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3,288,629

ORIENTED GRAPHITIC STRUCTURE

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Fig. 1

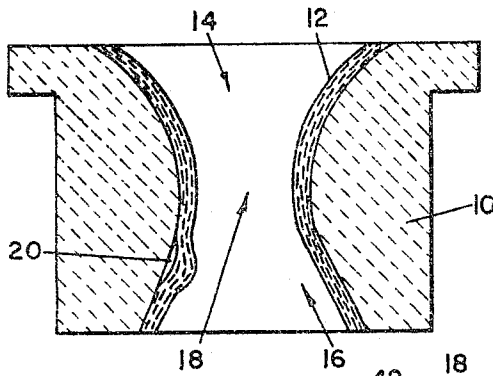


Fig. 2

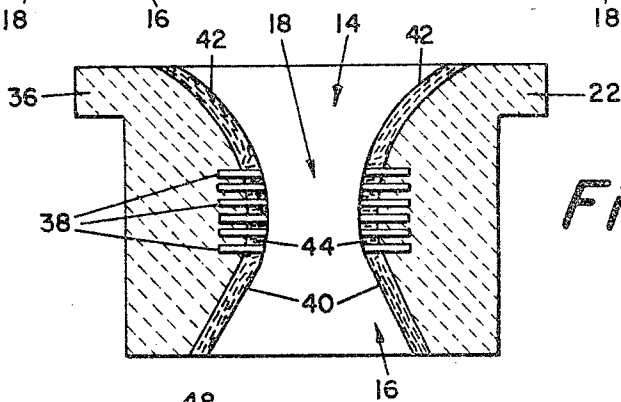
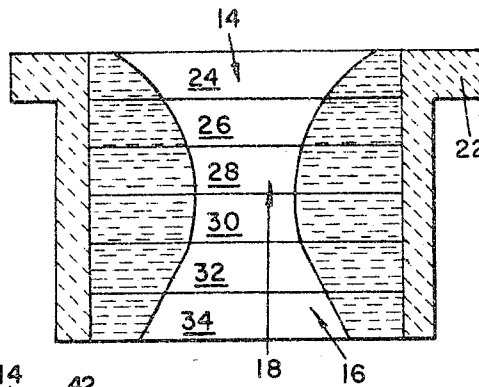


Fig. 3

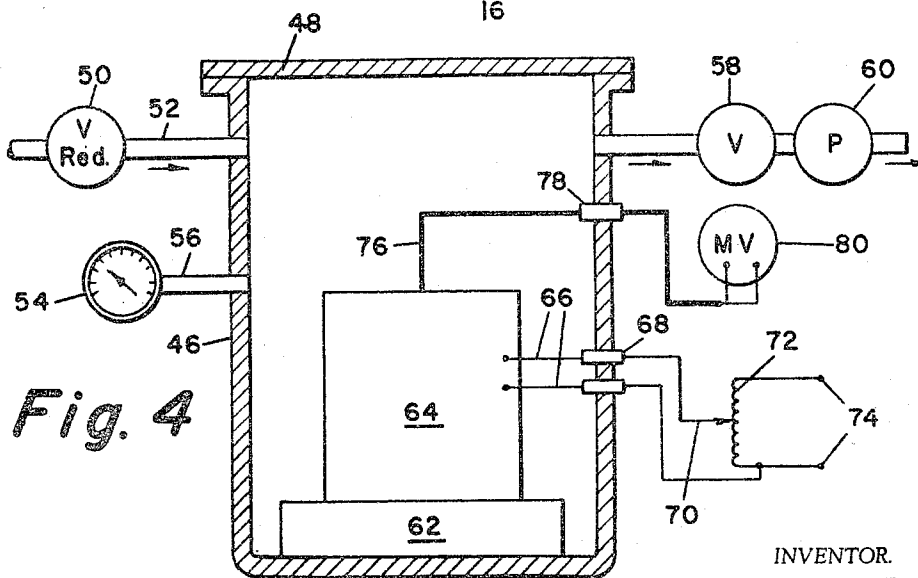


Fig. 4

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3,288,629

ORIENTED GRAPHITIC STRUCTURE

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3 Claims. (Cl. 117-46)

This invention pertains to the production of articles of carbon, more particularly to the production of articles of the graphitic form of carbon known from its usual technique of formation as "pyrolytic graphite."

