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Shear Strength of Grossly Deformed Solids

A simple empirical shear strength formula is related to several problems in applied science.

Laird C. Towle and Robert E. Riecker

A prime motivation for investigating the mechanical properties of grossly deformed materials is the desire to achieve a fundamental understanding of the physical processes involved. Studies of the mechanical properties of crystals have been intensively pursued during the last 30 years. Attention has been focused primarily on single crystals and lightly strained samples. Many practical problems involve gross rather than slight deformation, and the properties of materials undergoing gross strain cannot be derived from investigations of lightly strained materials. Therefore we need experimental studies of gross deformation which provide some empirical background for characterizing materials in this interesting state where work-hardening has been driven to saturation. There is also a pressing need to synthesize these data into general guiding principles which can be used to predict the properties of materials not yet tested, or at least not yet tested under all practical conditions of interest. A fundamental understanding of the mechanisms of gross deformation may not be too difficult to achieve because the grossly deformed material has reached a steady-state condition which may be relatively simple compared to the transitory states that characterize more moderate deformation.

Experimentalists have concentrated primarily on the behavior of materials at atmospheric pressure. Although studies have been made over very wide temperature ranges, the pressure variable has been largely ignored. This is unfortunate since, in many applications, states of triaxial stress exist which contain large hydrostatic components. Studies of the effect of pressure on mechanical deformation can yield information of both practical and theoretical value, and it is with this aspect of the problem that the authors have been particularly concerned.

The earliest extensive data on the effect of pressure on mechanical properties are based on measurements of the shear strength of several hundred elements and compounds at room temperature in the pressure range up to 50 kb (*1*, *2*). Bridgman used the shear press primarily to seek polymorphic transformations through variations in mechanical properties. As a consequence, his strength measurements tend to be qualitative in character. In those cases where Bridgman made quantitative tests, as in his tensile tests under hydrostatic pressure (*3*), the materials investigated were complex alloy systems that did not lend themselves readily to detailed analysis. However, two general conclusions follow from Bridgman's measurements: (i) the strength of most solids increases rather slowly with pressure (~ 2 percent per kilobar); and (ii) fracture is suppressed by the application of hydrostatic pressure. Both conclusions favor the application of high-pressure techniques to industrial metal-forming operations.

Subsequent investigators have corroborated these general conclusions (*4*). Tests made by Vereshchagin and co-workers have been confined almost exclusively to metals, because hydrostatic pressure has immense potential advantages in industrial metal-forming; similar objectives motivated Pugh and co-workers (*5*). Although metal-forming under pressure is a subject of vital economic importance, it is too extensive to be reviewed here.

We still need to know much more about the basic mechanisms that are at work when solids deform under pressure. The authors have pursued this problem for almost 10 years in an effort to collect and synthesize data on the shear strength of solids. The materials investigated have ranged from minerals to metals and solidified gases. Some of the discoveries made during the investigation of the basic mechanisms of deformation have found immediate application.

Experimental Techniques

We have measured the shear strength of grossly deformed solids by two distinctly different techniques: extrusion and opposed anvils. In extrusion the shear strength is determined by measurement of the load required to force a sample of the material through a constriction, whereas in an opposed-anvil apparatus the shear strength is calculated from the torque required to shear a thin wafer of the sample material while it is compressed between flat, circular anvils.

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The extrusion process takes several forms. The simplest is direct extrusion. The sample, which is contained in a cylinder with a die in one end, is forced through the die by a closely fitting piston. The shear strength is calculated from the observed extrusion pressure by plasticity theory (*6*). In direct extrusion the sample billet slides against the cylinder walls; this results in a large frictional resistance which varies with the length of the sample. Absolute measurements of shear strength require measurement of the extrusion pressure as a function of length with extrapolation to zero length. In inverted extrusion the die is held in the end of a hollow piston which itself advances into a cylinder containing the sample material. Since the sample billet does not slide against the cylinder walls and the friction problem is avoided, reliable measurements of strength require the extrusion of only a few millimeters of sample material. Measurements on solidified argon by both direct and inverted extrusion (*7*) are identical within experimental error (~ 5 percent). The inverted extrusion technique, however, is simpler, faster, and more accurate.

Both techniques are suited to the measurement of the temperature dependence of the shear strength only at atmospheric pressure. In order to determine the pressure dependence of the shear strength, we have employed a chamber-to-chamber extrusion device. The shear strength is calculated from measurements of the pressure differential required to cause flow of the solid through a tube which connects two high-pressure chambers. Measurements at high pressure are made by an initial application of an identical pressure to both chambers followed by superimposition of a pressure differential (*8*).

