ON THE NATURE OF THE OPAL-LIKE OUTER LAYER OF COATED DIAMONDS

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Abstract

A description is given of so-called coated diamonds which consist of a clear core surrounded by an opal-like layer or coating. From a careful microscopical study of this coating, which is pure diamond, wherein minute foreign particles are embedded, a suggestion is made as to the growth pattern of the diamond. Growth is found to occur not only in waves, which include angles of 60°, but growth angles of about 80° are also observed. Attention is drawn to curious string formations of the embedded particles in the coating.

Research carried out in this laboratory has included the examination of various types of so-called coated diamonds from various sources. The literature on this subject is rather sparse and we are attempting, in the first instance, to give a clear description of the kind of stones covered by this investigation.

Almost all the coated stones, which have been examined, are of the octahedral habit and even if they are not perfect octahedrons, all the eight octahedral facets are usually present. Some stones, however, are of an irregular shape and some of them may be twins, though the percentage of this type is very low.

When looking at these stones, which may have weights of about 0.1 to 1.5 grams, they do not appear to be clear, their color being grey and dull. On opening them one can verify, however, that they contain a core or interior part which is clear diamond, though this clear part sometimes contains one or more black spots, cracks, flaws and so on.

The core is surrounded by the so-called coating. Due to its light scattering properties, this coating gives the stone its dull opal-like or cloudy appearance, thus making it quite impossible to look into the stone. As a matter of fact, the coating consists of diamond in which foreign material in the form of very tiny particles is embedded. Though we are not yet certain about the nature of this foreign matter, it is probable it is pure carbon, either in the amorphous state, or in the form of graphite. These tiny particles with a refractive index different from the index of pure diamond, act as light scattering centres. Under the binocular microscope they appear as a milky cloud in reflected light, whereas one can distinguish them as fine brown, or black-brown specks in transmitted light.

This coating shows several interesting features, which throw moreover some light on the growth of the diamond.

Usually the boundary between the coating and the clear part of the stone is very sharp. When this is the case, one can be sure that the boundary plane is an octahedral (111) plane. The stone has grown from its center and the growth has been in layers parallel to the most densely packed "net" planes, the (111) planes. At a definite stage of the growth, precipitation of the foreign material commenced over the whole surface of an octahedral plane whilst, at the same time, the growth of the diamond crystal continued. This stage marked the start of coating formation.

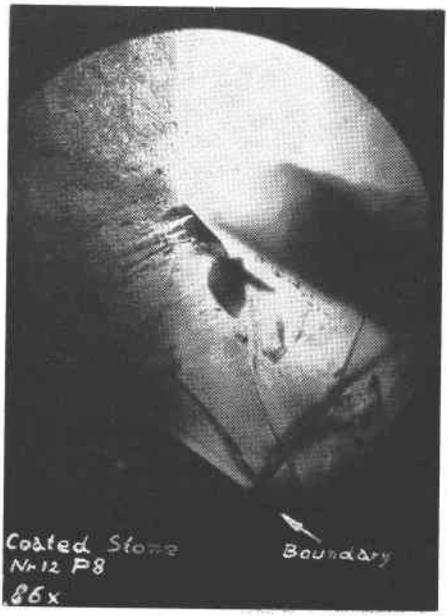

FIG. 1. Boundary between the coating and the clear part of a coated stone. Original magnification on the photograph reduced ½ on reproduction.

The sharpness of the coating boundary is represented in Fig. 1 which is a photograph of a stone taken normally at a "window". What is meant by a "window" is illustrated in Figs. 2*a* and 2*b*. It is a facet cut on a stone and is usually orientated so that it is parallel to one side of the girdle whilst being normal to the plane of this girdle.* As is evident from Fig. 2*a* the window intersects normally 4 of the 8 octahedral faces and it intersects, therefore, also the four coating layers. In Fig. 1 such an intersection is shown. The border line is in most cases as sharp as a knife edge, pointing to the fact that the one layer formed is still pure diamond

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* The so-called girdle of an octahedral stone is the plane of symmetry which divides the octahedron in two equal four-sided regular pyramids. It has, therefore, the form of a square and each octahedron has three girdles, the planes of which are mutually perpendicular to each other.

and that the next contains the foreign matter. The transition from the one layer to the other is less than about 0.5 micron.

