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Apparatus for High-Pressure High-Temperature X-Ray Powder Diffraction Studies

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A high-pressure high-temperature x-ray powder diffraction apparatus has been developed based on a modification of the belt apparatus, which is an internally heated compressible gasket device. The unique feature of this device is that the die-support ring assembly is fabricated in two parts which mate along a plane normal to the piston axis. The split-die design permits entry of the x-ray beam into the high-pressure volume and egress of both the diffracted rays and the undeviated beam through suitable grooves and fan-shaped slots ground in the mating surfaces. The high-pressure x-ray windows are either a beryllium ring with a wedge-shaped cross section or epoxy resin stops at the bore of the die. The high-pressure medium is "amorphous" boron, and the sample is in the form of a thin cylinder which is coaxial with the pistons and normal to the x-ray beam. The compressible gaskets between the pistons and the die are made of pyrophyllite, as they are in conventional devices, inasmuch as they are not part of the x-ray path. High sample temperatures are attained by resistance heating of carbon rods adjacent to the sample. Present limitations on pressure and temperature are 100 kilobars and 1000°C. High-intensity Mo K_α radiation is employed. The apparatus is portable and may be positioned on a conventional x-ray source.

INTRODUCTION

ONE of the potentially most promising areas of high-pressure research which is relatively unexplored is that of structural studies on crystalline solids at pressures in excess of 20 kilobars at sustained temperatures in excess of 300°C. Such studies could provide basic data on the equation-of-state, nonquenchable phase transitions, order–disorder phenomena, etc. of solids.

At present there are three basic designs being used for high-pressure x-ray diffraction measurements. The diamond cell[1–3] consists of a pair of diamonds in the configuration of Bridgman anvils and the x-ray beam is transmitted through the diamonds perpendicular to the anvil faces and the sample plane. Carbide Bridgman anvils are used for[4–6] x-ray diffraction measurements with the x-ray beam transmitted parallel to and between the anvil faces. The third design utilizes the tetrahedral high-pressure apparatus[7] to generate pressure and the x-ray beam is transmitted in and out of the high-pressure volume through the compressible gaskets. For high-pressure studies at elevated temperature the first two designs are restricted by the effect of external heating on the properties of the carbide or diamond anvils (less than 500°C). The tetrahedral device can be internally heated and is limited only by the combination of requirements fixed by the gasket material, i.e., low x-ray absorption, proper frictional qualities to effect a high-pressure seal, and high-temperature stability.

The apparatus described in this article utilizes a belt-type high-pressure cell[8] with a split die for entrance and egress of x rays from the high-pressure region. The essential feature of this design is the separation of the x-ray beam path from the compressible gasket region in an internally heated high-pressure high-temperature device. This permits the use of standard gasketing materials, such as pyrophyllite, to effect the pressure seal irrespective of their x-ray absorption characteristics. This design has been used to 1000°C and 100 kilobars.

APPARATUS

The high pressure is generated in a modified high-compression belt of the type developed by Bundy.[9] The high-pressure volume is 0.25 cm high by 0.5 cm in diameter, which is large enough for internal heating to over 1000°C. Fifty tons of ram force applied to the pistons produces over 100 kilobars internal pressure, so the whole assembly, 50-ton press, die, pistons, and binding rings, can be constructed with a total weight of less than 34 kg. The device, therefore, is portable and can be installed on an x-ray source. Figure 1 is a picture of the high-pressure apparatus aligned with the x-ray source, and Fig. 2 is a schematic representation of this assembly.

To provide entry for the x-ray beam and exit of both the diffracted rays and the undeviated beam, the die and the support ring assembly of the high-compression belt were fabricated in two halves which mate in a plane perpendicular to the piston axis. The entrance and exit ports are ground into the mating surfaces of the two halves (Fig. 3). The die halves (5 cm diam, 1.25 cm thick) are made of Carpenter–Hampton tool steel hardened to 60–62 R_c, and the binding rings (10 cm o.d., 5 cm i.d., 1.25 cm thick) are made of Vascojet 1000 hardened to 50 R_c. The die and binding ring halves fit together with 1° taper and 0.028 cm

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of interference. The faces are ground parallel. The die is made of tool steel to facilitate the grinding operations described below. A higher pressure range could probably be attained with the use of tungsten carbide.

An entrance–exit groove is ground across the mating surfaces of the two halves to a depth of 0.025 cm with a grinding wheel dressed to a 0.025 cm radius. The groove is centered on a diameter of the die and passes through the die center to within ± 0.001 cm. A fan-shaped slot for diffracted rays is ground into the assembly on each side of the groove. The fan on one side of the groove covers the 2θ diffracted angles 5 to 30° and the fan on the other side covers 2θ angles 20 to 45°. This provides a range of measurable "d" values with Mo K_α radiation from 8.1 to 0.93 Å with overlap of the two slots from 1.37 to 2.04 Å. The fans have a vertical taper of 2°, which, at a film distance of 57.3 mm, gives an x-ray pattern 3 mm high. An initial flat region 0.025 cm deep is left in the fan for a distance of 1.25 cm from the bore center before the vertical taper is started. The flat region aids in effecting the pressure seal. The two halves are placed together and aligned by placing a 0.05 cm drill rod in the entrance and exit groove.

