little chance of retaining the high-pressure structure at low pressures. With reconstructive transformations, however, the atoms must move relatively long distances and rearrange themselves. Since diffusion is slowed by high pressures, such transformations tend to be very sluggish and, indeed, may not occur at all even at pressures well above the appropriate value to stabilise the high-pressure form thermodynamically. The direct graphite-to-diamond transformation, for example, requires a pressure of 150,000 atmospheres, some 50% greater than for diamond stabilisation. In such cases it is often possible to bring down the pressure at which a measurable transformation occurs by the use of a suitable 'catalyst.' For the graphite-to-diamond transformation a carbon solvent such as nickel is used—this has the effect of dispersing the carbon atoms so that their reconstruction as diamond is made easier and can be achieved effectively under equilibrium conditions.

The new structures resulting from reconstructive transformations or pressure-induced reactions (such as Nb_3In) tend to persist metastably at atmospheric pressure. Thermodynamically they are unstable, but in practice they may be as inert and unchanging as diamond itself. This is because thermal energy at room temperature is insufficient to allow the reverse process to take place (although it will occur at higher temperatures where diffusion is facilitated). These conditions give us the possibility of 'bringing back alive' high-pressure phases for assessment and study.

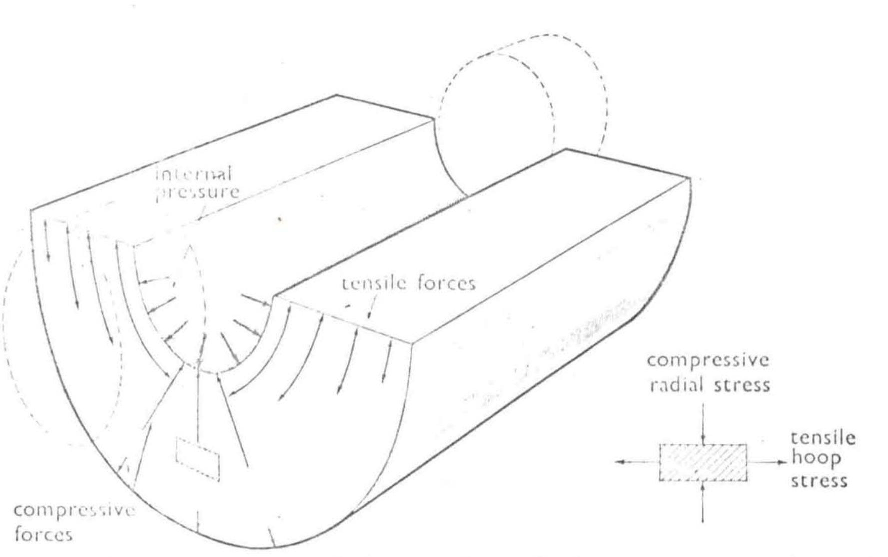

Fig 2 High pressure in a cylinder produces both compressive and tensile forces, both of which are greatest at the bore. Each part of the tube must be able to resist these forces: where stress differences are large, failure is likely to occur. One solution is to transfer tensile forces to outer parts of the cylinder

Producing high pressures

How can very high pressures be generated in the laboratory? One of the easiest methods is to use explosives or electric discharges to set up shock waves in a liquid (*see* "New ways of shaping metals," DISCOVERY, June 1963). These shock waves do produce very high pressures, but unfortunately they are of very short duration. Since we require metastable structures resulting from reconstructive transformations or pressure reactions, chemical synthesis at high pressure usually requires that pressures and temperatures be maintained for some minutes, or even hours.

One hundred thousand atmospheres is a pressure of about 650 tons per square inch—greater than the compressive strengths of most substances. This makes the design of equipment to contain these pressures exceedingly difficult. Obviously the most highly stressed parts must be made from substances of the highest strengths, such as alumina, cemented carbide and even diamond itself. Cemented carbide is the favourite material since it has a high compressive strength (up to 400 tons per square inch) and can be obtained in large uniform pieces. However, it is relatively weak in tension, and this brings us to the great design problem of ultra-high-pressure apparatus. Somewhere in the equipment there must be large tensile stresses, and if these occur in the same regions as high compressive stresses, the resulting stress difference is likely to cause failure.

Unfortunately this is just the situation which exists in pressurised cylinders and spheres. Take, for example, the simple thick-walled cylinder shown in Figure 2. As the pistons are pushed in to increase the pressure in the bore, each part of the cylinder must resist not only the compressive stress, but also the tensile stresses which arise in the circumferential direction as a result of the tendency of pressure to expand the cylinder. Both these stresses have their maximum values at the inside edge of the cylinder and decrease rapidly towards the outside. Looked at in another way, the material near the bore has to carry an unfair proportion of the stress compared with the outer regions, which are relatively lightly loaded. It is the designer's problem to reduce the high stress differences by transferring the tensile forces to the outer parts of the apparatus where the larger cross-sections can cope more easily with them.

There are several ways in which this may be done, and two fairly typical designs for reaching pressures of about 100,000 atmospheres are shown in Figures 3 and 5. Firstly we have an advanced type of piston and cylinder—the hybrid apparatus (*see Fig. 3*). Here the pistons have become blunt cones (known as 'anvils') and they push into a contoured ring. A compressible seal for the high pressure region is formed from pyrophyllite, a soft mineral which has a very high friction and will not extrude out in thin sections. The highly stressed regions near the high-pressure chamber carry primarily compressive stresses. They receive 'massive support' from the surrounding regions of larger cross-section which carry tensile stresses also. An apparatus of this type was used for the first diamond synthesis in 1955 and pressures up to 120,000 atmospheres can be reached.

Secondly, we have the tetrahedral anvil apparatus, in which the cylinder or ring has been dispensed with. Four triangularly-shaped anvils push against the faces of a regular tetrahedron of pyrophyllite (*see Fig. 5*). This is initially oversize and the excess material flows into the gaps between the anvils, forming a seal as in the hybrid apparatus. Although pyrophyllite is a solid, it transmits the pressures to the