Figure 2*b* gives a pair of stereoscopic pictures of an opened stone. A Both the window and the cloudy coating are clearly visible and one can look through the window into the interior of the stone.

That the coating mainly consists of pure diamond and forms part of the one large single crystal occupying the whole volume of the stone is evident from *x*-ray photographs. We have not been able to find any difference on Laue photographs between the clear part of the stone and its coating. Both give rise to a Laue-photograph with well defined spots.

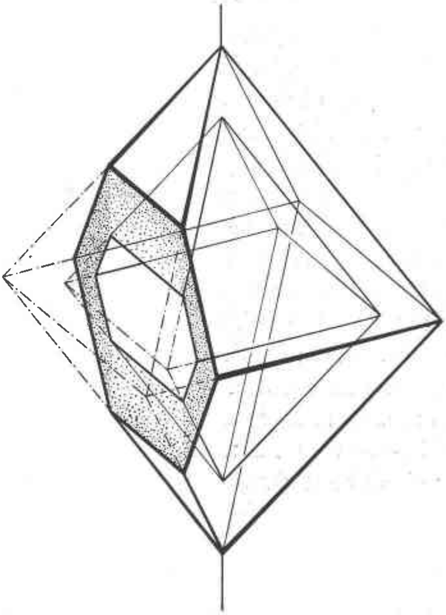

FIG. 2*a*. Drawing of a window on a coated octahedral stone. The coating is represented by dots.

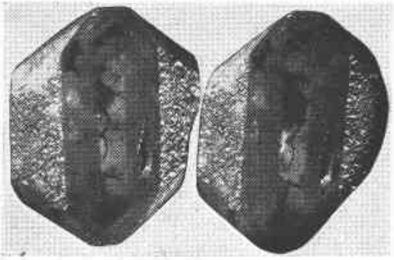

FIG. 2*b*. Stereoscopic pictures of a coated stone. The sharp boundary at the upper and lower sides can clearly be seen.

This points to the fact that the concentration of the built-in particles must be low. Otherwise, there should have been an indication of them either in the form of a pattern belonging to amorphous carbon or graphite, or to some other substance. However, when the coating is powdered and a Debye photograph taken, there is a slight indication of foreign material, for besides the ordinary diamond lines, some very faint lines with a low Bragg angle appear. We have not yet succeeded in identifying these lines.

Before going into the growth of the diamond in somewhat greater detail, we might remark about the thickness of the coating. This may vary between about 0.005 and 0.06 inch (0.1 and 1.50 mm. respectively). There seems to be no definite relation between the weight or volume of a stone and the thickness of its coating. Most frequently the thickness is about 0.02 inch (0.5 mm.). More than once we made the observation that not only the inner boundary of the coating is clear and sharp, but the outer one also. When this is the case, the outermost layer of the stone is again pure diamond. One way to verify this is to cut away the coating of one octahedral facet—(which, by the way, is a very tedious task, the octahedral plane being the hardest with respect to abrasion),—so that one can look through the whole clear core and observe under the binocular microscope the opposite facet. After lowering the tube of the microscope, one first distinguishes the window plane, then one may focus on the inner boundary of the coating and the core, distinguishing very clearly the black particles or specks and finally one focusses on the outside of the stone, that is the opposite octahedral facet mentioned above. The growth cavities in the form of triangles which are a very common feature of nearly all these coated stones, can then be seen quite clearly, but the coating particles are no longer visible.

