

Jan. 30, 1968

HIROSHI ISHIZUKA

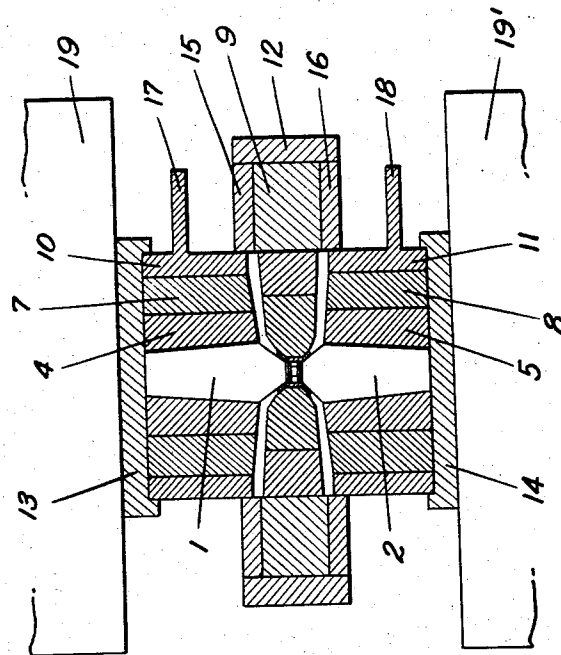
3,365,751

HIGH TEMPERATURE HIGH PRESSURE APPARATUS

Filed Nov. 22, 1966

3 Sheets-Sheet 1

Fig. 1



INVENTOR:
HIROSHI ISHIZUKA

BY *E. M. Squire*

ATTY

Jan. 30, 1968

HIROSHI ISHIZUKA

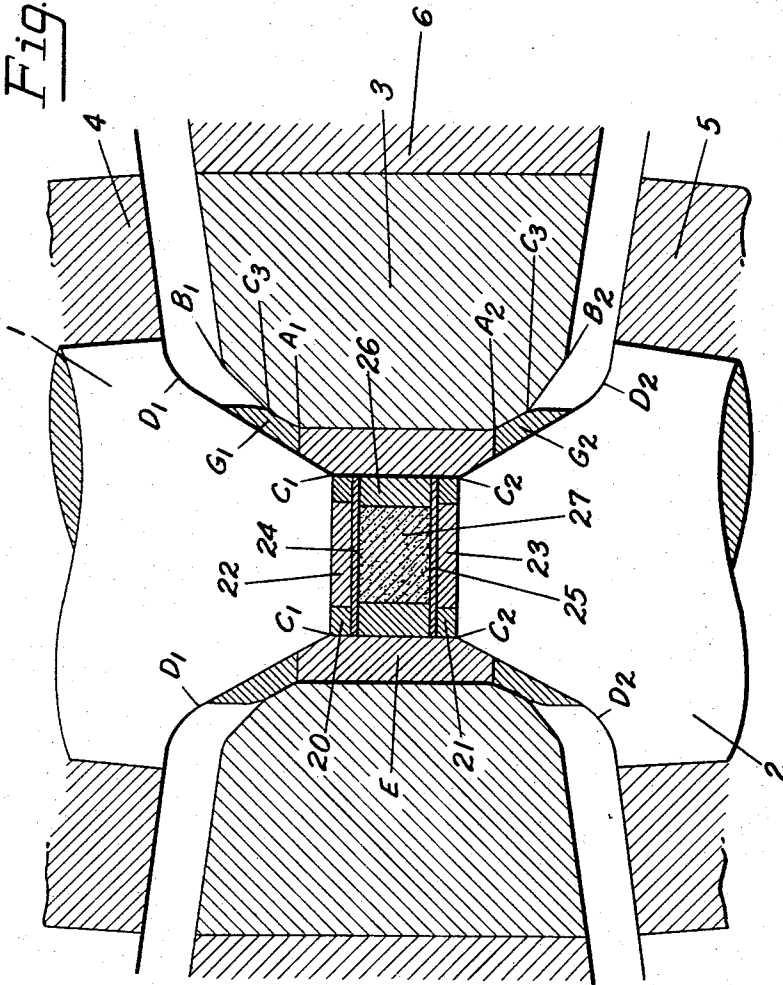
3,365,751

HIGH TEMPERATURE HIGH PRESSURE APPARATUS

Filed Nov. 22, 1966

3 Sheets-Sheet 3

Fig 3



INVENTOR:
HIROSHI ISHIZUKA

BY *E. M. Squire*

Att'y.

