the combustion was accompanied by light and the diamond was surrounded by a distinct flame.

Another curious fact was observed in these experiments. During the combustion of the diamond there was always observed to appear on its surface small, opaque particles, which indicate the transformation of the transparent into black carbon, while at the same time the combustion continues. . . .

How Are Diamonds Formed?

The geological studies made on the different rocks in which crystalline carbon is found establish indisputably that the diamond is not a vein mineral. . . .

It sometimes happens that the diamonds taken from the blue ground of the Cape are frequently cleaved or cracked open. Cannot this phenomenon be considered as indicating an unstable physical state due to a strong pressure which has acted at the time of formation of the diamond? None of the diamonds in all that I found show clearly a point attached to any rock whatever. It appears as though the diamond had formed in a liquid or pasty mass; consequently it is necessary to know the solvent which has been used.

According to the known properties of carbon and according to the experiments described in this work, it is mainly the metals which dissolve car-

bon, and best of all, iron. When it is remembered that the blue ground of the Cape contains, as I have shown, perfectly crystallized graphite, and that well-crystallized graphite is formed most readily in fused metals and not by volatilization, there is introduced the crystallization of carbon in fused iron under pressure.

I would add that the study of the ash of the diamond, in which iron is always found, leads to the same conclusion. . . .

Such are the ideas, true or false, which brought about the change in the direction of my investigations on the diamond and caused the intervention of pressure. I do not know if this theory will stand the tests of my successors, but it is to it that I owe the experiments which I will describe and that have brought about the preparation of the artificial diamond in microscopic crystals.

Detail of the Experiments

In order to make the experiments, I utilized the pressure produced by the increase of volume which a fused mass undergoes at the moment of passing from a liquid to a solid state. It is known that solid cast iron has a less density than liquid. It is a fact known in industry that pig iron floats on the surface of a bath of the fused metal.

Cast iron, like water, increases in volume at the moment of solidification. We begin these studies by heating in an oxyhydrogen blowpipe, a small quantity of iron in a carbon crucible, then immersing the whole in cold water.

Since the first experiment gave only doubtful results, we thought it was necessary to saturate the iron with carbon at a higher temperature. To obtain this result we used the electric furnace. At the high temperature furnished by this apparatus iron dissolves a large quantity of carbon, which is subsequently deposited as graphite when the iron again solidifies. This experiment was carried out in the following manner: 200 grams of soft Swedish iron cut into cylinders, 1 cm. to 2 cm. in length and about 1 cm. in diameter, were placed in a carbon crucible and completely covered with sugar carbon. Since, at the beginning of this work, we gave the arrangement of the electric furnace, it is not at present repeated. It was (*Turn to next page*)

Artificial Diamonds—Continued

heated from three to six minutes with a current of 35 amperes at 60 volts. The cover of the furnace was raised by the hand wrapped with a cloth, the edge of the crucible was grasped with a pair of iron tongs, and was plunged into a vessel filled with cold water. The crucible and contents remained at red heat for several minutes, with evolution of bubbles of gas which burst at the surface without taking fire. The temperature fell rapidly, the light faded and the experiment was ended (Fig. 24).

It was not without great care that we made this experiment the first time, for I wondered if there would not be an explosion when a crucible of molten iron, having a temperature of 3000°, was introduced into water. The experiment is actually without danger due to the great heat. We were able to prepare 250 to 300 ingots of iron by sudden cooling and we never had an accident. With other metals, bismuth in particular, this was not always the case.

The metallic ingot was treated with boiling hydrochloric acid until no iron remained. There then remained three kinds of carbon: A small quantity of graphite when the cooling was rapid; a brown colored carbon in very thin, distorted layers apparently having been submitted to strong pressure (we found the same variety in the specimens of iron from Canon Diablo); finally, a very small quantity of a somewhat denser carbon was formed, which we endeavored to separate.