There are several reasons for supposing that this foreign matter built into the crystalline diamond structure is the origin of stresses and strains set up in the crystal. One can frequently observe a crack running along the boundary between the coating and the clear part of the stone. Cracks are also found in other directions, though mostly coincident with (111) planes. It is well-known that when foreign atoms are built into a crystal, they can easily give rise to stresses, especially when their crystal structure is different, or if their atomic radius has another value. This is especially valid for metals where one of the methods to harden them is alloying with different elements. The foreign atoms deform the crystal lattice and increase the lattice energy.

For crystalline structures, such as ionic crystals and homopolar bond crystals, of which diamond is an example, one may expect the crystal to become brittle and more unstable if foreign atoms are present. In this connection, it may be mentioned that this brittleness is experienced on cleaving the coatings. It is only rarely that a flat surface is the result, on the contrary, it is nearly always of an irregular appearance.

It is frequently found that the black particles of the coating are arranged on strings. Figure 3 is a reproduction of such a string formation. In this reproduction, one looks normally on to the window and this is another illustration of the sharpness of the coating boundary.

These strings lie in (111) or octahedral planes, their direction is [110] which means that they run parallel to any of the sides of the equilateral triangle by which an octahedral face is bounded. This all points to a definite growth pattern and, if it may be assumed that the string formation is an indication of how growth occurred, the following process can be suggested. In Fig. 4 *ABC* is an octahedral plane, *pqrs* represent growth waves, and *v* and *w* give the directions of growth. These directions all belong to the form {110}. On this theory, a wave front such as *s* is parallel to a boundary line of coating, as can be seen in Fig. 3 whilst a direction of growth such as *v*. in Fig. 4 is parallel to the direction of the strings in Fig. 3. It is realized that this suggested theory of crystal growth of the diamond is only a theory and not a proven fact. It is, however, felt that the growth followed a definite pattern, as is made evident by this string formation, and it is a known fact that nearly all face-centered cubic crystals grow in layers parallel to octahedral planes, these being the planes of highest atomic density.

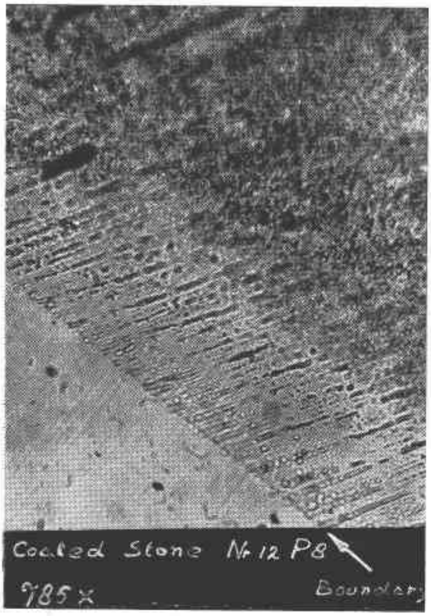

FIG. 3. String formation in a layer of coating. The boundary is indicated by an arrow. Original magnification on the photograph reduced ½ on reproduction.

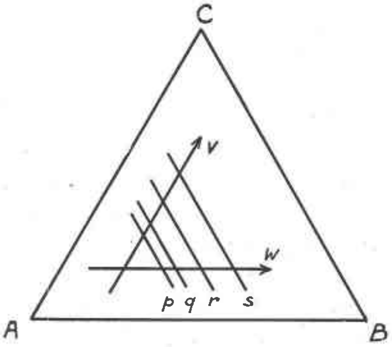

FIG. 4. Illustration of the growth of the diamond. *ABC* is an octahedral plane, *pqrs* are growth waves in the directions *v* and *w*.

After the crystal has been built up in this way to a certain size so that flat surfaces like *ABC* of Fig. 4 have been formed, for some reason unknown up to now, layers were deposited containing the black particles, and it is from the arrangement of these particles in strings that this picture of the growth of the whole monocrystal is obtained. This string formation went on for some time. Then it might happen again for an unknown reason that the crystalline formation went on quite regularly, i.e. without containing foreign particles. This affords an explanation of the formation of so-called prelayers of coating. Finally, the coating proper was crystallized. Temperature and pressure conditions must have played a predominant role in this process.

