May 3, 1966 J. D. BARNETT ET AL 3,249,753

HIGH PRESSURE-HIGH TEMPERATURE X-RAY DIFFRACTION APPARATUS

Filed Dec. 17, 1963 2 Sheets-Sheet 1

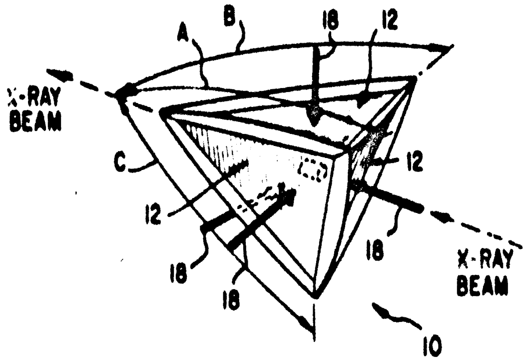

FIG 1

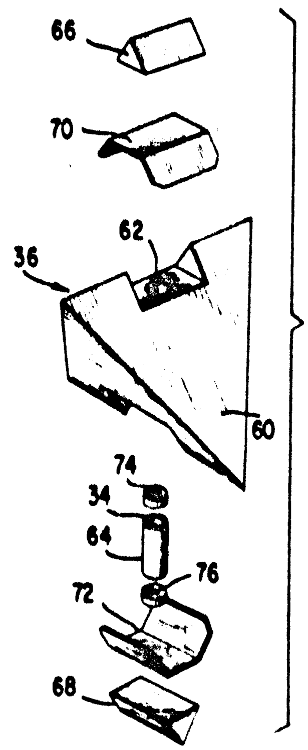

FIG 2

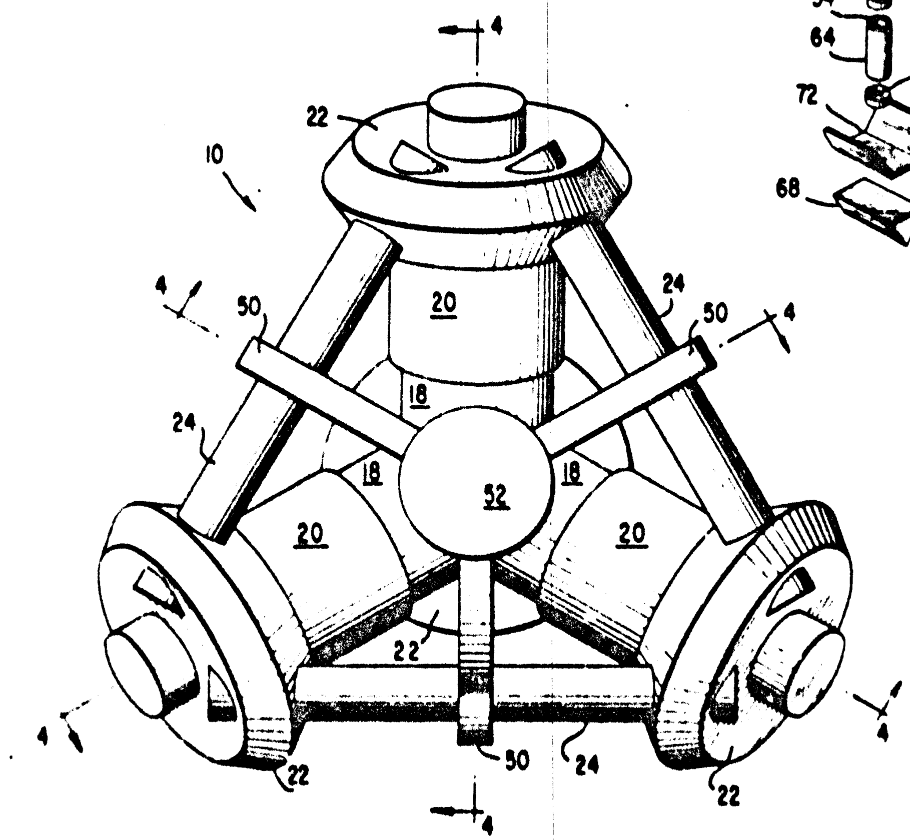

FIG 3

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HIGH PRESSURE-HIGH TEMPERATURE X-RAY DIFFRACTION APPARATUS

Filed Dec. 17, 1963 *2 Sheets-Sheet 2*

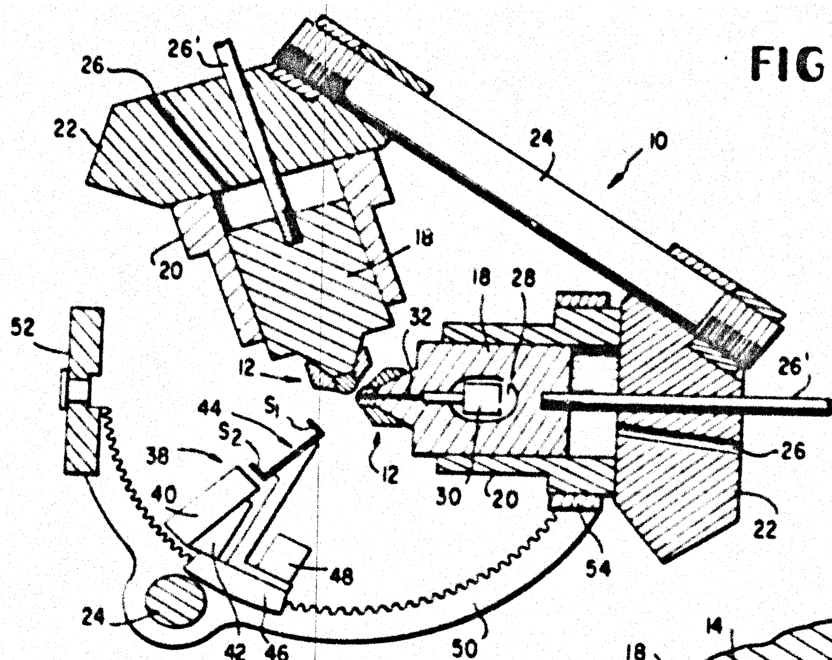

