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X-RAY DIFFRACTOGRAPH ENABLING DIAGRAMS TO BE TAKEN AT VERY HIGH TEMPERATURES

Filed Oct. 23, 1958 2 Sheets-Sheet 1

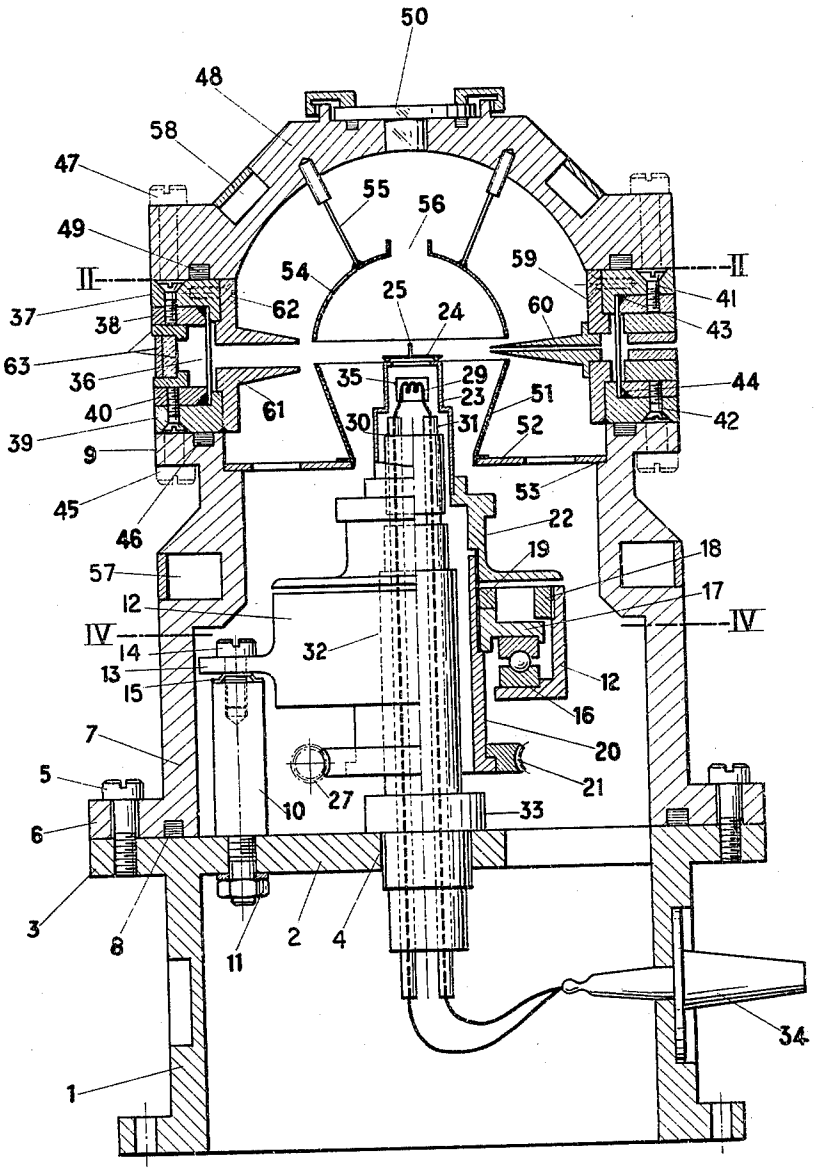



FIG. 1

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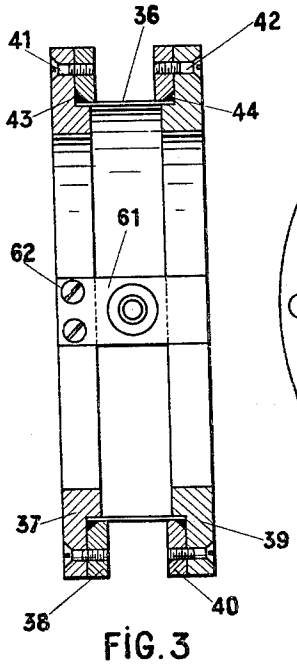



