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CURRENT PROBLEMS IN RESEARCH

Ultrahigh-Pressure Research

At ultrahigh pressures new and sometimes unexpected chemical and physical events occur.

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Pressure, defined as force per unit area, is a classical concept. A common unit used in the measurement of pressure is the atmosphere. One atmosphere is equivalent to 14.70 pounds per square inch or to 1.033 kilograms per square centimeter. Natural agencies and man-made devices wherein pressure is deliberately or indifferently generated abound. These pressures cover a tremendous range. For example, the pressure generated by a hand-operated tire pump may be 2 or 3 atm, that generated by a hammer blow may be 5000 atm; a rifle bullet impinging on armor plate, 100,000 atm; conventional explosive shock front, 300,000 atm; and the pressure at the earth's core boundary, 1.4×10^6 atm. Moreover, an "atomic-bullet" from a modern particle accelerator impinging on matter at rest may instantaneously generate 10^{10} atm, while the pressure on the interior of some stars may be as high as 10^{15} atm. Some of the above mentioned pressure generators produce static pressures, while others produce only transitory pressures.

Apparatus

For most experimental work static pressures are necessary. Today's laboratory machines are capable of generating pressures approaching 200,000 atm simultaneously with temperatures of 3000°C and maintaining these conditions for hours.

Progress in high-pressure research is directly dependent on progress in design of high-pressure apparatus. It is appropriate, therefore, to consider some of the problems of apparatus design and some recent developments in that area. The ordinary form taken by a high-pressure device is that of a piston and cylinder. The cylinder is closed on one end, and the sample contained therein is compressed by forcing a piston in the other end. Such a device, with the vital components constructed of cemented tungsten carbides, is capable of generating maximum pressures of 50,000 atm. Cemented tungsten carbides have the highest compressive strength of any available engineering materials in use today. The tensile strength of cemented carbides, however, is very low. Therefore, components such as cylinders, which are subjected to tensile loads in use, must be supported by alloy steel back-up rings or by some other means. The upper limit of 50,000 atm for a piston-and-cylinder apparatus is set by failure of the piston.

Theoretically, tremendous pressures could be reached by a cascading process whereby one piston-and-cylinder device is placed inside the chamber of a larger device, and so on. In such an arrangement the pressure differential between each stage would not exceed the maximum 50,000 atm. In practice, it has not been feasible to carry cascading beyond two stages. The experimental problems encountered in two stages are rather formidable, and at present such devices have been limited in use to the making of pressure-volume measurements at room temperature.

As has been mentioned, the upper limit of pressures obtainable in piston-and-cylinder devices is set by the strength of the best materials of construction currently available. Materials with higher compressive strengths would of course extend the range of any high-pressure device. Current effort in this direction is centered on the improvement of existing cemented carbides and the making of analogous cemented compositions of diamond or cubic boron nitride powders. Since diamond and cubic boron nitride have compressive strengths about three times as great as that of hard metal carbides, research on cemented compositions of these materials seems very worth while.

Apparatus currently available for use at pressures above 50,000 atm (other than the above-mentioned two-stage device) are based on the idea that a multistage effect can be obtained in a "single-stage" device.

P. W. Bridgman, Nobel laureate and long-time pioneer in the field of high pressure, first used this idea in the Bridgman anvil apparatus (Fig. 1). In this device, two cemented tungsten carbide "anvils" oppose each other. The working face of each anvil is the surface of a broad truncated cone. The included angle of a section through this cone is about 170°. The sample to be compressed is made in the form of a thin wafer approximately 0.010 inch thick and 0.375 inch diameter. A 0.500 inch (outside diameter) pipestone ring surrounds the sample. The assembly of wafer, sample, and pipestone ring is compressed between the anvil faces. The pipestone ring acts as a gasket to prevent loss of the sample by lateral extrusion between the anvils. This type of device has been used at pressures approaching 200,000 atm. These pressures are possible because the anvil faces receive "massive-support" from the adjacent carbide—that is, the intense load on