In the opposed-anvil technique the sample wafer shears between flat anvil faces. The upper anvil rotates at constant speed, and a strip chart records the torque required to prevent rotation of the lower anvil. Large strains are applied to the sample. The sample rapidly work-hardens, and after a few degrees of rotation a steady restraining torque appears. At low applied pressures surficial slippage between the anvil faces and the sample characterizes the steady state. As the applied pressure is increased, the frictional stress eventually exceeds the shear strength, and then internal flow predominates. A knee on the curve of stress plotted against pressure indicates the transition from surficial slippage to internal flow (Fig. 1).

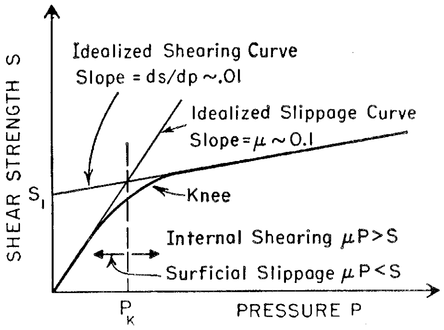


Fig. 1. Schematic representation showing the relation between the shearing torque and applied pressure (*9*).

The slope of the curve to the left of the knee equals the coefficient of friction between the sample and anvil. Data to the right of the knee represent valid measurements of the shear strength in a grossly deformed state. Results obtained on copper, silver, and gold at room temperature are shown in Fig. 2. The low slope of these curves to the right of the knees indicates that the strength of these metals increases slowly with pressure. The intercepts at zero pressure give reasonable values for shear strength when the metal is work-hardened to saturation at atmospheric pressure (*9*). Strain and strain rate vary across the radius of the sheared wafer, and pressure gradients may develop. When these factors do not cause difficulty (*10*), the opposed-anvil technique conveniently measures the pressure and temperature dependence of the shear strength of solids. We have run tests at room temperature to pressures of 150 kb, and at temperatures up to 950°C at simultaneous pressures up to 60 kb.

In general, extrusion processes are most convenient for strength measurements on soft materials at relatively low pressures. The opposed-anvil technique is more appropriate for measurements on strong solids at very high pressures and temperatures.

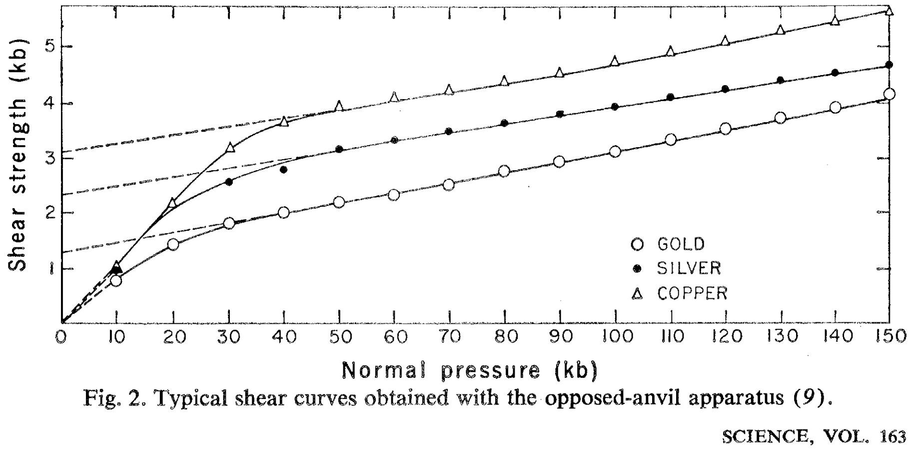


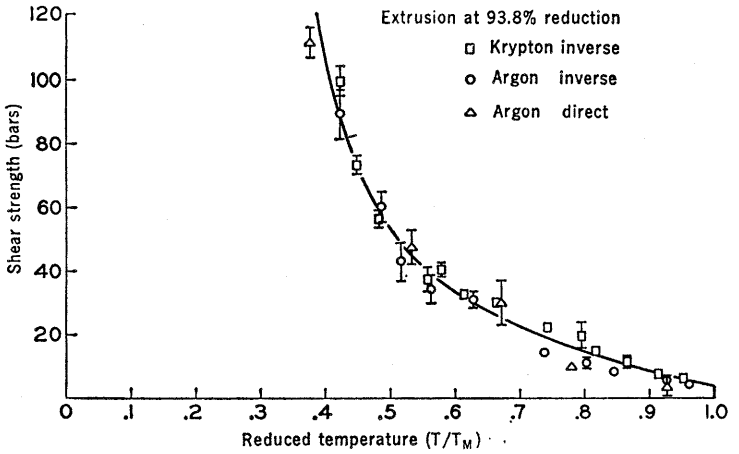
Fig. 2. Typical shear curves obtained with the opposed-anvil apparatus (*9*).

Fundamental Investigation of Mechanical Properties

We have obtained shear strength data on grossly deformed solids that exhibit several types of crystalline cohesion. Measurements have been made on molecular crystals such as argon, on metallic elements such as copper, and on minerals such as olivine that are bonded covalently and ionically. In spite of the diverse characteristics of these solids, the measurements conform to a simple and consistent pattern.