In many applications where moderate mechanical strength and the ability to withstand high temperatures are requisite, graphite has been employed. Thus, graphite was a common material for members functioning in the blast from early rockets, of a decade ago. It has frequently been included in designs for nozzles for rocket motors. (For example, U.S. Patent 2,958,184). However, microcrystalline graphite is subject to the disadvantage of materials having random orientation of their component crystals in that its strength is somewhat below that ultimately attainable, its physical properties such as thermal expansion and conductivity are incapable of being favorably oriented for a particular use, and it is subject to erosion by flow of high-temperature gases. Pyrolytic graphite, however, tends to be macroscopically anisotropic. When deposited by pyrolysis of a carboniferous gas (for which a procedure will be described in detail hereinafter) it produces crystals whose "a" and "b" axes are parallel to the substrate, the "c" axis being normal to the substrate. Since the crystalline structure and orientation of the deposit are not continuations of a structure of the substrate, but quite independent thereof, this phenomenon is *not* epitaxy. Because it is a self-orientation of the material it may reasonably be called idiotaxy, and the material be described as idiotaxial. Since the phenomenon obviously does not determine the orientation of the axes parallel to the surface of the substrate but only of the axis normal to the substrate, the orientation is defined only as regards the normal axis, the "c" axis in the case of pyrolytic graphite. Several suggestions have been made for the utilization of the anisotropic properties of pyrolytic graphite in structures, such as rocket nozzles. Nozzle throats have been coated, by pyrolysis, with pyrolytic graphite oriented with its "a" and "b" axes parallel to the coated surface, and their "c" axes normal to the surface. It has been found that this tends to produce failure by buckling or blistering at the nozzle throat where the effects of velocity and temperature, combined, are a maximum. Alternatively, it has been proposed to form a nozzle of disks of pyrolytic graphite held in a stack with their "a" and "b" axes parallel to the plane of the disk surface and the "c" axis pointing in the direction of the adjacent disks. This has good mechanical results; but the thermal conductivity along the "a" and "b" axes is much greater than that along the "c" axis. In consequence, heat leakage through the graphite rings to the substrate is excessive, to the damage of the substrate. In view of the cited tendency for pyrolytic graphite to be formed with "a" and "b" axes parallel to the surface upon which deposition occurs, it would appear to be difficult in the light of the known art to find any alternative to the two schemes described.

I have invented a way of lining a nozzle throat with arbitrarily oriented pyrolytic graphite, desposited upon the substrate, without the necessity of immediately forming large disks for subsequent assembly and machining. While this method is particularly well adapted to produce a novel improved rocket nozzle, it is equally applicable to produce other products of this new kind.

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I achieve this by extending from the substrate a plurality of protrusions, which may be rod-like or layered projections, in the area where I desire the "a" and "b" axes of the deposited graphite to be other than parallel to the main surface of the substrate. Deposition occurs with "a" and "b" axes of the graphite parallel to the surface of the rods, or layers, which surfaces are themselves non-parallel to the main surface of the substrate.

For the better understanding of my invention I have provided figures of drawing, in which

FIG. 1 represents in section a rocket nozzle with a lining of pyrolytic graphite, deposited in situ;

FIG. 2 represents in section a rocket nozzle formed of stacked graphite disks;

FIG. 3 represents in section a rocket nozzle embodying my invention; and

FIG. 4 represents apparatus for carrying out a deposition of pyrolytic graphite to form a variously oriented coating, according to my invention.