FIG. 3

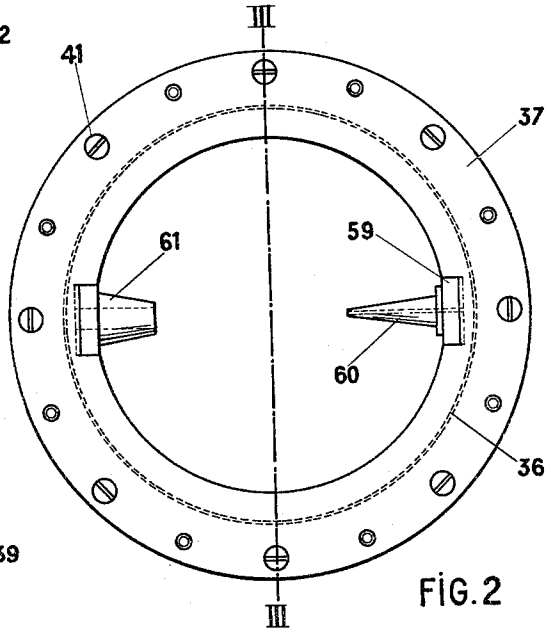



FIG. 2

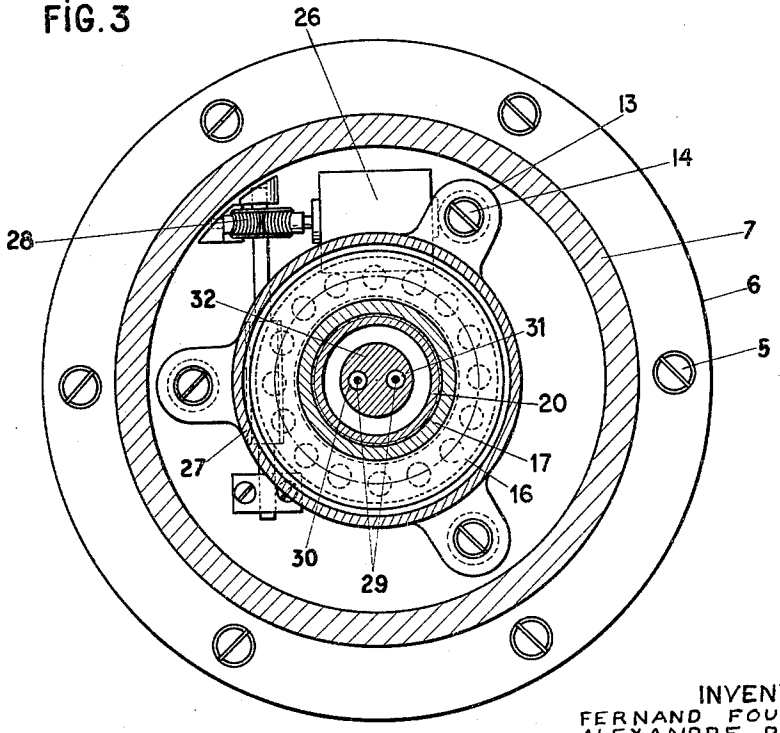



FIG. 4

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# X-RAY DIFFRACTOGRAPH ENABLING DIAGRAMS TO BE TAKEN AT VERY HIGH TEMPERATURES

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The present invention relates to improvements in X-ray diffractograph devices, and more especially to diffractographs intended for the application of the Debye and Scherrer method with the object of taking diagrams at very high temperatures.

It is well known that the application of the Debye and Scherrer method, known as the powder method, requires that the sample to be examined should be placed in the form of a small rod along the axis of a cylindrical member carrying a photographic film. The incident X-radiation, obtained from a suitable source, irradiates a part of the sample, and the diffracted radiation is collected on the photographic film. These devices are well known and are easy to carry out when the sample is examined at ambient temperatures.