FIG 4

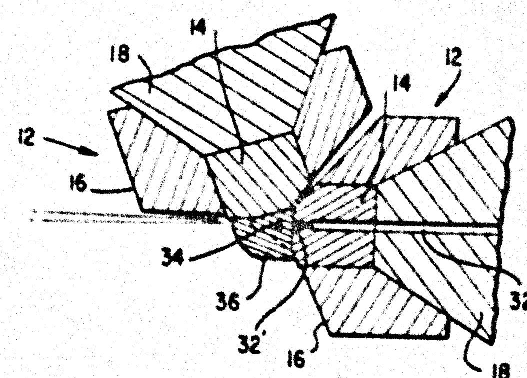

FIG 5

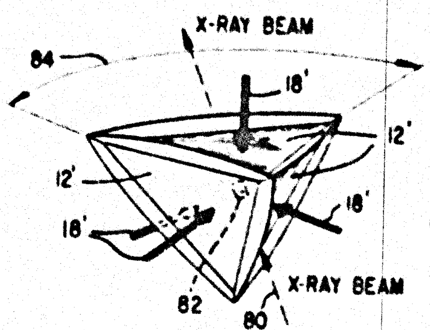

FIG 6

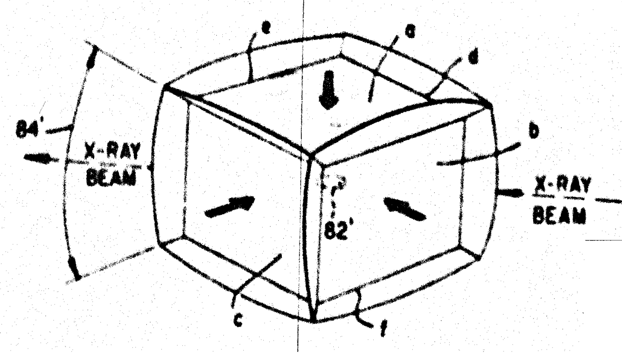

FIG 7

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HIGH PRESSURE-HIGH TEMPERATURE X-RAY DIFFRACTION APPARATUS

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This invention relates to improvements in high pressure or high pressure and high temperature X-ray diffraction apparatus.