Referring first to FIG. 1, there is represented a body portion 10 which is of some refractory material, either ceramic, graphite, metal, or a combination of these. Its inner surface is represented covered with particles of pyrolytic graphite 12, which are represented by straight lines, similar to the official symbol for the section of a ceramic, but lying parallel to the face of body 10. When pyrolytic graphite is formed upon a surface by methods to be described in detail hereinafter, it forms platelets of crystal whose "a" and "b" axes lie parallel to the surface of deposition, or substrate. The direction of the lines, therefore, is indicative of the plane of the "a" and "b" axes of the pyrolytic graphite 12. This deposit 12 forms a nozzle passage having an entrance 14, and exit 16, and a throat section 18. This form of rocket nozzle, known previously to my invention, has the advantage that pyrolytic graphite is refractory and is not readily eroded by the flow of hot gases. However, it has been found by experience that there is a tendency for a layer of pyrolytic graphite 12 as here represented to form blisters such as 20, tearing loose from its substrate, with consequent loss of mechanical strength, deformation, and consequent shortening of its useful life.

There is represented in FIG. 2 a structure which has been employed, previously to my present invention, to overcome some of the difficulties described as occurring in the embodiment of FIG. 1. In FIG. 2, there is represented a sleeve-like outer housing 22, which may conveniently be of metal. This sleeve holds a stack of disks 24 through 34 inclusive, which are formed by deposition upon a flat substrate and in consequence have their "a" and "b" axes located parallel to the upper or lower surfaces of the disk. The disks are mounted so that, when stacked, they form a chamber or passageway having entrance 14, exit 16, and throat 18 of the same shape as represented in FIG. 1. This type of structure has been found to possess some satisfactory properties, in that the ends of the "a" and "b" axes of the graphite are the ones primarily exposed to the action of the hot gases. Such exposure has been found to afford the highest possible resistance to erosion and abrasion by the hot gases. However, the heat transfer in the "a" and "b" directions is also a maximum. In consequence, it has been found that the heat losses from such a nozzle not only tend to reduce efficiency but are so great that they tend to be injurious to the outer housing 22.

It would be desirable to enjoy the benefits of poorer heat conductivity in the coating in entrance 14 and exit 16 and tolerate high heat conductivity in return for abrasion resistance only in the region of the throat 18 where such resistance is most urgently required, because of the higher gas velocity. FIG. 3 represents how I have

achieved this. Outer housing 36 is of some convenient refractory material which may be any one of those listed as possible for item 10 of FIG. 1. In the vicinity of the throat 18, there are inserted in housing 36 pins 38, which may be of some suitably refractory metal such as molybdenum. When the deposition of pyrolytic graphite upon the interior of housing 36 is conducted, the coatings 40 and 42 lie with the "a" and "b" axes parallel to the substrate. However, deposition in the vicinity of the throat 18 occurs primarily upon pins 38, producing a deposit 44 whose "a" and "b" axes lie parallel to the pins 38 and therefore normal to the surface of housing 36. Thus, as may be seen by reference to FIG. 3, I produce a nozzle having a lining of pyrolytic graphite, having low heat conductivity in the vicinity of the entrance 14 and the exit 16, but having higher abrasion resistance in the vicinity of the throat 18. It is, of course, apparent that the pins 38 need not be cylindrical, but may equally well be flat strips having their flat surfaces facing the top and bottom of the nozzle. Obviously, some crystal growth will occur from the substrate itself until it is stopped by interference with crystals growing out from the protruding pins. (This phenomenon is classically illustrated in every treatise on elementary metallurgy as an example of how crystals grow from the sides and bottom of an ingot during freezing.) If the crystals growing out from the protruding pins actually sealed off the substrate hermetically from access of the carboniferous gas before the substrate was solidly coated with graphite, there would, obviously be voids in the graphite immediately adjacent to the substrate. Succinctly, for a given spacing between pins: If the pins are too long, the graphite would not contact the refractory base, and if the pins are too short, the orientation would be parallel to the base. However, it is obvious by elementary kinematics (in addition to the teachings of elementary metallurgy) that materials growing at the same speed from two surfaces at an angle to each other will intersect along a plane which bisects the angle between them. Thus for uniform growth rates, the height of undesired growth from the substrate cannot be more than half the spacing between adjacent pins; clearly any pin length greater than this will result in an upper surface which has grown exclusively from the pins. Actually, the sensitivity of deposition rate to temperature makes these considerations somewhat academic. If heat is applied via the substrate, the rate of growth at the substrate may first exceed that at the pins if these rise more slowly in temperature, so that the deposition will first occur on the substrate and the parts of the pins near the substrate. However, as the deposit grows thicker it will conduct heat from the substrate to the pins, and the exposed parts of the pins nearest the deposit will receive deposits. It is thus evident that the process will be largely self-stabilizing, even if pins very long relatively to their spacing are used.