In the case in which an examination is required to enable the structure of a crystalline system to be studied as a function of temperature, it is necessary to take the diagrams in accordance with carefully controlled programs of heating and cooling. It is frequently advantageous to this end to protect the sample from the action of air. In order to effect the heating of the sample, a number of devices have already been proposed, for example an oven using the Joule effect, heating by high frequency, a hot-plate, etc. These devices all have the drawback of being so positioned with respect to the sample that there is a substantial loss of heat; in addition, the mass of metallic or refractory material is so great that the temperature reached by the sample rarely exceeds 1500° K.

The present invention is intended to provide a remedy for these drawbacks by virtue of a diffractograph device, in which the construction of the sample support and the method of heating the sample enable the highest temperatures utilizable in the technique to be obtained and also enables precise heating and cooling programs to be followed. One of the most interesting advantages of the said diffractograph device resides in its very low inertia from the heat point of view, which results in an economy of energy and in the possibility of following very closely a predetermined program of heating or cooling.

Finally, the said device is designed so as to permit rapid dismantling of the various parts of which it is constituted, which provides for easy replacement of these parts.

In general, the present invention has for its object a device characterized by the fact that in the center of a diffraction chamber in which a vacuum can be created, and in which are established the conditions permitting the observation and irradiation of a sample to be examined, the sample is fixed on a metal support having a very high melting point, and it is heated by electronic bombardment of the support, an assembly of means being provided in order to prevent losses of heat.

In addition, the device may have one or more of the following features:

(1) The support is electrically connected to the anode of an electron gun and is heated by electronic bombardment when a suitable electric field is created between the cathode and the anode;



(2) The connection between the support and the anode is made in such manner as to avoid losses by conduction;

(3) The sample support which, for example is formed from tungsten, is preferably given the shape of a thin plate having a low heat inertia;

(4) Means are provided to permit of the adjustment of the support and to bring the sample into the axis of the apparatus;

(5) The sample and its support are driven in rotation by a motor;

(6) Judiciously-placed mirrors enable the radiation emitted by the sample at high temperature to be reflected back on the sample;

(7) The diffraction chamber comprises a transparent window intended to permit the measurement of the temperature of the sample to be made;

(8) The chamber may be cooled by circulation of a suitable fluid;

(9) The recording device, for example, a film, is external to the chamber, the wall of which is transparent to X-rays at that place.

In accordance with a particular form of embodiment, the diffractograph device comprises in combination:

(*a*) A vacuum-tight diffraction chamber, in which a vacuum can be created, comprising a cylindrical zone permeable to X-rays, along the axis of which is placed the sample to be examined, the said sample receiving perpendicularly to its axis a beam of incident X-rays, the diffracted radiation of which is recorded on a sensitive surface mounted on a cylindrical support external to the said chamber, and that axis of the chamber which is normal to the incident beam passes through the sample.

(*b*) A sample support formed by a thin plate of tungsten resting through the intermediary of supporting points on the straight section of a metal cylinder which plays the part of the anode of an electron gun, the cathode of which is suitably located inside the said cylinder, the potential applied to the terminals of the gun being sufficiently low so as not to cause the emission of parasitic X-rays.

(*c*) A motor, preferably located inside the chamber, and enabling the cylinder forming the anode to be driven in rotation together with the sample support;

(*d*) A system of mirrors which reflect back on the sample the radiation emitted by the said sample, the said mirrors being formed by reflectors of polished metal, unaffected by heat and arranged in such manner as to prevent heating of the diffraction chamber while leaving the sample visible so that its temperature can be measured.

The electron gun occupies a position which enables the distance between the source and the sample to be reduced to a minimum, thus ensuring maximum energy on the sample to be studied.

Further features and advantages of the present invention will be brought out from the description which follows below of one preferred form of embodiment of a diffractograph in accordance with the invention.

Reference will be made to the accompanying drawings, in which:

FIG. 1 shows a vertical view, partly in cross-section and partly in elevation of a preferred form of construction of a diffraction chamber in accordance with the invention;

FIGS. 2 and 3 show respectively a plan view and a view in transverse section along the axis III—III of FIG. 2, of the assembly constituted by the beryllium ring and the rings which serve as its base;

FIG. 4 shows a view in transverse section of the diffraction chamber, taken along the plane IV—IV of FIG. 1.