The temperature dependence of the shear strengths of argon and krypton are very similar. The two sets of data can be superimposed by application of a suitable scale factor to the temperature axis (*7*) (Fig. 3), where shear strength is plotted against reduced temperature T/T_m; T is the temperature at which the strength was measured, and T_m is the melting point of the material. The shear strength follows a law of corresponding states in which temperature, as measured relative to the melting point, determines the strength.

The reduced temperature is an implicit function of pressure because the melting point is pressure-dependent. As pressure is applied, the melting point is raised which lowers the reduced temperature. According to Fig. 3, a lower reduced temperature should increase shear strength. Measurements of the pressure dependence of the shear strength of argon and krypton (*8*) are plotted on a reduced-temperature scale (Fig. 4). Melting curves (*11*) were used to transform the pressure variable to the reduced temperature variable. The smooth curve (Fig. 4) is transcribed from Fig. 3. A comparison of these data indicates that the pressure dependence of the melting point entirely accounts for the pressure dependence of the shear strength of these molecular solids and, hence, that the shear strength



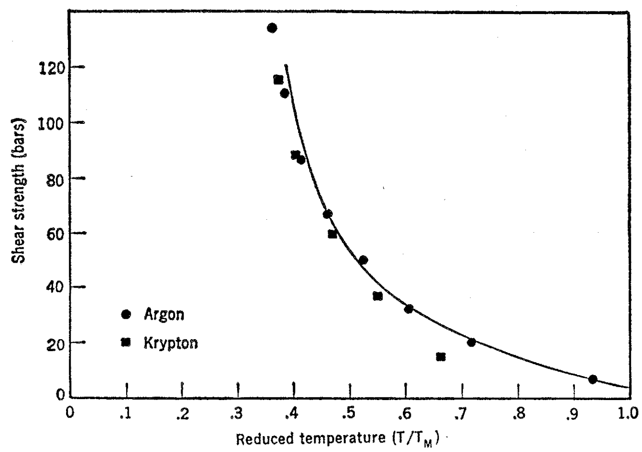


Fig. 3 (left). Shear strength of argon and krypton plotted against reduced temperature (*9*). Fig. 4 (right). Shear strength of argon and krypton plotted against reduced temperature. Data shown by solid circles and squares were obtained under high pressure and were converted to the equivalent reduced temperature using the known melting curves of these materials. The curve was transcribed from Fig. 3.

of these materials is a function of reduced temperature at the strain rates employed here.

The functional form of this dependence has been found to be an exponential (*12*). Thus when the natural logarithm of S is plotted against the reduced temperature T/T_{m}, the data fall along a straight line within experimental error. Hence, the pressure and temperature dependence of the shear strength of these solids can be represented by the following empirical law

$$S(T,P) = S_0 \exp\left[bT/T_{\mathrm{m}}(P)\right] \qquad (1)$$

where S_0 and b are constants characteristic of the material. When these data are plotted on a semilogarithmic scale, S_0 is the intercept on the shear strength axis when T/T_{m} is equal to 0 and b is the slope of the straight line.

In addition to the data on argon and krypton discussed above, measurements on silver chloride (*12*) and copper, silver, and gold (*9*) are consistent with Eq. 1. Thus experimental data on widely different materials indicate that Eq. 1 may be a generally valid expression for the shear strength of grossly deformed materials.

Since we are interested in the gross deformation of materials at relatively high rates of strain, we will assume that ductile behavior results from crystalline glide. A variety of detailed mechanisms have been suggested to explain glide phenomena. The flow stress is limited either by the stress required to move dislocations through the lattice or by the stress required to generate new dislocations (*13*). In either case the flow stress is proportional to the shear modulus of the material. Thus in Eq. 1 we expect S_0 to be proportional to $G(P,T)$, where G is the shear modulus, a slowly varying function of both temperature and pressure.

The temperature dependence of the shear modulus is relatively small. For example, in metals G varies by about a factor of two between absolute zero and the melting point (*14*), whereas shear strength varies by a factor of a hundred or more. Hence, we neglect the temperature dependence of the shear modulus in what follows. This approximation may lead to a small error in the parameter b which controls the temperature dependence of the shear strength in Eq. 1.

The pressure dependence of the shear modulus is also small. It increases approximately linearly with pressure for many materials at a rate of about 1 percent per kilobar (*15*). For materials with a high or pressure-insensitive melting temperature (or both), the exponential term in Eq. 1 becomes practically independent of pressure. The pressure dependence of the shear modulus then becomes important. Hence, we may rewrite Eq. 1 in a more general form

$$S(T,P) = aG_0(1 + \gamma P) \exp\left[bT/T_{\mathrm{m}}(P)\right] \qquad (2)$$

where a is a proportionality factor, G_0 is the shear modulus when P is equal to 0, and γ is a material parameter.