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the anvil faces is "fanned-out" throughout the carbide bulk beneath the faces. Some of this load will be tensive and is absorbed by cylindrical steel binding rings which surround the carbide anvils. The relative motion along the anvil line of centers which is necessary to effect compression of the sample is made possible by the remarkable properties of the pipestone (catlinite). This material—a hydrous, iron-bearing aluminum silicate related to pyrophyllite and talc—compresses linearly with the load and at the same time possesses sufficient internal and surface friction to "contain" the sample and prevent its extrusion from between the anvils.

Bridgman anvils have been effectively used in measuring electrical resistances of materials as a function of pressure at room temperature. With external heating they have been used in mineral synthesis problems. The pressures obtainable with external heating must of necessity fall off with increasing temperature because of loss of strength of the carbide. Thus, at 1000°C, the maximum pressure obtainable is reduced to about 20,000 atm.

The massive-support and "motion-via-compressible-gasket" principles have been utilized in a device known as the "tetrahedral-anvil apparatus" (Figs. 2, 3, and 4). This equipment provides a larger working volume than the Bridgman anvils and in addition provides for internal heating and entrance of electrical leads for use in making temperature and other measurements. At this writing this device has been used at pressures as high as 130,000 atm. The arrangement for internal electrical-resistance heating allows for temperatures of 3000°C to be maintained at the higher pressures for periods of several hours.

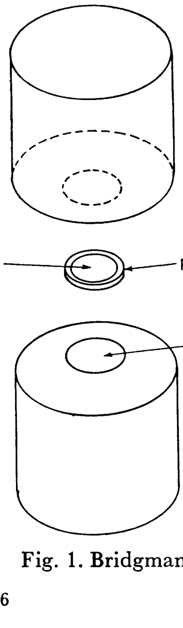

Fig. 1. Bridgman anvils.

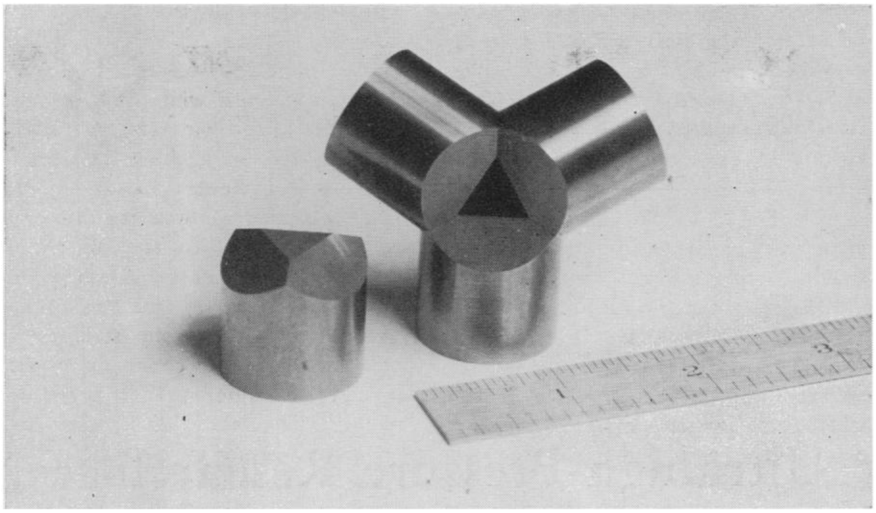

Fig. 2. Details of tetrahedral anvils.