1

2

3,365,751

HIGH TEMPERATURE HIGH PRESSURE APPARATUS

Hiroshi Ishizuka, 106 5-chome, Hiratsuka Shinagawa-ku, Tokyo, Japan

Continuation-in-part of application Ser. No. 300,338, Aug. 6, 1963. This application Nov. 22, 1966, Ser. No. 602,446

Claims priority, application Japan, Aug. 10, 1962, 37/34,631

3 Claims. (Cl. 18—16.5)

ABSTRACT OF THE DISCLOSURE

A high temperature high pressure apparatus for use, for example, in the synthesis of diamonds. Two cooperating punch members with frusto-conical end portions and flat circular confronting faces cooperate with a hollow cylindrical insulating member to form a pressurized reaction chamber. The insulating member is uniformly supported throughout its length in a cylindrical portion of the die aperture. The faces of the punch members are of the same diameter as the internal diameter of the insulating member so that the insulating member is not subjected to axial compressive stresses.

This application is a continuation-in-part of my co-pending application Ser. No. 300,338 filed on Aug. 6, 1963, now abandoned.

The present invention relates to a high temperature high pressure apparatus. More particularly the present invention relates to a high temperature high pressure apparatus comprising a pair of tapered pistons and a die.

An object of the present invention is to provide a high temperature high pressure apparatus comprising a die and wherein the die has a construction which will endure through many operations.

An object of the present invention is to provide a high temperature high pressure apparatus having a die of a long life made of inexpensive pressure resisting metal.

Still another object of the present invention is to prolong the life of the die by protecting the hole of the die with a hollow cylindrical insulator.

In order to convert graphite to diamond, there is required an apparatus generating a high temperature of more than about 1200° C. and a high pressure of more than about 50,000 atmospheres. In order to carry out the conversion more efficiently, there is required an apparatus generating a high temperature of more than about 2,000° C. and a high pressure of more than about 100,000 atmospheres. Such apparatus is also useful to carry out a physical conversion or a chemical reaction under a high temperature and pressure of any other substance.

As such high temperature high pressure apparatus are known a high pressure apparatus of Poulter, Bridgman anvil apparatus, Belt apparatus and tetrahedral anvil apparatus. Among them, the Belt apparatus and tetrahedral anvil apparatus are practical.

However, in the latter tetrahedral anvil apparatus, the mechanism is complicated and the reaction chamber is small as compared with the size of the anvil. Therefore, it has defects that it is not economical and is difficult to make larger.

The Belt apparatus is a high temperature high pressure apparatus wherein an annular pressure supporting member having a hole of an outwardly spreading conical inner surface is arranged coaxially between a pair of opposed tapered punches.

In this apparatus, a pair of gaskets is provided between the pair of tapered punches and the annular pressure

supporting member. Said gasket acts to prevent the high pressure in the reaction chamber from leaking out, to insulate electricity and heat between the punch and the annular pressure supporting member and to make the movement of the punch smooth. Thus the gasket is made of such pressure resisting and comparatively easily deformable material as pyrophyllite so as to make the movement of the punch smooth. Therefore, due to this easily deformable property, there is a defect that, if the gasket is thick, the high pressure in the reaction chamber will escape to the part of the gasket and no pressure will concentrate in the center of the reaction chamber.

Further, as regards the shape of this gasket, as the hole in the annular pressure supporting member has an outwardly spreading conical surface and is of a shape expanding inward in the central part, the gasket is the thinnest in the part near the central part in the reaction chamber where the temperature and pressure are the highest. Therefore, in spite of the gasket, the inner surface of the hole in the annular pressure supporting member is liable to be influenced by the high temperature and high pressure. Further, in such part, as the upper and lower gaskets are merely in contact with each other in the end parts, the high temperature and high pressure in the reaction chamber are likely to escape through the clearance between the gaskets and to be transmitted to the above mentioned inner surface of the hole.