This generalized equation has been applied to shear measurements on the minerals diopside, labradorite, and olivine (*16*). We illustrate this application for diopside in Fig. 5; shear data are plotted in the upper part of the figure on a semilogarithmic scale. The temperature dependence of the shear strength at some fixed pressure agrees with Eq. 1, as shown by the line drawn through the points at a pressure of 40 kb. Test results taken at several constant temperatures as a function of pressure are connected by short line segments. Equation 1 does not account for the large pressure dependence because the melting point of diopside is high and relatively insensitive to pressure. Hence the pressure dependence of the shear modulus becomes important.

The data for diopside were fitted to Eq. 2 by a least-squares procedure. The constants aG_0, γ, and b assumed the values 5.9 kb, 0.032 kb^{-1}, and $-$ 1.1, respectively, which are the expected orders of magnitude. The calculated and experimental values of the shear strength are compared by considering the strength ratio R, defined as

$$R = S/aG_0(1 + \gamma P) = \exp\left[bT/T_{\mathrm{m}}\right] \qquad (3)$$

This ratio is plotted in the lower part of Fig. 5. The data fit the generalized formula very well. Similar results were obtained on olivine and labradorite.

Equation 2 has also been applied to shear data on copper, silver, and gold. The pressure coefficient of the shear modulus γ and the other parameters in Eq. 2 are of the expected magnitudes. Since γ is small for these materials, Eq. 1 also fits the data reasonably well (*9*).

We conclude that Eq. 2 is a useful empirical equation relating the pressure and temperature dependence of the shear strength of solids. It fits data on the molecular crystals argon and krypton; on the metals copper, silver, and gold; and on the ionically and covalently bonded minerals olivine, diopside, and labradorite. The possible theoretical basis of Eqs. 1 and 2 has been discussed elsewhere (*17*).

Evaluation of Pressure-Transmitting Media

We now consider the evaluation of soft solids for use as pressure-transmitting media. During an investigation of the effect of high pressure on the properties of materials, the sample is usually placed in a chamber where it is surrounded by an inert pressure-transmitting medium. Load is then applied to the medium by one or more pistons. The pressure transmitted to the sample is hydrostatic, only if the medium is fluid and the load is applied slowly. If the medium is not fluid, the pressure on the sample is nonhydrostatic and the mechanical properties of the medium become important.

Silver chloride has been used as a pressure-transmitting medium near room temperature for many years. Bridgman made measurements of the pressure dependence of the shear strength of this solid at room temperature to 50 kb (*2*). He observed a moderate increase in strength at high pressures. We determined the temperature dependence of the shear strength of silver chloride by the inverted extrusion technique (*18*) (Fig. 6). A sharp increase in strength at temperatures below about 200°K restricts the usefulness of this material as a pressure-transmitter at low temperatures.

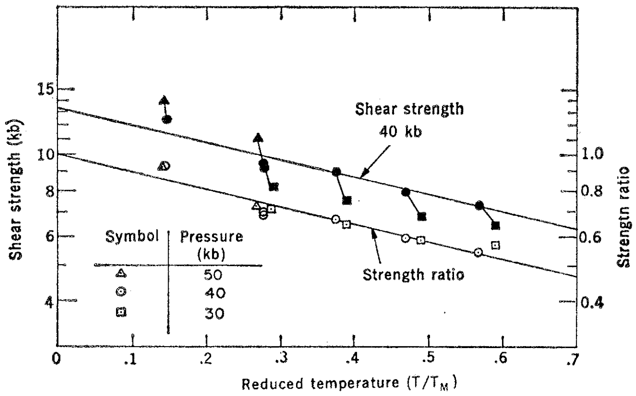
Selection of low-temperature pressure-transmitting media is particularly difficult. Stewart made a qualitative comparison of the shear strengths of a variety of soft solids at low temperatures (*19*). He found that the solidified rare gases and solid hydrogen are the most promising materials for studies at low temperature. Although liquid helium can be used at moderate pressures, it cannot be reliably confined by a piston with any known packing. Helium solidifies at relatively low pressures, and the solid is also difficult to confine in a piston-and-cylinder apparatus. We have determined the shear strength of argon and krypton by extrusion techniques (*7, 8*). Strength increases dramatically as the temperature decreases or as pressure rises. These solids remain soft and plastic only at pressure-volume conditions close to their melting curves.