In the tetrahedral-anvil apparatus, four cemented tungsten carbide anvils (Fig. 2) are driven together by hydraulic rams along center lines normal to their triangular faces. These center lines intersect at tetrahedral angles in the center of a regular tetrahedral volume enclosed by the anvil faces. The carbide anvils are surrounded by steel binding rings that absorb the tensive loads. In this device, a regular, pyrophyllite tetrahedron (Fig. 3), the edges of which are 25 percent longer than the corresponding edges on the triangular anvil faces, serves as pressure-transmitting medium and as thermal and electrical insulation and also provides the necessary compressible gasket. The sample container, a tube which also serves as the electrical-resistance heater, is located within the pyrophyllite tetrahedron and runs diagonally from opposite edges as is shown in Fig. 3-I. Electrical connections are made to the sample tube (*C*, Fig. 3-II) through metal tabs shaped as shown in cross section at *B* (Fig. 3-II). These tabs are spot-welded to the ends of the metal tube *C*, thus sealing in the contents. The metal tabs from each end of the sample tube make electrical contact with the faces of a pair of anvils which bring in the heating current. Prisms of pyrophyllite (*A*) provide thermal insulation at the ends of the sample container. A thermocouple (*E*) is spot-welded to the sample container, and the leads are brought out through edges of the tetrahedron as shown. Friction of the pyrophyllite on the fine wires is sufficient to hold them in place during high-pressure operation.

In operation, the pyrophyllite tetrahedron is centered on the anvil faces. The anvils are then simultaneously forced together. Since the triangular faces of the pyrophyllite tetrahedron are larger than the triangular anvil faces, some pyrophyllite is forced between the sloping sides of the anvils, and a gasket is automatically formed. Continued motion of the anvils compresses the gasket and tetrahedron, and consequently, the sample.

Pressure calibration of this device is based on locating the hydraulic ram load required to cause certain known abrupt changes in electrical resistance to occur in materials such as bismuth, barium, and thallium.

Some General High-Pressure, High-Temperature Considerations

The concept of pressure is clear-cut when one is dealing with a continuous fluid medium but becomes somewhat hazy when atomic phenomena are involved. For example, 1 mole of helium gas at 0°C, when confined to a volume of 22.4 liters, exerts a nominal pressure at 1 atm on the containing walls. According to kinetic theory, this pressure is generated by molecules of gas rebounding from these walls. At any instant, however, the fraction of the total wall area covered by rebounding helium atoms is only about 0.013 percent. Therefore, the instantaneous average pressure per helium atom generated at the point of contact on rebound is approximately 7500 atm.

Pressure, like temperature, is an intensive property, and when it is multiplied by a capacity factor, an energy is obtained. When temperature is introduced into a system, the corresponding capacity factor is, of course, the specific heat. When pressure is applied, the corresponding capacity factor is the volume, and the integral

$$\int P dV$$

gives the energy introduced into the system by the pressure.

Pressure and temperature are opposites in their general effect upon matter. Increasing temperature tends to "loosen" systems and increase their entropy, whereas increasing pressure tends to densify systems and decrease their entropy. A solid at low temperature will, upon heating, successively change its crystalline structure, become a liquid, a gas, and then proceed through molecular dissociation to electronic ionization. On the other hand, a gas, when it is subjected to progressively higher pressures, may be condensed to a liquid, various solid phases, and then, when the atoms are in closest packing, proceed through various electronic rearrangements, and finally, at pressures of billions of atmospheres, atoms may be brought within the critical distance of 10^{-13} centimeter at which nuclear fusion may occur.

The profundity of the changes that can be produced in a quantity of matter by injection of energy is qualitatively related to the magnitude of the intensive factor for the type of energy concerned. Heat energy is a type of energy that man has deliberately applied for ages to effect transformations in materials. Temperatures of 1000° to 1500°C, readily obtainable in flames and furnaces, introduce energies of order of magnitude 10 kilocalories. These energies correspond to the ordinary energies of chemical bonds; hence, interaction of this heat energy with matter will produce atomic and molecular rearrangements.