On the other hand, it is reasonable for the generation of the high pressure that the inner surface of the hole in the annular pressure supporting member is an outwardly spreading conical surface. But the shape is so complicated as to be difficult to make. It is all the more difficult to make the hole specifically because the annular pressure supporting member is made of a very hard material (very hard alloy) to resist pressures.

Further, in this type of apparatus, in order to generate a high pressure, it is considered to be necessary to make the clearance between the punch and the annular pressure supporting member as small as possible so far as the movement of the punch is allowed. Therefore, the diameter of the end surface (truncated part) of the punch and the diameter of the narrowest part of the hole of the annular pressure supporting part are so set as to be as equal to each other as possible. Therefore, the generated high pressure will be applied directly to the annular pressure supporting member. Thus the annular pressure supporting member will be often broken and its life is short. The annular pressure supporting member is made of a costly very hard alloy and the cost of making is also high as described above. Therefore, if its life is short, the diamond produced with it will be very dear.

Further, as the very hard alloy which is a constituting material of the punch and annular pressure supporting member can not endure such high pressure as several ten thousand atmospheres, it is difficult to enlarge the apparatus in order to generate a higher pressure or to increase the production.

The present invention is a high temperature high pressure apparatus in which these problems have been solved and a die corresponding to the above described annular pressure supporting member is so made as to be durable to many times of uses and to be able to be made of a material comparatively low in the pressure resistance.

That is to say, in the present invention, in order to attain the above mentioned object, there is used a hollow cylindrical insulator for protecting the inside wall of the hole of the die. Further, the hole of the die to be used is cylindrical so that the die may be easily made.

More particularly, according to the present invention, in order to protect the inside wall of the circular hole of the die, there is used a hollow cylindrical insulator made of a rigid and electrically and thermally insulative

refractory metal oxide. It is fitted in the above mentioned cylindrical hole. The thickness of the wall of said hollow cylindrical insulator determines the pressure applied to the inside wall of the hole of the die. On the other hand, the diameter of the truncated part of the tapered piston is made substantially equal to the inside diameter of the above mentioned hollow cylindrical insulator. Therefore, the reaction chamber to be at a high temperature and high pressure is formed of the truncated parts of the above mentioned pistons and the inside wall of the hollow cylindrical insulator.

Therefore, the high temperature high pressure apparatus of the present invention comprising a pair of tapered pistons or punch members each having a truncated part and opposed to each other and a die having a central cylindrical hole and conical holes adjacent to it and each having a tapered surface of an apex angle larger than an apex angle of the above mentioned piston is characterized in that

- (1) a hollow cylindrical insulator is fitted in the above mentioned cylindrical hole of the die,
 - (a) said hollow cylindrical insulator is made of a rigid and electrically and thermally insulative refractory metal oxide,
 - (b) its outside diameter is substantially equal to the inside diameter of the above mentioned cylindrical hole so that it is uniformly laterally supported by the die,
 - (c) the thickness of its wall is large enough to protect the inside wall of the above mentioned cylindrical hole from the high temperature and high pressure of the reaction chamber,
- (2) the diameter of the truncated circular face portion of the tapered piston is made substantially equal to the inside diameter of the above mentioned hollow cylindrical insulator and
- (3) the pressurized reaction chamber is defined by the circular end faces of the truncated parts of the tapered pistons and the inside wall of the above mentioned hollow cylindrical insulator.

A modification of the high temperature high pressure apparatus according to the present invention consists of the apparatus described above, wherein said cylindrical hole and conical holes are separated by intermediate frustoconical holes at angle to the first mentioned holes, the surfaces of the second mentioned intermediate conical holes having an apex angle equal no greater than the apex angle of the tapered part of the pistons and the surfaces of the second mentioned conical holes.