Two methods are used to prevent extrusion of the pressure medium into the slots and grooves. The first method employs epoxy resin to fill the slots and grooves to a distance of 0.5 cm from the periphery of the bore of the die. A clear epoxy loaded with 50–70% by weight of amorphous boron is suitable. An excess of the mixture is applied and then lapped parallel to the die face after curing. The epoxy–boron mixture has a linear absorption coefficient for Mo K_α x radiation of approximately 1.0 cm^{-1}, which results in an attenuation of intensity for the described configuration of 65%. When using the epoxy seal the internal temperature of the sample is limited to 500–600°C, since the temperature of the bore is approximately one-third the internal temperature and the epoxy begins to soften above 200°C.

The second method of sealing the pressure is by means of a beryllium ring with a wedge-shaped cross section. The bore is tapered where the two die halves mate so that the

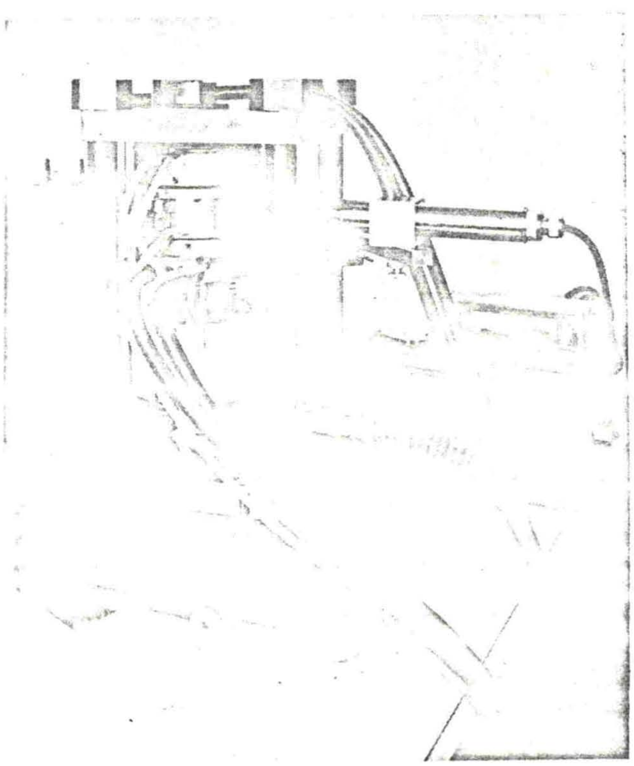

Fig. 1. Photograph of the high-pressure apparatus showing the press frame and hydraulic ram, the positioning table, the x-ray tube head (left), and the Geiger tube for aligning the press. The Debye–Scherrer camera is not in position so that one of the slots for the diffracted rays is shown. The scale is in centimeters.

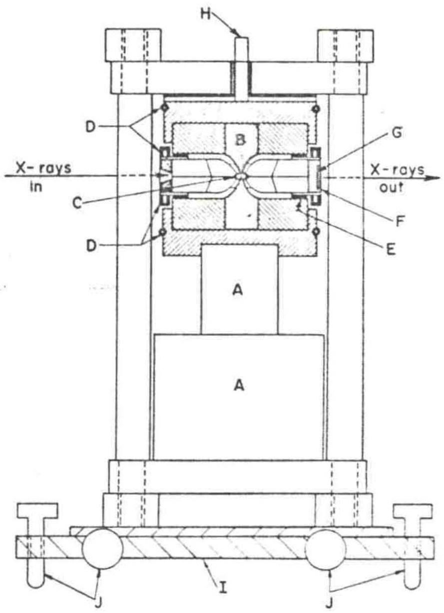

Fig. 2. Schematic drawing of the high-pressure apparatus. A—hydraulic 50-ton ram; B—WC pistons; C—die assembly; D—water cooling tubes; E—rubber shim to position die water-cooling tube; F—film cassette; G—x-ray film; H—insulated current lead; I—press positioning table; J—adjusting screws for vertical and horizontal positioning.

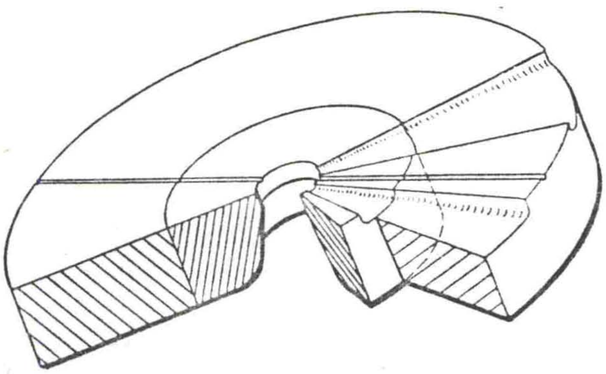

Fig. 3. One-half of split-die assembly showing mating surface with groove for entrance of x-ray beam and egress of undeviated beam and fan-shaped slots for egress of diffracted rays.