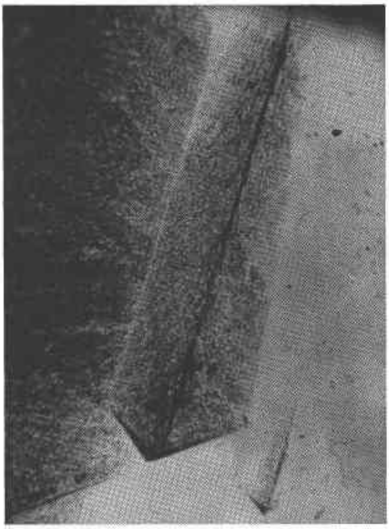

Fig. 5. Coating formation in the form of "fish bones." Original magnification on photograph reduced $\frac{1}{2}$ on reproduction.

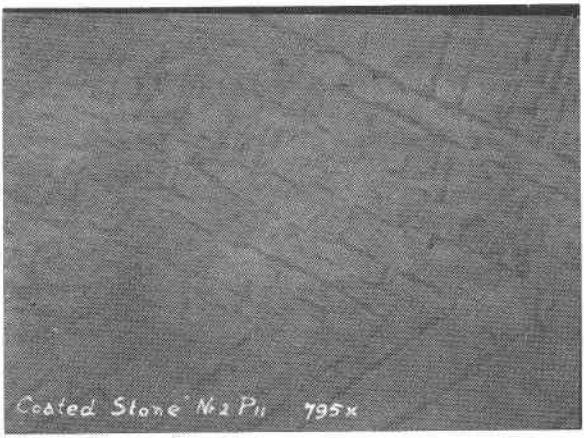

Fig. 6. Example of a regular string formation. The strings mostly include an angle of 60°. This picture shows, however, also strings which include an angle of about 80°. Original magnification on photograph reduced $\frac{1}{2}$ on reproduction.

Another example of coating formation is given in Fig. 5. Here two "fish-bone" formations can be seen. "Growth of the coating has occurred in two plane waves in each "fish-bone." The front lines of these waves can be seen to include an angle which is actually 90 degrees (angle between two different [110] directions) but is seen here as projected on a (110) plane (plane of a window), the projected angle being about 110 degrees, which is the angle between the normals to two adjacent octahedral planes. The two halves of the "fish-bone" lie in two different planes, which are not coplanar and which are also adjacent (111) planes. From Fig. 5 it can be seen that only the sides of the "fish-bone" are in focus, whereas the center line is not. This center line along the whole length of the "fish-bone," which is actually the line of intersection of the two waves, may be explained as the line at which the two waves were halted by each other. The center line indicates the direction of growth.

An optical analogy is found in the propagation of light in a doubly-refracting medium. Here the extraordinary wave is propagated in a direction which is not normal to the wave front. This curious "fish-bone" formation is very striking and occurs frequently.

In Fig. 6 the coating formation is shown under a higher magnification. Whereas the arrangement of the particles on strings is sometimes very irregular, a formation of frequent occurrence is shown here at a magnification of 795 ×. This photograph is interesting for it shows not only the growth lines including an angle of 60 degrees with each other as may be expected because the plane of these strings is a (111) plane, but it shows, moreover, growth lines including an angle of about 83 degrees with each other. This value is the average of five determinations, the extreme values being 81.0 degrees and 83.7 degrees, respectively.