In FIG. 1, there has been shown at 1 the base of the

diffraction chamber, of generally cylindrical shape, and which in the present form of embodiment is mounted directly on a vacuum pump (not shown). The upper part of the base 1 forms a platform 2 made up of three limbs separated by hollowed portions, and has a circular edge 3. A threaded hole 4 is provided in the center of the platform 2. By means of a series of screws 5, the base 6 of a metallic body 7 is fixed on the edge 3, an annular joint 8 being provided in order to form a vacuum-tight seal between the base 1 and the body 7. The body 7, of generally cylindrical shape, forms the central wall of the diffraction chamber, and terminates at its upper portion in a widened edge 9.

Three vertical columns 10 are fixed respectively in any suitable manner, for example by means of nuts 11, on the three limbs of the platform 2. These three columns are intended to serve as a support for a casing 12 which has the general shape of a ring and comprises three fixing tongues 13 (see FIG. 4). Screws 14 serve to fix the tongues 13 to the upper parts of the column 10, metal washers 15 being provided between the tongues 13 and the tops of the columns 10. These washers 15, the particular function of which in the adjustment of the device will be more clearly shown in the remainder of this description, are of any suitable metal or alloy, and may be given any suitable form which gives them a certain elasticity.

On the bottom of the casing 12 is supported a ball thrust bearing 16 intended to support, through the medium of the threaded rings 17, 18 and 19, or by any other suitable device, a socket member 20 which is externally threaded toward its other portion and is fixed at its lower portion on a toothed wheel 21. The socket member 20 is surmounted by a cap 22 forming on the one hand the cover of the casing 12 and serving on the other hand as a support for a metal cylinder 23 of smaller diameter. On the upper portion of the metal cylinder 23, a thin metal plate 24 is supported solely through the intermediary of a few points of support, in order to avoid losses by conduction, this plate being of metal having a very high melting point, for example, tungsten, and having the function of supporting the sample. It is at the center of the horizontal plate 24 that the sample 25 to be examined is fixed vertically, the sample having the form of a small rod or stick following the usual practice.

A small motor 26 (see FIG. 4), which in this form of embodiment is provided in the interior of the diffraction chamber, has the function of driving the toothed wheel 21 in rotation through the intermediary of any appropriate system. In this case there has been provided an endless screw 27 cooperating with the toothed wheel 21, the said endless screw being coupled to the motor 26 through the intermediary of a reduction gear 28 of standard type. By means of the system which has just been described, it will be understood how the motor 26 drives the assembly 20, 22, 23, 24 in rotation together with the sample 25 which is to be examined. The step-down gearing is provided in such manner as to ensure a speed of rotation of the sample of about one revolution per minute.

The upper part of the cylinder 23 carries out the function of the anode of an electron gun intended to heat the sample by electronic bombardment of the support 24. The cathode 29 of the gun is constituted by a spiral filament of any appropriate material, for example, tungsten, which is placed in the interior of the cylinder 23 at a suitable distance from the sample support plate 24. The filament 29 passes through two vertical sheaths 30 and 31 formed in a cylinder 32 of Teflon, threaded towards its lower extremity. The cylinder 32 is screwed into the central orifice 4 of the platform 2, and it is vertically fixed along the axis of the diffraction chamber by means of a locking-nut 33, formed for example of insulating material. The extremities of the filament 29 are connected to a high tension source shown diagrammatically at 34. In order to avoid stray electrons, a small ring 35 may be provided,



of tantalum for example, which is fixed at a single point of the spiral filament 29.