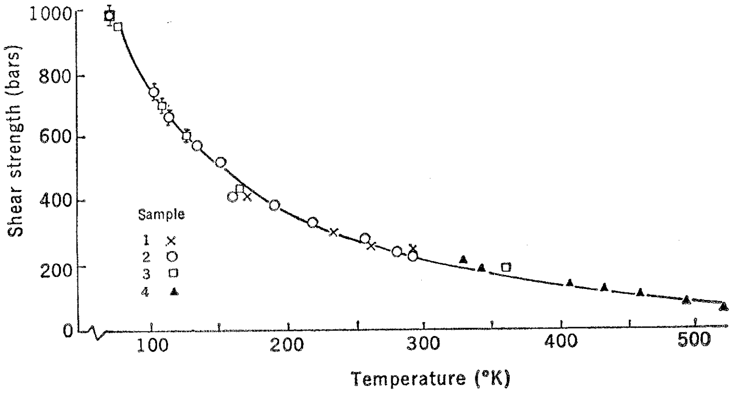
Haynes measured the effect of pressure on the shear strength of solid methane at 77.3°K by the chamber-to-chamber extrusion technique (*20*). Figure 7 shows his results and includes our argon data for comparison. At 77.3°K, methane is stronger than argon at atmospheric pressure. Above about 1 kb, argon is strongest. At very high pressures, methane becomes a much better pressure-transmitter than argon at 77.3°K. When these data are plotted on a semilogarithmic scale and reduced temperatures calculated from the known melting curve are used, we find agreement with Eq. 1. The slow increase of the melting point of methane with pressure accounts for the difference in behavior between methane and argon.

Some of the solidified gases are quite soft and ductile as compared to silver chloride, and these gases serve as satisfactory pressure-transmitting media at low temperatures. When held under pressure-volume conditions close to their melting curve, they are extremely soft and can be used like hydraulic fluids. Towle and Stajdohar (*21*) illustrated this behavior with a force intensifier which operates on hydraulic principles with a solidified gas as working fluid.

Seismic Events and Earth Mechanics

A second area in which mechanical data on grossly deformed solids find practical application is geophysics. Although man has lived on this planet for millennia and now samples distant space, he knows very little about the nature of the earth's interior. The deepest direct penetration by drilling or mining is less than one one-thousandth of the earth's radius. Elastic waves gen-





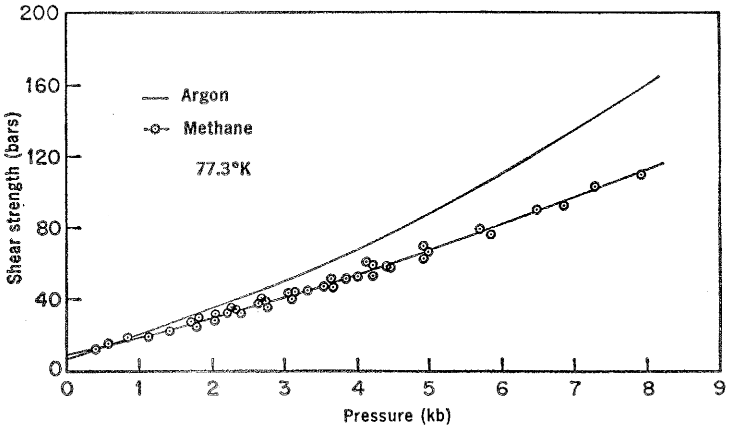


Fig. 5 (top left). Shear strength plotted against reduced temperature for the mineral diopside. The shear strength data are shown with solid symbols; the open symbols are the strength ratio calculated from Eq. 3 plotted with the right-hand vertical scale (*16*).

Fig. 6 (top right). Temperature dependence of the shear strength of silver chloride. Data are shown for four samples of high-purity polycrystalline stock (*18*).

Fig. 7 (right). Pressure dependence of the shear strength of argon (*8*) and methane (*20*) at 77.3°K.

erated by earthquakes and explosions reveal that the earth is much more heterogeneous, dynamic, and interesting than we might have expected. Still, we know little about the mechanism for the origin of earthquakes, the causes of mountain building, and whether the continents have been stationary for 4.5 billion years or have drifted around the earth's surface under the influence of internal solid-state currents. What is the nature of the earth's heat engine which underlies all tectonophysical phenomena?

Many of these fundamental questions about the earth's interior may be partially answered by studies of the mechanical properties of rocks and minerals exposed to geologically realistic conditions of high pressure and temperature. Do rocks at a depth of 100 km fracture when stressed and thereby generate earthquakes, or do rocks become ductile under the influence of high pressure and temperature so that brittle behavior is precluded? Does faulting cause earthquakes, or are faults the results of earthquakes?

Most of the dynamic geological and geophysical processes that we see at the earth's surface originate at depths of less than 300 km. These processes and related phenomena include the presence of most earthquake foci, the low-velocity channel of the mantle, the Mohorovicic discontinuity, parts of the mantle transition zone, the development sites for magmas which manifest in volcanism and plutonism, the level of isostatic compensation, the major concentrations of radioactive elements, and many more. Unfortunately, apparatus limitations prohibit exploration of the mechanical properties of rocks and minerals at conditions simulating depths much greater than several tens of kilometers. Present maximum test conditions reach at most several hundred kilobars and a few thousand degrees Kelvin and usually not simultaneously. This is equivalent to much less than 1000 km depth—far from the megabar pressures and extremely high temperatures present in the earth's core. Available alloys and cermets now prohibit exploration of these very deep regions in the laboratory, because sufficiently strong temperature-resistant components are unavailable. We require major breakthroughs from the materials scientists before really deep earth environments can be simulated in the laboratory by the use of static tests.