FIG. 4 represents schematically the basic elements of apparatus suited for the deposition of pyrolytic graphite. There is represented a chamber 46 having the cover 48 which may be hermetically sealed to it, forming a closed chamber. From a source of hydrocarbon gases at high pressure, not represented, a tube or pipe leads to reducing valve 50 which is connected by pipe or tube 52 to discharge gas into the interior of container 46. A pressure gauge 54 is connected by a pipe 56 to measure the pressure in the interior of container 46. In order to provide for possible operation at less than atmospheric pressure, there is also connected to container 46 a valve 58 which is connected to an exhaust pump 60, which discharges to the atmosphere. Inside of container 46 and resting upon its bottom, there is a refractory support 62, which may be a piece of ceramic of any convenient kind, since it serves only as a support. A rectangle 64 represents a housed induction coil of an induction furnace inside or

around which a conductive piece such, for example, as that represented in FIG. 1 or FIG. 3 may be placed, providing that the material 10 or 36, respectively, is conductive, such as a metal or graphite. Terminals from the coil in housing 64 are connected by conductors 66 to feed-through terminals 68, which carry the electrical circuit through the wall of container 46, and are further connected by conductors 70 to a tapped coil 72 which is connected to terminals 70, which are connected to a source of high frequency energy not shown. By adjusting the tap on coil 72, the energy input to the body placed inside 64 may be adjusted. Reference 76 represents thermocouple leads which pass through stuffing box 78 through the wall of container 46 to millivoltmeter 80, whose reading will give an indication of the temperature of the junction of the thermocouple. The thermocouple junction may be placed in contact with the work piece to be heated in order that its temperature may be measured. If the work piece is made of a non-conducting material, a suitable conductive coating may be applied to its interior portions, as by spraying a thin layer of molybdenum upon it by known metal-spraying processes; or, alternatively, a simple furnace element may be placed inside shield 64 and the ceramic piece may be heated directly as in a muffle furnace. Direct resistive heating is a third alternative. A published reference upon the deposition of pyrolytic graphite is to be found in "Industrial Carbon and Graphite," published in 1958 by the Society of Chemical Industry, London, S. W. 1. On pages 86 through 100 of this volume, there may be found a paper by Brown and Watt entitled "The Preparation and Properties of High-Temperature Pyrolytic Graphite." In accordance with the teaching of this paper, pyrolytic carbon may be deposited at a rate of about 2.5×10^{-5} centimeters per second of deposit thickness growth upon a substrate maintained at a temperature of 2100° C., by providing an atmosphere of methane at a pressure of 15 centimeters of mercury (page 88, Table I). This procedure results in the production of a graphite deposit of density approximately 2.2 grams per cubic centimeter. This may be performed with the apparatus of FIG. 4 by placing the work piece inside the heating device represented by 64, opening valve 58 and operating pump 60 to substantially exhaust the container 46, topped by closure 48; and adjusting valve 50 to maintain a reading equivalent to 15 centimeters of mercury upon pressure gauge 54. Energy may be applied to terminal 70 and the tap on inductor 72 may be adjusted as required to produce a temperature of approximately 2100° C. as indicated by the reading of millivoltmeter 80. An alternative, sometimes preferable, method of determining the temperature of the work piece is to provide cover or closure 48 with a suitable window to permit observation of the work piece and the measurement of its temperature by means of an optical pyrometer. The techniques of heating materials to high temperatures in gaseous atmospheres at moderate pressures and measuring their temperatures are all very well known, and there are numerous ways available from the art for performing each of the functions described. The particular procedure described here has been included pro forma for completeness of disclosure. In actual practice, convenience and availability of equipment are more likely to determine the choice of the particular procedure used than any particular technical requirements. It may be observed from the reference that pyrolytic graphite may be deposited at a number of different temperatures and at a number of different pressures from a number of different carboniferous gases. The Brown and Watt reference teaches this, and specifically indicates the idiotaxial nature of the deposits at page 99 thereof, under "Conclusions (2)" with the statement, "The deposited carbons have a structure of hexagonal layer planes of carbon atoms as in graphite, the layer planes all lying parallel to each other and the surface of the substrate but being otherwise randomly