As has been previously indicated, the diffraction chamber comprises a zone permeable to X-rays, which should on the one hand allow the sample 25 to be irradiated, and on the other hand it should collect the radiation diffracted by the said sample. In the present form of embodiment this zone is constituted by a cylinder 36 of beryllium. As can be more clearly seen from FIGS. 2 and 3, the said beryllium cylinder is mounted between two pairs of rings (37, 38 and 39, 40) which are assembled together in pairs by series of screws 41 and 42 respectively. An annular joint 43 is provided between the rings 37 and 38 and the cylinder 36, in order to obtain vacuum-tightness between these various parts. An annular sealing member 44 plays a similar part between the rings 39 and 40 and the cylinder 36. The ring 39 forming part of the unit constituted by the beryllium cylinder 36 and the rings which serve as a base for it, is fixed on the edge 9 by a series of screws 45, vacuum-tightness being obtained by means of an annular sealing member 46 inserted in a groove formed on the edge 9. On the ring 37 is fixed in its turn by a series of screws 47 a metal cover 48 which closes the diffraction chamber. An annular sealing member 49 inserted in a groove provided in the cover 48 ensures vacuum-tightness between the said cover and the ring 37. The cover 48 is provided at its upper portion with a transparent surface 50 of any suitable material, fixed in a vacuum-tight manner on the said cover; the said surface permits of observation of the sample and measurements of its temperature by means of an optical pyrometer for example.

In order to avoid heating of the diffraction chamber, reflectors of polished metal, unaffected by high temperatures, of tantalum for example, are arranged in such manner as to reflect back on the sample 25 the high temperature radiation emitted by this latter. In this form of embodiment, there has been provided a lower reflector 51 in the form of a truncated cone which surrounds the cylinder 23 and reaches the level of the sample support 24. This reflector 51 rests on a support 52 mounted on a shoulder 53 of the cylindrical body 7. The support 52 is provided with hollow portions so as to enable a vacuum to be produced throughout the whole of the diffraction chamber. A second reflector 54, which is given the shape of a half-sphere, is suspended from the cover 48 by means of rods 55. It is provided with a central orifice 56 so as to permit observation of the sample 25 through the window 50.

There may be provided as an optional feature a cooling device for the diffraction chamber by circulation of an appropriate cooling liquid. This device may be constructed in any suitable manner; there has been shown diagrammatically at 57 and 58 a circulation of water in the walls of the cylinder 7 and of the cover 48 respectively.

There is directed on the sample 25 the radiation emitted by a standard X-ray tube which has not been shown, and which is mounted on the outside of the diffraction chamber, at the level of the beryllium cylinder 36. There has been shown at 59 a part fixed by brazing on the ring 39 and by screws on the ring 37, serving as a support for a member 60 intended to channel the incident X-rays on the sample 25. Diametrically-opposite to the member 59, a part 61 (see FIG. 3) fixed by brazing on the ring 39 and by screws 62 on the ring 37, cooperates with an assembly of parts 63 forming a trap, of brass or bronze for example, these parts being fixed on the outside of the cylinder 36, between the rings 38 and 40. By virtue of this arrangement, the direct radiation emitted by the member 60 associated with the X-ray tube is received by the member 61 and absorbed by the member 63 and is thus prevented from interfering with the recording of the radiation diffracted by the sample 25, which is collected on a sensitive film which is mounted exter-

nally of the diffraction chamber, at the level of the beryllium cylinder 36 on a cylindrical support, the axis of which passes through the sample. The support of the film on which is recorded the said radiation diffracted by the sample may either be fixed or it may be given a vertical movement of translation which permits of continuous recording of the variations of the crystalline structure as a function of the temperature.

The method of operation and the advantages of the diffraction chamber which has just been described are clearly apparent from the foregoing description.

The diffraction chamber which has been shown can be entirely dismantled, which enables its various parts to be replaced and considerably facilitates the initial adjustment. Once it has been closed, the said chamber is perfectly vacuum-tight, and by reason of the hollowed portions provided in the platform 2 and in the support 52 of the reflector 51, the depression which exists is the same throughout the whole chamber.

For the purpose of simplicity, provision has been made in this form of embodiment for mounting the X-ray tube and the diffraction chamber on the same vacuum pump (not shown).

When it is desired to proceed to the study of the radiation diffracted by a sample as a function of time and/or temperature, the sample 25 in the form of a small stick is fixed in any appropriate manner at right angles to the support 24 at its center. The sample 25 is then brought into the axis of the diffraction chamber by acting on the screws 14 which, by virtue of the presence of the elastic washers 15, enable the relative positions of the sample 25 and of the incident beam to be regulated in a precise manner.