What magnitude of pressures corresponds, in energy, to temperatures of 1000° to 1500°C and, hence, might be expected to produce changes in scope and magnitude comparable to those that are produced by these temperatures? For condensed systems—that is, liquids and solids (gases are not generally interesting because large energy changes may be involved in which the only effect is that of producing a large change in the volume)—corresponding pressures would be of the order of 100,000 to 200,000 atm. In energy, 1 cubic centimeter kiloatmosphere is equivalent to 12.19°K (where degrees are equal to the energy divided by the Boltzman constant *k*.).

Two problems confront the scientist who is concerned with the transformation of matter from one chemical or physical state to another. The first of these is the thermodynamic problem, and the second concerns the rate of reaction, transition, change, and so on. The thermodynamic equations give information concerning the possibility of transformation from one state to another under certain conditions of temperature, pressure, external fields, and so forth. The rate equations give information concerning the time required for the equilibrium dictated by the thermodynamics to be obtained.

Application of thermal energy to systems to obtain proper thermodynamics and rates for the production of desired changes has been widespread. However, the use of pressure to effect such changes has been quite limited. The use of pressure and temperature together as "levers" to manipulate systems (thermodynamically and rate-wise) to obtain a desired result offers far greater possibilities than the use of either alone. In fact, many transformations (graphite → diamond, for example) can only be brought about by application of the two types of energy.

The general diametrically opposite behavior of pressure and temperature has been mentioned. This carries, generally, into the realm of reaction rates. Whereas rates of reaction are increased by increasing temperatures, increasing pressures decrease the rates. Consequently, it becomes very desirable to have apparatus available that can produce high pressures and high temperatures simultaneously.

Synthesis of Diamond

For almost 100 years great impetus has been given to high-pressure research by the desire to synthesize diamonds. Success in this field has been very elusive. Evidence that the goal has finally been attained, however, is abundantly available in the many diamond grinding wheels now in use for which the wheel's diamond powder was made by the General Electric Company's Metallurgical Products Division. General Electric announced in October 1957 that 100,000 carats of diamond powder had been made as of that date and that they expected to manufacture over a million carats during 1958. The current price of the man-made diamond grit is $3.48 per carat, whereas the price of natural material is about $2.80 per carat. The 24 percent higher price for man-made diamonds is not a deterrent to their use, however, because extensive tests have shown that the grinding efficiency of the man-made diamonds exceeds that of natural diamonds by 35 percent. Diamonds large enough for use as gems have

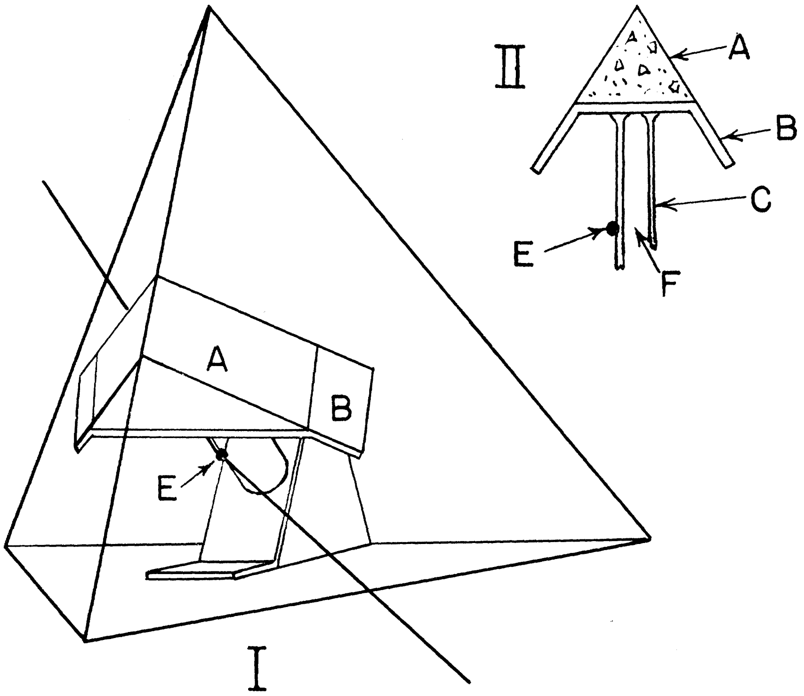

Fig. 3. (I) Details of pyrophyllite tetrahedron with diagonal edge-to-edge heater-and-sample tube. (II) Details of heater-and-sample tube.