The present invention will be illustrated by the following description, taken in connection with accompanying drawing, in which:

FIGURE 1 is a front elevational view of an oil-operated hydraulic press with a high temperature high pressure apparatus with embodies the present invention;

FIGURE 2 is an enlarged sectional view of one form of the high temperature high pressure apparatus of the present invention; and

FIGURE 3 is an enlarged sectional view of a further form of the high temperature high pressure apparatus of the present invention.

In FIGURE 1, **1** and **2** are tapered pistons made of a tungsten carbide-cobalt alloy, reinforced with spring steel rings, **4**, **7** and **5**, **8**, having a high tensile strength and protected outside with rings **10** and **11** made of a soft steel to prevent danger in the case of damage caused at the time of pressure application, **3** is a die having a cylindrical hole and conical holes, made of tungsten carbide-cobalt alloy, reinforced with spring steel rings **6** and **9** having a high tensile strength and protected outside with a ring **12** made of a soft steel for safety at the time of pressure application. **13** and **14** are electrical insulators made of phenol (-formaldehyde) resin to insulate the pistons **1** and **2** from press plates **19** and **19'**,

respectively. **15** and **16** are guides made of phenol-formaldehyde resin to hold the die in the regular position in pressing the pistons **1** and **2** and to insulate the die from said pistons. **17** and **18** are bars made of copper and connected to an electric source (not shown) so as to be conductors to feed an electric current to heat the reaction chamber.

FIGURE 2 shows a high temperature high pressure apparatus according to first embodiment of the present invention. In FIGURE 2, the reference numerals have same significance as in FIGURE 1. **3** is a die, A_1A_2 is a surface of the cylindrical hole (parallel to the compression direction, A_1B_1 is a (surface of the) conical hole having an angle larger than that of the piston. **E** is a hollow cylindrical insulator made of rigid and electrically and thermally insulative refractory metal oxide. The hollow cylinder $C_1C_1C_2C_2$ is a reaction chamber to be filled with graphite and a metal in the synthesis of diamond. **1** and **2** are pistons having truncated flat end surfaces C_1C_1 and C_2C_2 and frusto-conical tapered surfaces C_1D_1 and C_2D_2 , respectively.

Now, when this apparatus is set in a (oil-operated) hydraulic press and a pressure is applied from the pistons **1** and **2**, the reaction chamber will be compressed by the truncated parts of pistons. In such case, the cylindrical insulator **E** located in the clearance between the pistons and the die will be partly pushed out to serve as a seal. The coefficient of compression of the cylindrical insulator **E** is so small that so much compression of the insulator will not be required in applying the pressure. Therefore, the compression stroke will not be increased. In such case, the pressure in the truncated parts of the pistons will be the highest. The wall A_1A_2 of the cylindrical hole of the die will be subjected to only a pressure inversely proportional to the square of the diameters of C_1C_1 and A_1A_1 .

When the reaction chamber is heated by directly passing an electric current through the pistons **1** and **2**, the heat will reach A_1A_2 through the cylindrical insulator **E** and therefore the temperature rise of the wall will be less than in the conventional apparatus.

FIGURE 3 shows a high temperature high pressure apparatus according to a second embodiment of the present invention in which the pressure resistance and capacity that of the apparatus is larger than that of the apparatus shown in FIGURE 2. In FIGURE 3, the reference numerals have significance as FIGURE 1. **3** is a die, A_1A_2 is a surface of the cylindrical hole parallel to the compressive direction, A_1C_3 is a surface of the second-mentioned conical hole having an apical angle equal to or smaller than the angle of the tapered part of the piston, C_3B_1 is a (tapered) surface of the conical hole having an angle larger than that of the piston, **E** is a hollow cylindrical insulator made of said material and the hollow part $C_1C_1C_2C_2$ is a reaction chamber. **1** and **2** are pistons each having a tapered part. G_1 and G_2 are gaskets located between the pistons and the second-mentioned conical hole.