It is a principal object of the present invention to provide apparatus by which X-ray diffraction data may be obtained while a sample under consideration is subjected to pressures in the order of 100,000 bar.

A further object of the present invention is to provide such apparatus which permits X-ray diffractometry analysis of samples while they are subjected to such high pressures and to temperatures to, for example, 1000° C.

These and other objects and advantages are provided in a high pressure-high temperature X-ray diffraction apparatus comprising at least four anvil devices, each having a planar press face, means mounting each of the anvil devices for rectilinear motion along axes normal to the planar press faces and converging to a common intersection whereby the press faces form a closed polyhedron in their position of contact, X-ray producing means, means mounting the X-ray producing means to direct a beam of X-rays into the polyhedron formed by the planar press faces of the anvil devices, at least one X- ray detection device, means mounting the X-ray detection device for controlled movement along a plane passing through the line of intersection of a pair of adjacent anvil devices, and means for heating a press sample to be contained within the polyhedron formed by the press faces of the anvil devices.

The invention Will be more fully described with reference to the illustrative embodiments shown in the drawings wherein:

FIG. 1 is a diagrammatic view of the system of the invention applied to a high pressure-high temperature tetrahedral anvil type press;

FIG. 2 is an exploded perspective view of a solid pressure sample holder for a tetrahedral anvil type press;

FIG. 3 is a perspective view of a tetrahedral anvil type press employing hydraulic rams, as the pressure developing means which incorporates the X-ray diffraction apparatus of the present invention;

FIG. 4 is a Section along any line 4-4 of FIG. 3;

FIG. 5 is an enlarged fragmentary detailed view of the pair of anvil devices illustrated in FIG. 4;

FIG. 6 is a diagrammatic perspective view of another form of high pressure-high temperature X-ray diffraction apparatus applied to a tetrahedral anvil device; and

FIG. 7 is a view similar to that illustrated in FIG. 6 of the high Pressure-high temperature X-ray diffraction apparatus applied to a cubic press.

The polyhedral press, having at least four anvil devices each having a planar press face, has been found to be particularly adaptable to high pressure-high temperature X-ray diffraction analysis work. Of the polyhedral presses, the tetrahedron press disclosed and claimed in U.S. Patent 2,918,699, H. T. Hall, represents the simplest of the polyhedral presses as the tetrahedron has only four faces, thus requiring only four anvil devices. The anvil devices are movable along axes normal to the triangular faces thereof and converge to a common intersection at equal solid angles whereby the four triangular faces, of the anvil devices define a regular tetrahedron.

The polyhedral multiple anvil presses, are particularly suited for high pressure-high temperature X-ray diffraction analysis as there are substantially uniform pressure gradients over the entire sample region, eliminating preferred orientation among the crystallites of a sample. Further, since the compressible gaskets of the multiple anvil presses form in planes rather than in cylinders, cones, or other shapes, there are a number of possible arrangements for the samples, electrical leads and contacts for heating elements and the like and the compressible gaskets provide a number of zones for X-ray entry and exit of the diffracted rays.

Referring to FIGS. 1 through 5, the illustrated tetrahedral press 10 includes four anvil devices which are identical in construction and are designated 12. Each of the anvil devices 12 includes an anvil member 14 having an equilateral triangular face at the extended end thereof with the side walls of the members 14 sloping away from the equilateral triangular faces along each of the edges thereof,

Each of the anvil members 14 is supported in a binding ring 16 with each of the binding rings being provided with a bore for snugly receiving the extended end of a rectilinearly movable piston rod 18. The piston rods 18 are slidably mounted in cylinders 20 having base members 22. Each pair of the pistons 18 and cylinders 20 form hydraulic rams which hydraulic rams are interconnected through their respective base members 22 by tie-rods 24. Means generally illustrated at 26 are provided in each of the ram base members 22 for directing pressure fluid into the cylinder spaces. In this form of the invention, the spatial arrangement of the four hydraulic rams is such that the rectilinear movement of each of the ram piston rods 18 thereof is along a line normal to the triangular face of its respective anvil device so that the triangular faces of the anvil devices intersect at equal solid angles to define a regular tetrahedral space formed by the four triangular faces of the four anvil devices 12.