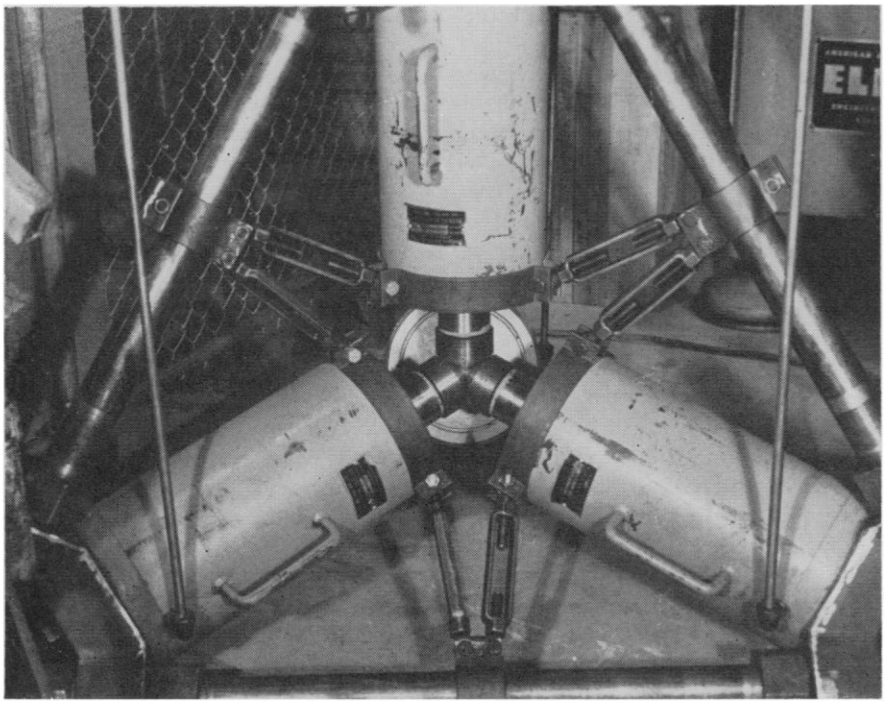

Fig. 4. Tetrahedral anvil apparatus.

not been synthesized up to the present time.

It has not been possible to disclose the details of the methods used to synthesize diamonds because of a government security classification on the patent applications. However, it is generally known that the synthesis is effected by pressures near 100,000 atm and temperatures near 2000°C.

Other Minerals

Naturally occurring high-pressure minerals other than diamond that have been synthesized in recent years include the garnets: pyrope, andradite, almandite, spessartite, grossularite, and uvarovite. These garnets are readily synthesized from the metallic oxides in the presence of water at pressures ranging from 20-000 to 35,000 atm at temperatures near 1000°C. In addition to the naturally occurring garnets, several garnets unknown in nature have been made at high pressure and high temperature. The value of laboratory synthesis of minerals in elucidating the nature of geological processes is self-evident.

Two extremely interesting "minerals" not found in nature have been synthesized in the laboratory. The first of these is Coesite. The chemical composition of Coesite is the same as quartz—SiO_2. However, Coesite has a refractive index of 1.6 and a density of 3.0, whereas the corresponding quantities for quartz are 1.5 and 2.7. In addition, Coesite is remarkably stable toward long heating in hydrofluoric acid. Coesite is readily formed from quartz or other silicates at pressures of 35,000 atm and temperatures of 750°C in the presence of mineralizers such as water, diammonium phosphate, or boric acid. Coesite has been synthesized directly from quartz without the aid of a mineralizer at pressures of 90,000 atm and temperatures of 2000°C.