As described above, as different from the conventional gasket having it as a principal object to seal the pressure, the hollow cylindrical insulator used in the present invention has it as an object to protect the die. Therefore, it is necessary that the above mentioned hollow cylindrical insulator should be made of a rigid substance so as to protect the die from the high pressure and should be made of an electrically and thermally insulative substance so as to protect the die from the high temperature. The term "rigid" used here does not mean "theoretically rigid (not deformable by any pressure)." In order to make the movement of the piston made of the very hard alloy easy, the hardness of the insulator had better be lower than of the very hard alloy. Said term means the hardness of such substance to be actually used as a refractory metal oxide as made as high as possible and is used to distinguish such substance from commercial

hard refractory metal oxide. However, high a substance satisfying such properties as are mentioned above may be in the hardness, it must be electrically insulative. Therefore, metals and alloys can not be used. Such refractory metal oxide as alumina or magnesia is favorable. A hollow cylindrical body is made by such means as molding its powder and sintering it under a high pressure. The hollow cylindrical insulator is made of such material, is to be used as replaced for each operation and is not a component part of the die. In the actual operation, a container containing a specimen is put into the hollow cylindrical insulator and then the insulator is fitted into the cylindrical hole of the die. The insulator is so cheap that, even if it is replaced for each operation, it will be economical as the life of die will elongate.

As the present invention is formed as mentioned above, it has such effects as are described below.

First of all, the pressure applied to the inside wall of the hole of the die can be remarkably reduced by the use of the hollow cylindrical insulator. Speaking comprehensibly though not technically correctly, when the wall of the hollow cylindrical insulator has a certain thickness, the inside diameter of the cylindrical hole of the die will become larger than the diameter of the inside wall (corresponding to the inside wall of the reaction chamber) of the hollow cylindrical insulator by the above mentioned thickness, the inside wall of the above mentioned hole will be that much away from the center of the reaction chamber which is at the maximum temperature and pressure and therefore the pressure applied to the inside wall of the hole will reduce. According to the dynamical calculation, it is approximately presumed that a pressure inversely proportional to the square of the ratio of the inside diameter C_1-C_2 of the above mentioned hollow cylindrical body to the inside diameter A_1-A_2 of the above mentioned hole will be applied to the inside diameter A_1-A_2 of the cylindrical hole of the die.

Therefore, the rate of the reduction is large. Therefore, by selecting the thickness of the wall of the above mentioned hollow cylindrical body and properly setting the ratio of the diameters of both of those mentioned above, the pressure applied to the die can be reduced so that the die may be made of a material low in the pressure resistance. Further, reversely, even if the same material is used for the die, the pressure in the reaction chamber will be able to be elevated within the endurable limit of the material. In such case, when the above mentioned hollow cylindrical body is not made of a rigid material, the inside diameter C_1-C_2 will expand due to the pressure and the above mentioned ratio will become so small that the above described effect will not be obtained.

Secondly, as the above mentioned hollow cylindrical body is made of a thermally insulative substance, the high temperature in the reaction chamber will be hard to conduct to the inside wall of the hole of the die and therefore the strength reduction of the die by heat can be prevented. Therefore, the die will be little broken during the operation. According to the present invention, even when the die was used more than 1500 times, it was not damaged and its life was 30 times as long as of any conventional one.

Thirdly, as the diameter of the truncated part of the piston is made substantially equal to the inside diameter of the above mentioned hollow cylindrical body, the above mentioned truncated part will be all used only to press the reaction chamber and therefore the pressure energy applied to the piston will be effectively used. Specifically, in the present invention, as the above mentioned hollow cylindrical body is made of a rigid substance (such as a refractory metal oxide), when the truncated part is to push the above mentioned hollow cylindrical body as heretofore, a large energy will be required due to its deformation.

Fourthly, the part of contact of the die with the piston is so small that breaks occurring due to the deviation of

the positions of the piston and the die from each other are considerably less than in the conventional apparatus.

Further, as the above mentioned hollow cylindrical body is of an electric and thermal insulator, when the reaction chamber is to be charged with reaction substances of the same diameter, the temperature applied to the inside wall of the hole of the die can be extremely reduced as described above. However, if the temperature applied to the inside wall is made somewhat lower than before, the amount of the charge will be able to be considerably increased and the yield will be able to be increased.

An example of a reaction carried out by using the apparatus of the present invention in a high temperature and high pressure state will now be described.