It was repeatedly treated with aqua regia, then alternately with boiling sulphuric and hydrofluoric acids. The residue was introduced into sulphuric acid and heated to 200°, while small quantities of powdered potassium nitrate were added. All of the amorphous carbon was destroyed. The heavier portion, examined with the microscope, contained only very little graphite and the different varieties of carbon. It was treated six or eight times with potassium chlorate and fuming nitric acid, which we prepared as free from water as possible. After a final treatment with boiling hydrofluoric acid, then after decantation with boiling sulphuric acid, to destroy the fluorides formed, it was washed, the residue dried and the heavier particles separated by means of bromoform.

After the first separation with bromoform, the small residue that

sank to the bottom of the liquid was washed with ether and introduced into a small tube containing methylene iodide. Some small, transparent particles sank to the bottom, and black fragments swam on the surface. Both were collected and separately introduced into a conical wine-glass with a large excess of distilled water.

It was taken up with a pipette, brought on a glass slide, covered with a slip and examined with the microscope. The opaque particles had a rough appearance, a gray-black color, similar to the specimens of black diamond. Their density varied between 3 and 3.5, since some sank in methylene iodide and others in bromoform. Some had a less roughened surface and a deeper black; one showed curved edges. Others had well-terminated angles and which at first sight appeared to be cubical. . . .

In general, when the iron used in these experiments was free from silicon and when the crucible did not contain aluminum, the black or transparent particles left no ash when burned in oxygen. . . .

Experiments in Iron Filings

It appeared to us that the rapidity of the cooling had an important influence on the formation of crystalline carbon. On cooling the crucible in water, the heating completely prevented contact between the red-hot iron and the liquid. At the beginning the cooling was mainly by radiation. In order to more quickly lower the temperature we attempted to cool the liquid fusion by conduction. To this end, 200 grams of iron, saturated with carbon in the electric furnace, were poured in a cavity made in the center of a mass of iron filings and then completely covered with the filings. The fusion was surrounded by fused iron and the whole rapidly cooled, due to the conductivity of the filings. After action of the acids, the treatment with potassium chlorate and nitric acid, and the action of hydrofluoric acid, then with boiling sulphuric acid, there remained small diamonds having a rounded form and rarely showing a crystalline appearance and almost always enclosing small black points which are called spotted diamonds in jewelry.

These spotted diamonds had a density of 3.5, scratched the ruby and burned readily in oxygen, giving carbon dioxide. In this experiment the pressure appears to have been less and the conversion of carbon into diamond

less complete; the yield, moreover, is always very small. The experiment of cooling in iron filings was repeated a large number of times (about forty times). When the fusion had been regularly formed and when it contained no cavities, the result was always the same. The form of the spots was variable, sometimes forming small, black spots distributed by chance, sometimes forming local regions.

We regard this formation of diamonds with spots as very important, since it gives results similar to those found in nature. Moreover, from their peculiar appearance, it was possible to recognize at once that the fragments were diamonds. In fact, it sometimes occurred that small, transparent grains were obtained whose density was greater than methylene iodide and which resisted all of the treatments with the acids and potassium chlorate, and which were not formed of carbon. These particles never showed definite angles, striations, or triangular impressions; they were rounded and did not burn in oxygen. After combustion they were found in the platinum cups, their form was not changed, frequently their surface was only slightly corroded. This substance was formed especially with irons rich in silicon, or when the electrode contained a considerable quantity of silica or alumina.

*The oxygen was prepared in the laboratory from a mixture of potassium chlorate and manganese dioxide, the latter having been first strongly heated. Before each combustion, this oxygen was tested with potassium pyrogallate. It should not contain more than 3 per cent of other gases.

Henri Moissan was born September 28, 1852, in Paris, and died in the same city February 20, 1907. Educated at the Museum of Natural History, he began teaching toxicology at the age of 34. The same year he isolated fluorine for the first time, by means of electrolysis. Turning to inorganic chemistry, he invented the electric furnace and prepared in it many new compounds. Carbides, silicides and borides were made, and the production of artificial diamonds was attempted. The minute crystals which he made passed his three tests for the diamond: hardness, specific gravity and combustion in oxygen with a definite yield of carbon dioxide. He also made other crystals of an obscure silicide with some of the properties of the diamond and an even greater hardness. The question of whether or not he really did produce diamonds has recently been reopened in England by the discovery that his method of quickly chilling the outside of a mass of cast iron does not result in great pressure in the interior as he had supposed.