The second remarkable "mineral" is Borazon, a cubic form of boron nitride with the chemical composition BN. Boron nitride is isoelectronic with graphite, and the normal hexagonal form—a white, slippery solid—has a crystal structure similar to that of graphite. Borazon can be prepared at pressures near 65,000 atm and temperatures near 1500°C. This material is completely analogous to diamond. It is comparable to diamond in hardness and apparently has properties superior to those of diamond with regard to oxidation, resistance and thermal stability. The material thus far prepared is comparable in size to the diamond grit being manufactured for use in grinding wheels. No doubt this material will eventually take its place alongside diamond in industrial grinding applications.

There is no doubt that future research at high pressures and temperatures will produce many new materials that will possess new and useful properties.

Many materials synthesized by the use of high pressure and high temperature are thermodynamically unstable at room temperature and atmospheric pressure. Diamond, a remarkably stable substance from a practical standpoint, is the supreme example of this type of phenomenon, for it is unstable with respect to graphite by some 450 calories under ordinary conditions. Such thermodynamically unstable materials whose rate of transformation to a stable form under ordinary conditions is infinite in terms of human experience are referred to as being metastable.

Metastable materials that become stable under high-pressure conditions can be synthesized in the laboratory by the following sequence of events: (i) subject the starting material to high pressure; (ii) while maintaining pressure, subject the material to a temperature sufficiently high to obtain a reasonable rate of transition or reaction (the pressure and temperature must be such that the metastable end-product desired is stable); (iii) decrease the temperature to room temperature; and (iv) decrease the pressure to atmospheric. Step iv, of course, removes the end-product from stable conditions and subjects it to unstable conditions. However, the temperature had been reduced in step iii so that a material possessing metastability would not revert to the stable form at the completion of step iv. Now, in nature's high-pressure laboratory, this sequence is rarely followed. As materials are brought from the depths of the earth, where they were under high-pressure, high-temperature conditions, pressure and temperature fall together and materials that may have been stable at depth will revert to the unstable form as they rise to the surface. Rare as the diamond is, it is a marvel that it exists at all.

Independent control over pressure and temperature in the laboratory gives man the opportunity to synthesize many things not found in nature.

Interior of the Earth

An indirect investigation of the interior of the earth has become possible with the advent of high-pressure, high-temperature apparatus. Man's direct access to the earth's interior is, of course, very limited. Personal excursions can be made to depths of about 1 mile, this being the depth of the deepest mines. Oil wells have been drilled to depths of 4 miles, and the drill cores and readings from instruments lowered in the holes yield information concerning these depths. A pressure of 130,000 atm corresponds to a depth of about 260 miles. There is some uncertainty about the temperatures at these depths; but they very likely do not exceed the temperatures now simultaneously obtainable with pressure in the laboratory.

It is probable that some of the seismic discontinuities within the earth are due to the presence of phases not known, under ordinary conditions, to be existent at the earth's surface. For example, it has recently been postulated that the core of the earth is not composed of iron-nickel as is usually assumed, but instead is essentially olivine, which, at the tremendous pressure of 1.4×10^6 atm existing at the core boundary, has been converted to a metallic material of density near 10. Support for this theory is found in the fact that the two smallest planets in the solar system, Mars and Mercury, do not have a core. Calculation shows that these planets are not large enough to maintain the pressure of 1.4×10^6 atm necessary to support the core, even at their centers.

Pressures required to test this postulate are out of reach of present-day apparatus. However, metallic and nonmetallic forms of some elements are known. Gray tin is nonmetallic and has a density of 5.75. Application of pressure to this material transforms it to a metallic white variety of density 7.28. Arsenic is known both as a low-pressure nonmetallic material of density 2.0 and as a high-pressure metallic substance of density 5.73. Phosphorus has a low-pressure yellow form of density 1.82 and a high-pressure black form of density 2.70.