In this example, in FIGURE 3, each of the pistons 1 and 2 had a truncated surface 15 mm. in diameter, a tapered length of 40 mm. and was made of a 5% WC-Co alloy. The core ring 3 was made of a 7% WC-Co alloy, 40 mm. thick, 80 mm. in diameter and 24 mm. in inner diameter. The thickness at C_3C_3 was 27 mm. The angle of A_1C_3 was 27 degrees. The angle of C_3B_1 was 45 degrees. The insulator E was made of dense MgO of small coefficient of compression and its porosity was less than 3%. Each of the gaskets G_1 and G_2 was made of agalmatolite and was inserted between metal gaskets made of an iron sheet 0.25 mm. thick.

The rings 20 and 21 were made of a carbon steel of 0.45% C. The insulators 22 and 23 were of agalmatolite. The plates 24 and 25 were of nickel. The charge 27 consisted of 10 parts by volume of nickel particles of 20 to 30 mesh/in., 1 part by volume of chromium carbide powder of less than 325 mesh/in. and 20 parts by volume of graphite of 60 to 80 mesh/in. These substances were mixed and the mixture was packed into the insulator 26 which is the container of charge 27. Thereafter the insulator 26 containing charge 27 was compressed to mould its shape to that of the reaction chamber. The compressed insulator 26 was inserted within the insulator of small coefficient of compression E. The assembly constructed by the means illustrated above was put in the core ring.

Such apparatus was arranged as in FIGURE 1 and was put in an oil operated hydraulic press. A pressure was applied to the apparatus through the pistons and plates 19 and 19' of the press so as to produce about 52,000 to 54,000 atmospheres in the reaction chamber. An electric current of 1,200 to 1,500 A. in 1.5 to 1.8 v. was fed to the pistons through the bars 17 and 18. The charge was thus heated for 10 to 15 minutes and was then cooled. When the product was extracted by a conventional chemical treatment, a light green diamond could be obtained in a yield of more than 50%.

When such operation was repeated more than 1,500 times in the present apparatus, no damage appeared at all in the die.

On the contrary, when the above example was repeated except that agalmatolite, whose coefficient of compression was several times that of the rigid substance described above, was used as the material of E, the pressure was applied directly to the inner wall of the die and as a result the die was damaged after being used about 50 times.

What I claim is:

1. A high temperature high pressure apparatus comprising:

(1) a die having a central aperture formed therein, said aperture comprising a central cylindrical portion and two frusto-conical end portions which diverge outwardly from the ends of said cylindrical portion;

(2) a hollow cylindrical insulator member removably fitted coaxially into said cylindrical portion of said aperture, the external diameter of said insulator being substantially equal to the diameter of said cy-

- lindrical portion and its length being substantially coextensive with said cylindrical portion;
- (3) a pair of aligned punch members comprising frusto-conical end portions terminating in flat parallel confronting circular faces, the diameters of said faces being substantially equal to the inside diameter of said insulator member, the apex angles of said frusto-conical portions of said punch members being smaller than the apex angles of said frusto-conical portions of said aperture;
- (4) pressure means for forcing said faces toward each other to close the ends of said insulator member, thereby defining a pressurized reaction chamber in the interior of said insulator member; and
- (5) means for passing an electric current between said faces for producing resistive heating of an electrically conductive charge in said reaction chamber.
2. Apparatus according to claim 1, wherein said central aperture comprises two intermediate frusto-conical portions located intermediate the ends of said cylindrical por-

tion and said first-named frusto-conical portions, the apex angles of said intermediate portions being no greater than the apex angles of said frusto-conical portions of said punch members; said apparatus further comprising gasket means positioned in said intermediate portions of said central aperture.

3. Apparatus according to claim 1, wherein said insulator member is formed of a refractory metallic oxide selected from the group consisting of alumina and magnesia.

References Cited

UNITED STATES PATENTS

2,554,499	5/1951	Poulter.
2,941,241	6/1960	Strong.
2,941,248	6/1960	Hall.
3,067,465	12/1962	Giardini et al.
3,137,896	6/1964	Daniels.

WILLIAM J. STEPHENSON, *Primary Examiner.*