Each of the pressure fluid rams is also provided with rod means 26' which is connected to a small hydraulic ram, not shown, for retraction of each of the ram pistons.

In the form of the invention illustrated in FIGS. 1 through 5, one of the ram pistons is provided with an opening, as at 28, which opening receives in X-ray producing device 30. Any conventional form of X-ray producing means may be employed with the invention and excellent results have been obtained with an X-ray diffraction tube manufactured by General Electric Company and designated General Electric CA-7 X-ray Diffraction Tube.

The primary X-ray beam passes along the axis of the piston rod carrying the X-ray diffraction tube through a bore 32 in the piston rod 18 and a mating bore in the anvil member 14 to impinge upon the sample 34 maintained in the pressure transmitting element and the sample holder combination generally designated 36. The diffracted X-rays then pass out through the compressible gasket formed from a portion of the pressure transmitting element and enter one or more X-ray detection devices generally designated 38 and more clearly illustrated in FIG. 4 of the drawings.

In the form of the invention illustrated In FIGS. 1 through 5 of the drawings, three X-ray detection devices 38 are employed. Each of the X-ray detection devices 38 includes a scintillation counter 40, a pre-amplifier for the scintillation counter 42, means 44 for decreasing background pickup, a movable carrier for the X-ray detection device 46, a motor 48 for driving the carriage 46 and track means 50 for supporting and guiding the carriage 46,

In the illustrated form of the invention, where three X-ray detection means are employed, three curvilinear tracks 50 are utilized. Referring particularly to FIGS. 3 and 4, the tracks 50 tire spaced 120° apart from a common point on the primary X-ray beam adsorbing plate 52. The three spaced tracks 50 correspond to the three planes which bisect the line of intersection of adjacent pairs of anvil devices as more clearly illustrated in FIG. 1 of the drawings. Thus, it will be seen that the center of the primary X-ray beam adsorbing means 52 lies on a line passing through the vertex of one of the tetrahedral angles of the closed tetrahedron formed by the four anvil members. The other end of each of the three tracks 50 is secured to a ring 54 carried by the cylinder of the ram piston housing the X-ray producing means 30. Each of the tracks is also supported by the three tie-rods 24 shown in FIG. 3 of the drawings.

As illustrated in FIG. 4, the trackways 50 are in the form of curvilinear racks and each carriage 46 includes gear means driven by the reversible motors 48 whereby each of the X-ray detection means may be positioned in an arcuate path in the plane passing through the line of intersection of its respective pair of adjacent anvil devices. These paths are indicated by the letters A, B, and C in FIG. 1 of the drawings.

The background eliminating element 44 includes two bosses having slits S_1 and S_2 therethrough. The two detected slits S_1 and S_2 restrict the zone of pickup of X-rays by the scintillation counter 40. It has been found that the use of the pair of slits S_1 and S_2 decreases the background pickup by a factor of 2 or 3, depending upon the size of the slits and the sample under study.

Probably one of the most difficult problems encountered in high pressure-high temperature X-ray diffraction apparatus involve the selection of a material for constructing the pressure chamber and sample holder 36. The pressure chamber forming material in addition to its requirement for withstanding extremely high pressures, must be relatively transparent to X-rays. Suitable materials for enclosing the sample 34 and forming the high pressure gaskets are: carbon, graphite, diamond, beryllium carbide, LiH, amorphous boron or combinations thereof.

Pressures of 75 kb's. have been maintained for several hours in both 50-50% by weight and 25-75% by weight LiH-B containers.

Satisfactory results have also been obtained using pressure containers constructed of phenolic thermosetting plastic and boron; polyethylene and polyethylene mixed with hexagonal BN. It has been found that the polyethylene produces a somewhat diffused low-angle diffraction pattern which can be easily distinguished from the sharper lines characteristic of inorganic structures.

The particular material selected for gasket formation and pressure transmission is formed into a regular tetrahedron 60 (FIG. 2) with edges about 25% larger than the corresponding edges of the triangular faces of the anvil members 14. The tetrahedron serves as a pressure transmitting medium and as a thermal and an electrical insulation, and provides the necessary compressible gasket for the system. The tetrahedron is bored as at 62 to provide an opening for a material container 64.