If we cannot directly explore the properties of the very deep earth, then perhaps it is possible to examine these properties by careful extrapolation from known conditions or by the use of analogs. With the opposed-anvil technique we have explored the shear strength of a wide variety of rocks and minerals of the crust and upper mantle. Most of the tests reached maximum simultaneous conditions near 1000°C and 60 kb. Two special experimental problems complicate geologic studies on the mechanical properties of rocks—the effect of size or scale and the effect of time. Most experiments can be properly scaled to a laboratory test. Some scaling yields surprises, as when continental-sized rock bodies exhibit properties more like butter than rocks. Time is more difficult to handle. The slowest strain rates in the rock mechanics tests approach 10^{-8} per second. This is a long way from the so-called "geologic test" at 10^{-14} sec^{-1}. At the other end of the spectrum of strain rates, explosives yield strain rates of 10^{5} sec^{-1} or more. The behavior of many materials depends strongly on strain rate as well as on pressure and temperature; thus rate effects become extremely important when dealing with natural earth processes where strain rate varies from "fast" earthquake rates to "slow" creep rates relevant to continental drift. We performed almost all of our tests at a constant strain rate of 10^{-1} sec^{-1}. Variations as slow as 10^{-4} sec^{-1} produce only slight displacement of the data in harmony with the experience of Bridgman (*2*) and Heard (*22*).

Several of the shear results suggest important applications in geology and geophysics. Geologists have been concerned by the laboratory observation that most rocks exhibit great strength, whereas analysis of stress drops associated with earthquakes suggests weakness. We need to find ways to make strong rocks weak. The earth contains many hydrous minerals. When the dehydration temperature of these minerals is exceeded, pore pressure develops and reduces the effect of confining pressure with a concomitant decrease in strength (*23*).

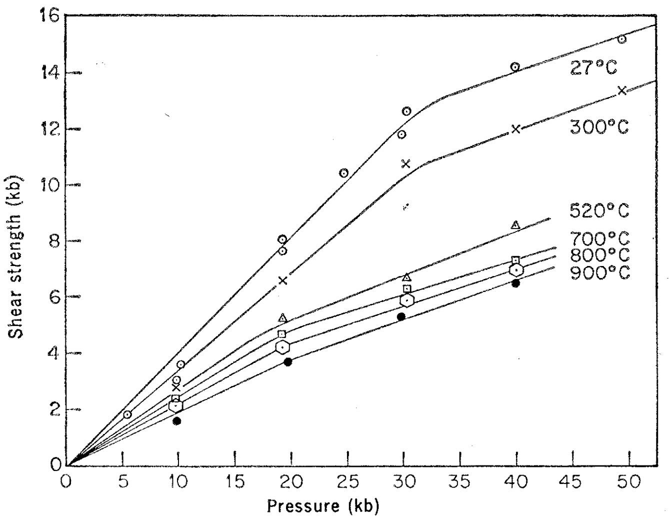
Shear testing on olivine associated with less than 5 percent hydrous serpentine revealed that dehydration weakens the otherwise strong olivine enormously (*24*). The pore pressure effect is illustrated in Fig. 8. Our samples are not completely gasketed to totally prevent the escape of water vapor during a test. If we could prevent the vapor escape while obtaining the shear strength, we would observe still smaller values of strength. Pure hydrous serpentine exhibits the same effect (*25*). This is one possible process by which strong rocks can become weak.

Another application of pore pressure phenomena pertains to the explosion of nuclear devices underground. Most of these detonations have been set off in tuff—a soft, easily mined, hydrous alteration product of volcanic rock. The shear properties of this rock (*26*) revealed anomalous weakening induced by dehydration. This behavior becomes important near the detonation point where ambient temperatures may rise above the required dehydration temperature.

In addition to the mechanical behavior of natural materials, the modes of deformation and the polymorphism exhibited by deformed rocks are of interest. Only a few minerals, such as quartz, calcite, and dolomite, have been studied systematically. During shear testing of the mineral enstatite we observed peculiar behavior in the shear curve at room temperature (Fig. 9). Optical and x-ray analysis revealed that a polymorphic transition had occurred from an initial orthorhombic form to a final monoclinic form (*27*). The transition was rapid, requiring less than a second under the influence of shear stress. However, the transition would not occur under the influence of static pressure alone, even over test periods as long as several days. Furthermore, the transition was associated with a small but finite change in volume. This is significant because a potential source mechanism for earthquakes must release up to 10^{24} ergs of energy in 1 second. Using a sufficiently large volume (1 km^3) of enstatite, we suggested that rapid transformation could produce a modest earthquake (*27*). This phase transition thus provides another alternative to the fault source for the generation of seismic energy.