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oriented." My invention professes only to make use of the techniques for depositing pyrolytic graphite and to teach a method of producing a desired result in the course of such deposition; it is pointed out that the deposition of pyrolytic graphite *as such* is part of known art, including additions such, e.g., as boron.

Returning once more to a consideration of FIG. 3, it is evident in the light of the description I have just given of the procedure for depositing pyrolytic graphite that as the carbon bearing gas comes in contact with the internal surface of 36 and the surfaces of pins or strips 38, the deposition of pyrolytic graphite will occur upon the exposed surfaces and the thickness of the layer will increase by further deposition upon the graphite already deposited. Thus, the graphite deposited at points 42 and 40, that is, the entrance and exit of the nozzle, will simply grow thicker, but the deposition occurring in the throat region 18, represented by 44, will begin primarily upon the surfaces of pins or strips 38 and will extend until it forms a bridge from one pin to the next and will continue until the interstices are filled, so that the graphite represented by reference number 44 will be compact and dense comparably with the density of the graphite represented by reference numbers 40 and 42, differing therefrom primarily in its crystal orientation. The junctions between the graphite masses 40, 42 and 44 will, of course, also be filled by deposition of graphite through decomposition of the carbon bearing gas. Therefore, there will be found a continuous mass of graphite, having the orientation of its crystals arbitrarily controlled, being different in different places. Since it may not be possible to achieve sufficient uniformity of the deposition process to produce a completely symmetrical nozzle by the procedure I have described, I envisage the possible necessity of finishing the surface of the graphite so deposited by ordinary machining processes. While my invention has been described with respect to embodiment in a rocket nozzle, it is obvious that it may be usefully applied in any application where graphite as such may be used. Such applications, based upon my teaching, lie within ordinary skill in the art.

The appended claims are written in subparagraph form, in compliance with a recommendation of the Commissioner of Patents, to render them easier to read. This particular manner of division into subparagraphs is not necessarily indicative of a particular relative importance or necessary subdivision of the physical embodiment of the invention.

What is claimed is:

1. The method of forming deposits of pyrolytic carbon so attached to a substrate that the normal axes of the deposit are at a predetermined acute angle with the surface of the substrate which comprises:

providing the said substrate with protrusions each of circular symmetry around a central axis, the central axis of each protrusion making with a normal to the surface of the substrate an angle equal to the said predetermined angle,

said protrusions having lengths sufficient to ensure orientation parallel to the surface of the protrusions in the interstices between the protrusions,

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said protrusions also having limited space therebetween to prevent any substantial amount of orientation parallel to the surface of the substrate, causing the deposition of pyrolytic carbon by destructive decomposition of carboniferous gases to occur on the said protrusions until the interstices between the protrusions are filled with pyrolytic carbon.

2. The method claimed in claim 1 in which the therein said central axes of the protrusions are all parallel to each other.

3. The method of forming deposits of pyrolytic carbon so attached to a substrate that the normal axes of the deposit are at a predetermined acute angle with the surface of the substrate which comprises:

providing the said substrate with protrusions having surfaces of single curvature whose generating straight lines intersect the surface of the substrate at an angle which is the complement of said predetermined angle,

said protrusions having lengths sufficient to ensure orientation parallel to the surface of the protrusions in the interstices between the protrusions, said protrusions also having limited space therebetween to prevent any substantial amount of orientation parallel to the surface of the substrate, causing the deposition of pyrolytic carbon by destructive decomposition of carboniferous gases to occur on the said protrusions until the interstices between the protrusions are filled with pyrolytic carbon.

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