The material container 64 may be made in tubular form and constructed of graphite where the material is to be heated while under pressure. Where the material is to be heated, the tetrahedron 60 is cut to remove from the tetrahedron prism shaped portions 66 and 68, the bases of which are in abutting relationship to the material container 64. Electrical connections are made to the container 64 by electrical conductors 70 and 72. The electrical conductors 70 and 72 may be made of metal or graphite. Where metal elements are used, they are placed so as not to obstruct the X-ray passage in the primary region of X-ray entrance and X-ray detection. However, it will be appreciated that the X-ray beam will penetrate a graphite heater without prohibitive intensity losses, thus allowing a greater freedom in sample heater construction.

In operation of the form of the invention illustrated in FIGS. 1 through 5, a sample to be studied is placed in the container 64, the end caps 74 and 76 are placed thereon and the sample within the container placed in the bore 62. The graphite electrical conductors 70 and 72 are then inserted in the slots provided therefor and the end pieces 66 and 68 are placed on top thereof to complete the formation of the tetrahedron sample holder and pressure transmitting means. The tetrahedron with the sample therein is centered on the triangular faces of the anvil devices and the anvil devices are simultaneously forced together and since the triangular faces of the tetrahedron 60 are larger than the triangular faces of the anvil devices, some of the tetrahedron 60 is forced between the sloping sides of the anvil members and a sealing gasket is automatically formed. Continued motion of the anvils compresses the gasket and the tetrahedron, the pressure on the tetrahedron being transmitted to the material contained therein. Powered amorphous boron may be placed in the anvil device end of bore 32 as illustrated at 32 to prevent tile gasket material from squeezing into the bore. At the desired pressure, electrical current is directed to the pair of electrical conductors 70 and 72 through their respective anvils, the X-ray producing means 30 is energized and the diffracted X-rays are detected by the three X-ray detecting means 38 as the carriages 46 thereof are traversed through the arcuate paths A, B and C. Thus, three separate patterns are simultaneously available. Obtaining three separate diffraction patterns increases the reliability and also gives added versatility to the apparatus by making possible the simultaneous observation of three different points in the intensity pattern.

It will be apparent that while three separate X-ray detection means are employed in the above-described form of the invention, only one of the three may be employed and further other detectors may be similarly mounted adjacent the other three planes bisecting lines of intersection of adjacent pairs of the anvil devices. Therefore, where a tetrahedral press is employed in accordance with the teachings of the present invention, as many as six detection zones may be utilized.

It will also be recognized by those skilled in the art that it is not necessary to mount the X-ray producing means 30 within one of the hydraulic rams as the primary beam of X-rays may enter the sample along a plane passing through the line of intersection of a pair of adjacent anvil devices. This form of the invention is illustrated diagrammatically in FIG. 6 wherein the anvil members are designated with the reference character 12 and the ram axes by the arrows 18. The primary X-ray beam, designated by broken arrow 80, enters the sample 82 along the line of intersection of a pair of adjacent anvil devices 18 and the X-ray detection means is mounted for travel about the arc 84 which bisects a plane of intersection of a pair of anvil devices opposite the line of intersection into which the X-ray beam is directed. As discussed with reference to the form of invention shown in FIGS, 1 through 5, while the diffraction beam is most intense along the arc 84, diffracted X-rays may be picked up along planes bisecting the intersection of faces of the other anvil devices forming the closed tetrahedron.

The principles disclosed with reference to FIGS. 1 through 5 of the drawings are also applicable to the other polyhedra and in FIG. 7, the principles of the invention are illustrated with reference to a cubical press which includes six anvil devices and six hydraulic rams. Referring to FIG. 7, the six anvil devices are designated with the letters *a, b, c, d, e,* and *f*. Further, the X-ray producing means is illustrated as directing an X-ray beam into the sample 82 through the gasket formed between adjacent edges of anvil devices *b* and *d*. The diffracted X-rays are illustrated as being picked up along an arc 84 which lies in a plane passing through the line of intersection of the edges of adjacent anvil devices *c* and *e*. Other diffraction patterns may be picked up along planes passing through the lines of intersection of other pairs of adjacent edges of the anvil devices *a, b, c, d, e* and *f*. Further, the primary X-ray beam may enter the sample through any one of the ram axes of the plural anvil devices as illustrated with reference to the form of the invention shown in FIGS. 1 through 5.