Solid Lubricants

Solid film lubricants are finding extensive applications in environments where conventional oils break down or are inconvenient to use. Solids can function as lubricants when their resistance to shear is small. Since the localized pressures between contacting parts can be quite high, a need exists for data on the pressure and temperature dependence of the shear strength of solid lubricants.



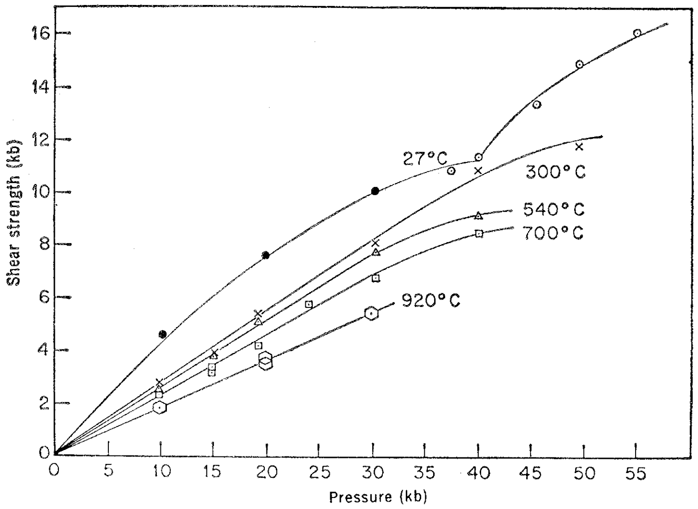


Fig. 8 (left). Pressure dependence of the shear strength of olivine at several temperatures. The large drop in strength between 300°C and 520°C is caused by the dehydration of about 5 percent (by weight) serpentinite in the samples (*24*). Fig. 9 (right). Pressure dependence of the shear strength of enstatite at several temperatures. X-ray and optical examination revealed that the orthorhombic starting material had undergone a polymorphic transition to a monoclinic form at all test conditions except those shown by solid circles (*27*).

The coefficient of friction μ is the ratio of the frictional force F to the normal load W. Microscopically, solid surfaces are always rough; when two bodies are placed together, contact occurs only where the asperities on each of the surfaces meet. As a consequence, the contact area A is normally much smaller than the macroscopic dimensions of the contact region. Bonding occurs at superposed asperities. The frictional force arises because sliding of the surfaces requires shearing of these asperities. The magnitude of this force is given by the product of the actual contact area and the shear strength of the weaker solid. The area of contact is given approximately by the ratio of the normal load to the yield stress Y of the weaker material:

$$\mu = F/W = SA/YA = S/Y \tag{4}$$

Lubrication occurs when a thin film of soft solid separates harder substrates because of the low shear strength of the film S_f and the high yield stress Y_s of the substrate. If we assume that the film is very thin (so that the area of contact is equal to the area of the asperities which must be sheared), then the friction coefficient becomes

$$\mu = S_f/Y_s \tag{5}$$

whereas the friction coefficient for the film material in bulk would be

$$\mu_f = S_f/Y_f \tag{6}$$

These equations combine to give

$$\mu = \mu_f\,(Y_f/Y_s) \tag{7}$$

which indicates that the coefficient of friction will be small if a very soft film is placed on a very hard substrate (*28*).

Because the contact areas are small, the contact pressures can be quite large (of the order of the strength of the substrate) for rather nominal loads. The shear and yield strengths of solids increase with pressure, and hence, the coefficient of friction will be pressure-dependent. A knowledge of the pressure dependence of these properties is essential for an understanding of the frictional properties of solid lubricants. The yield strength and shear strength of materials are essentially proportional, and hence their ratio is nearly independent of pressure. Thus μ_f should be independent of pressure, which is in agreement with experiment. However, μ depends on the properties of both the lubricant film and the substrate (Eq. 7). Since they may be influenced to different degrees by pressure, we expect μ to show some pressure dependence.

Although friction has been studied extensively, relatively little effort has been devoted to an investigation of the effect of pressure on the commonly used solid lubricants and substrates. The most extensive measurements available are those of Boyd and Robertson (*29*) which compare 24 solid lubricants. The general conclusion to be drawn from their work and also that of Bridgman (*1, 2*) is that inorganic materials exhibit a much smaller increase in shear strength with pressure than is observed with organic materials.