In this same connection, calculations have shown that hydrogen should transform to a metal at pressures beyond 400,000 atm and that $NH_3 + \frac{1}{2}H_2$ should become metallic at pressures beyond 200,000 atm. In such phenomena, pressure is affecting the electronic structure. Such effects offer exciting prospects for future high-pressure research. Since the chemical behavior of an element depends on its particular electronic configuration, gross disruption of this configuration by extremely high pressures could cause the element to behave quite differently. In effect, from a chemical standpoint, extremely high pressures could create a new periodic table.

The melting temperature of a substance is considerably altered by application of high pressure. For example, the melting point of germanium, which is 936°C at 1 atm, is depressed to 360°C (a change of 576°) by a pressure of 180,000 atm. Of course, germanium is an exception to the general rule that the melting point increases with pressure. High pressure has increased the melting point of some refractory materials by well over 1000°C. This fact makes it possible to work at higher temperatures at high pressures than would be possible at 1 atm (provided that the refractory insulation material surrounding the sample is subjected to high pressure, as it is in the tetrahedral anvil apparatus). As a matter of fact, it is quite possible to work with a "liquid" refractory under high-pressure conditions. A substance can flow only if it contains holes into which molecules can move. At pressures exceeding 100,000 atm the number of holes in a molten refractory can be severely reduced. Consequently, the material will be extremely viscous.

Work on the melting points of substances at high pressures has considerable significance in that it should throw some light on the old question about the possible existence of a critical point between liquid and solid which is analogous to the critical point between a gas and a liquid. Furthermore, since melting seems to be a phenomenon in which holes are introduced into a solid, and, since pressure has a strong influence on hole concentration, such studies should aid in obtaining a better understanding of the melting process.

Metallurgy

Metallurgy is an area in which "heat-treatment" has been extensively used to produce alloys with desired physical properties. The heat-treatment has of course been carried out at atmospheric pressure. Now many unsuspected solid phases exist under high-pressure conditions. For example, where only one phase of bismuth exists at 1 atm, eight phases are known in the area bounded by 130,000 atm and 500°C. The existence of additional solid phases, plus the fact that solubilities are greatly affected by pressure, offers exciting possibilities for the use of "pressure-treatment" in addition to heat-treatment in the metallurgy field.

The calculated yield strengths of many metals are 100 to 10,000 times greater than those measured. Yield strength is a structure-sensitive property—that is, the strength is dependent on the existence or nonexistence of vacant sites, dislocations, small and large-angle boundaries, and other factors. The elimination of the above-mentioned structures would result in an improvement of the yield strength of metals. Such an elimination would produce a decrease in volume of the material; and, since the application of pressure tends to drive processes in the direction of decreasing volume, such application might prove beneficial. There are undoubtedly activation (rate) barriers opposing the removal of the above structures. These barriers could be reduced by use of high temperature and catalysts (fluxes) in order to carry out the eliminations at a reasonable rate.

Most materials are polycrystalline. This is another factor causing lower than calculated yield strengths. Of course, a given weight of a single crystal would occupy a smaller volume than the same weight of polycrystals, since the density of the grain boundaries is about 10 percent less than that of the grains (crystals). There is also a certain amount of free energy associated with the grain boundaries. Application of high pressures would favor the elimination of grain boundaries and the growth of single crystals from polycrystals.

Electrical Conductivity

Pressures of 100,000 atm increase the electrical conductivity of most metals by about 20 percent. However, the conductivity of some metals is increased by as much as 400 percent. This phenomenon, of course, is in accord with the general fact that high pressure behaves similarly to low temperature. This raises the question: Is room-temperature superconductivity possible at sufficiently high pressure?

Conclusion

Research at ultrahigh pressures offers many possibilities in many disciplines for obtaining solutions to old problems and for the observance of new phenomena. Only a few possibilities have been suggested here. One thing is certain: in the ultrahigh-pressure field, there are vistas on the horizon.

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