While only one form of drive means for the plural anvil members has been specifically shown in the drawings, it is contemplated that other forms of drive means may be effectively employed without departing from the scope of the present invention. For example, screw means may replace the hydraulic rams or combination screw means and hydraulic rams may be effectively employed.

It is further evident that various modifications may be made in other specific features of the high pressure-high temperature X-ray diffraction apparatus without departing from the principles of the present invention.

We claim:

1. A high pressure X-ray diffraction apparatus comprising at least four anvil devices, each having a planar press face, means mounting each of said anvil devices for rectilinear motion along axes normal to said planar press faces and converging to a common intersection whereby the press faces define the faces of a polyhedral sample receiving space in their position of contact, X-ray producing means, means mounting said X-ray producing means to direct a beam of X-rays into the polyhedral sample receiving space formed by the planar press faces of the anvil devices, at least one X-ray detection device, means mounting said X-ray detection device for controlled movement along a plane passing through the line of intersection of opposed edges of a pair of adjacent anvil devices and a point within the polyhedral sample receiving space.

2. The invention defined in claim 1 wherein the polyhedron comprises a tetrahedron.

3. The invention defined in claim 1 wherein the polyhedron comprises a cube.

4. A high pressure-high temperature X-ray diffraction apparatus comprising at least four anvil devices, each having a planar press face, means mounting each of said anvil devices for rectilinear motion along axes normal to said planar press faces and converging to a common intersection whereby the press faces define the faces of a polyhedron in their position of contact, X-ray producing means to direct a beam of X-rays into a press sample maintained at the center of the polyhedron formed by the planar press faces of the anvil devices, at least one X-ray detection device, means mounting said X-ray detection device for controlled movement along the plane passing through the line of intersection of opposed edges of a pair of adjacent anvil devices and bisecting the angle formed by the intersection of the faces of the said pair of adjacent anvil devices, and means for heating a press sample to be contained within the polyhedron formed by the press faces of the anvil devices.

5. A high pressure-high temperature X-ray diffraction apparatus comprising at least four anvil devices, each having a planar press face, means mounting each of said anvil devices for rectilinear motion along axes normal to said planar press faces and converging to a common intersection whereby the press faces define the faces of a polyhedron in their position of contact, X-ray producing means, means mounting said X-ray producing means to direct a beam of X-rays through one of the anvil devices into a press sample maintained at the center of the polyhedron formed by the planar press faces of the anvil devices along one of the axes normal to one of the planar press faces of said one of the anvil devices, a plurality of X-ray detection devices, means mounting each of said X-ray detection devices, for controlled movement along different planes passing through the lines of intersection of opposed edges of certain pairs of adjacent anvil devices and bisecting the angle formed by the intersection of the faces of said certain pairs of adjacent anvil devices, and means for heating a press sample to be contained within the polyhedron formed by the press faces of the anvil devices

6. A high pressure-high temperature X-ray diffraction apparatus comprising at least four anvil devices, each having a planar press face, means mounting each of said anvil devices for rectilinear motion along axes normal to said planar press faces and converging to a common intersection whereby the press faces define the faces of a polyhedron in their position of contact. X-ray producing means, means mounting said X-ray producing means to direct a beam of X-rays into a press sample maintained at the center of the polyhedron formed by the planar press faces of the anvil devices along a plane passing through the line of intersection of opposed edges of a first pair of said anvil devices and bisecting the angle formed by the intersection of the faces of said first pair of adjacent anvil devices, an X-ray detection device, means mounting said X-ray detection device for movement along the plane passing through the line of intersection of opposed edges of a second pair of adjacent anvil devices and bisecting the angle formed by the intersection of the faces of the said second pair of adjacent anvil devices, and means for heating a press sample to be contained within the polyhedron formed by the press faces of the anvil devices.

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