When the diffraction chamber is finally closed, the vacuum pump is set in operation so as to produce a vacuum of the order of $10^{-5}$ mm. Hg. Good results have been obtained by working with a difference of potential of the order of 2,500 volts between the cathode 29 and the anode 23 of the electron gun. Working is also carried out with a very powerful X-ray tube with focusing by electrostatic lenses for example, since the atoms are extremely disturbed and diffract very badly at high temperatures. The temperature of the sample rises very rapidly and a temperature of 2,900° can be reached in about 40 seconds. The judicious arrangement of the tantalum reflectors 51 and 54 entirely prevents heating of the walls 7 and 48 of the diffraction chamber and also prevents heating of the Teflon tube 32 which carries the cathode.

It will be understood that the form of embodiment which has just been described has been given only by way of example and that a large number of detail modifications may be contemplated without thereby departing from the scope of the invention.

What we claim is:

1. An X-ray diffractograph device comprising: a vacuum-tight diffraction chamber; means for creating a vacuum within said chamber; means for guiding a beam of X-rays across the space within the chamber; a metal support within said chamber for holding a sample to be examined in the path of said beam; an electron gun within said chamber for bombarding said support with electrons so as to heat said support and a sample thereon to a high temperature, said support being electrically connected with the anode of said gun and being highly heat conductive and having a melting point higher than any temperature to be imparted to it by the electron bombardment; mirror means within said chamber for reflecting back to the sample, heat radiation from the sample; X-ray pervious window means for transmitting X-ray diffraction from the sample to a radiation-sensitive member disposed about said chamber; and means in said chamber outside the paths of X-rays enabling measurement of the temperature of the sample at any moment.

2. An X-ray diffractograph device as claimed in claim 1, the anode of said electron gun comprising a metal cylinder disposed in an upright position below said sample support, the cathode of said gun comprising a metallic filament inside said cylinder, said sample support being supported on the upper extremity of said cylinder.

3. The device of claim 2, said sample support being a thin plate of tungsten.

4. The device of claim 2, said sample support being supported on said cylinder at spaced points only to inhibit heat losses from said support by conduction.

5. An X-ray diffractograph device comprising: a diffraction chamber; means for guiding a beam of X-rays across the space within the chamber; a thin plate of refractory metal within said chamber for supporting a sample to be examined in the path of said beam; an electron gun within said chamber for bombarding said plate with electrons so as to heat said plate and a sample thereon to a high temperature, said plate being electrically connected with the anode of said gun and being highly heat conductive and having a melting point higher than any temperature to be imparted to it by the electron bombardment; spherical mirror means within said chamber for reflecting back to the sample, heat radiation from the sample; means for locating a radiation-sensitive member about said chamber in the path of X-ray diffraction from the sample; means enabling measurement of the temperature of the sample at any moment; and means for applying between the cathode and the anode of said gun a difference of potential insufficient to cause the emission of parasitic X-rays.

6. An X-ray diffractograph device comprising: a vacuum-tight diffraction chamber having a cylindrical side wall; means for guiding a beam of X-rays across the axis of said chamber; a support within said chamber on said axis for holding a sample to be examined in the path of said beam; an electron gun within said chamber for bombarding said support with electrons so as to heat said support and said sample to a high temperature, said support being electrically connected with the anode of said gun and being highly heat conductive and having a melting point higher than any temperature to be imparted to it by the electron bombardment; mirror means within said chamber for reflecting back to the sample heat radiation from the sample, said mirror means leaving unobstructed a cylindrical section of said chamber traversed by said beam and a path of heat radiation from the sample transverse to said cylindrical section; X-ray pervious window means in said side wall about said cylindrical section for transmitting diffraction from the sample to a radiation-sensitive member outside said chamber; window means in an end wall of said chamber across said path of heat radiation to enable observation of the temperature of the sample; adjustable means for positioning said support so as to locate the sample accurately on said axis; motor means for rotating said support to rotate the sample on said axis; and means for circulating a cooling fluid through walls of said chamber.

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