Miscellaneous Applications

Investigations of the effect of pressure and temperature on grossly deformed solids can also be used to study the phase diagrams of solids, to search for polymorphic forms, and to assist in the synthesis of particular compounds. Bridgman used an opposed-anvil shear

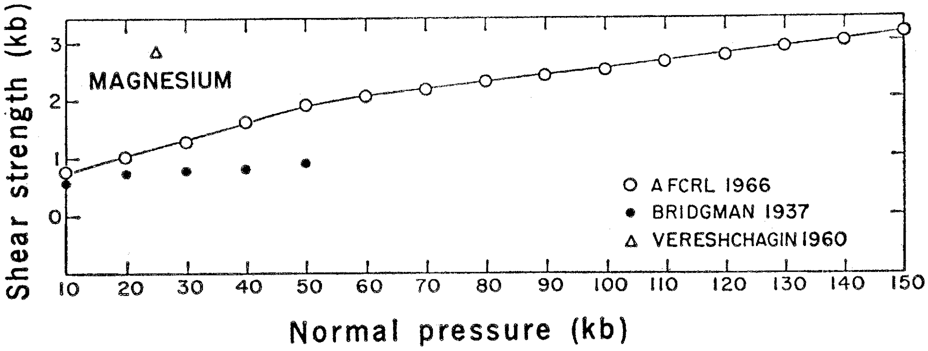


Fig. 10. Pressure dependence of the shear strength of magnesium at room temperature. The discontinuity in the slope of the curve is indicative of a phase transformation (*30*).

apparatus in an extensive search for polymorphic forms (*1*, *2*).

We have recently observed a solid-solid phase transformation in magnesium by use of the anvil technique (*30*). The shear strength of this metal is plotted against pressure in Fig. 10. The phase transformation is indicated by a distinct change in slope at about 52 kb. The lattice constants and volume of magnesium vary smoothly with pressure and give little indication of any phase transformation (*31*). However, there is a small anomaly in the crystallographic c/a ratio at about 50 kb. A new line was subsequently seen in the x-ray powder patterns at about 50 kb which suggests a structural change from the hexagonal close-packed (hcp) to the double hexagonal close-packed (dhcp) structure (*32*). A minimum in electrical resistance at about 50 kb also reflects this first-order phase transformation.

Although electrical measurements indicate qualitatively similar behavior in isomorphous zinc, x-ray determinations of structure under pressure have failed to establish the occurrence of the hcp to dhcp transition in zinc (*31, 32*). Shear data at present indicate a phase transformation at about 113 kb. Thus relatively simple and direct mechanical measurements can frequently give unequivocal indications of polymorphic transformations in cases where more difficult and sophisticated techniques lead to ambiguous results.

Shear strains in gross deformation experiments produce both beneficial and detrimental side effects. Many phase transformations and solid-state reactions proceed more rapidly in the presence of shear stresses. In moving from one equilibrium state to another during the transformation or reaction, the molecular units may overcome energy barriers. Although thermal activation energy is a major factor in overcoming these barriers, the mechanical work done by the shear stress can also make a significant contribution (*33*). Some transformations and reactions occur only in the presence of shear. Minerals which exhibit this exclusive behavior are called stress minerals. The clinoenstatite discussed above is one example (*27*). On the other hand, shear tends to change not only the rate at which transformations occur but the pressure-volume-temperature conditions as well. Phase boundaries established by shear tests do not necessarily coincide with equilibrium phase boundaries. Thus far, few practical applications have taken advantage of the catalytic effect of shear stress.

Finally we mention some indirect applications of Eq. 2. If the equation is valid, then by making measurements of shear strength on a solid over a wide range of temperatures and pressures, we can determine the value of the parameter γ which determines the pressure coefficient of the shear modulus G. This parameter is difficult to measure under high pressure by any other technique; hence, the validity of this procedure is important.

Thus far we have applied Eq. 2 to three metals and to three minerals and have obtained reasonable values for the parameter γ. However, the data are neither sufficiently extensive nor sufficiently accurate to establish whether Eq. 2 is valid to within limits closer than about ± 10 percent. As a consequence, the values of γ are of only limited practical value now. One potential application may be the determination of the equation of state through measurements of shear strength.

Ultrasonic measurements on several polycrystalline metals show that the bulk and shear moduli increase linearly with pressure at essentially the same rate (*15*). Thus

$$G = G_0 (1 + \gamma P) \qquad (8)$$

and

$$K = K_0 (1 + \gamma P) \qquad (9)$$

where G_0 and K_0 are the shear and bulk moduli, respectively, at zero pressure. Equation 9 can be integrated to derive an equation of state

$$V/V_0 = (1 + \gamma P)^{-1/\gamma K_0} \qquad (10)$$

where V_0 is the volume at atmospheric pressure. Since we know K_0 for most materials, we can determine the equation of state by evaluating γ in shear tests. We have applied this technique to copper, silver, and gold and have observed good correlation between calculated and experimental compressions V/V_0 for copper and silver. The results for gold were less satisfactory. However, the value of γ for gold was quite uncertain because the data did not fit Eq. 2 as well.

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