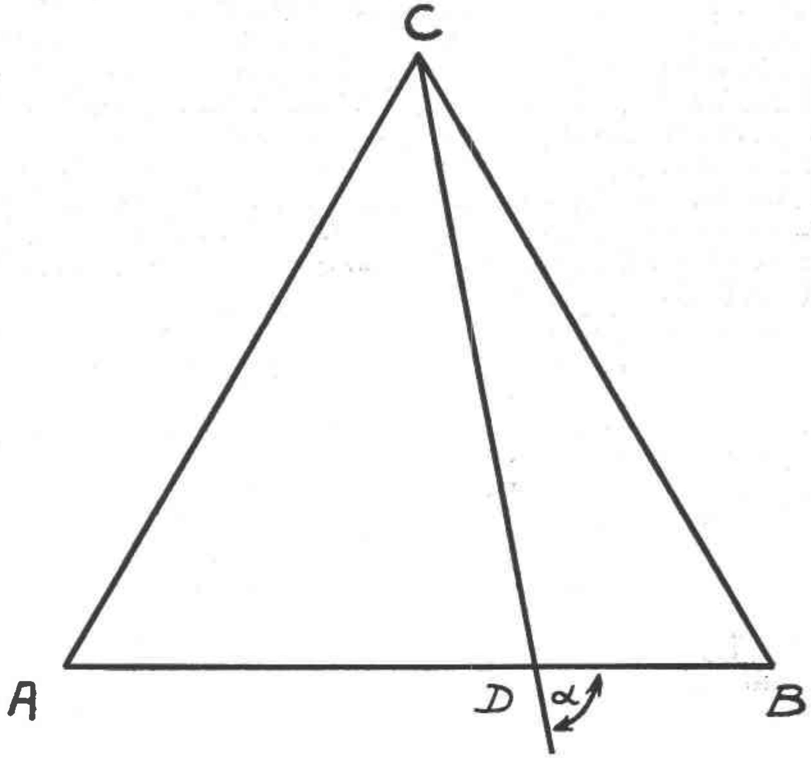

FIG. 7. The direction of the 80° strings in the octahedral plane of a coated stone is obtained by dividing *AB* in about three equal parts.

One may ask what crystallographic direction is coincident with these growth lines. In Fig. 7 *AB*, *BC* and *CA* are assumed to be growth waves. If now we divide, for example, *AB* in three equal parts and draw the line

CD then the angle α is about 80 degrees, to be exact 79° 6′. One can easily verify that the direction represented by this line is a [123] direction. Assuming then that the strings represent lines along which the growth of the crystal took place, so that layers were formed parallel to octahedral planes, we must assume also that growth can take place along lines unknown up to now (the 80 degree angle). Finally we might remark that these observations support those authors who are of the opinion that the triangular pits on the surface of so many diamonds are growth cavities and not etch pits.[1] The sides of these triangles are the fronts of the growth waves which grew no further. The only remarkable point here is that many times a face contains hundreds of these triangles so that there must have been about the same number of centers from which growth started. And why did growing stop? By lack of material? Our opinion is that this cannot have been the only reason.

We have never observed growth triangles on the surface of diamonds other than equilateral ones. What we did find, however, were lines making again an angle of about 80 degrees with each other. This remarkable angle between lines of growth is, therefore, to be found not only in the interior of a crystal, but also at its surface.

In this connection, it is worth while drawing attention to an article on the cleavage properties of diamond by Ramaseshan.[2] This investigator established definitely the following cleavages: (111), (221), (110), (322), (331), (211) and (332).

One might ask if there is any relationship between the above mentioned direction [123] and one or more of these cleavage planes. The only relation found is that the planes $(11\bar{1})$, $(\bar{3}3\bar{1})$ and $(1\bar{2}1)$ of the forms $\{111\}$, $\{331\}$ and $\{211\}$, respectively, belong to the zone [123], though according to Ramaseshan, cleavages (221) and (110) were the most frequent after the (111) cleavage.

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[1] Tolansky, S., and Wilcock, W. D., *Proc. Roy. Soc. London* (A) **191**, 182–194 (1947).

[2] Ramaseshan, S., Sec. Symp. on the Structure and Properties of Diamond, pp. 114–121. Reprinted from: *Proc. Indian Acad. of Sci.*, Bangalore (1946).