

What are the, COMBINED EFFECTS OF TEMPERATURE AND VERY HIGH PRESSURE ON METALS?

The inception of high-pressure, high-temperature operations has opened many new avenues of investigation. The author discusses the possible effects of both on electrical resistance, ductility, hardening, and other mechanical and structural properties of metals.

by R. B. Fischer

One of the greatest potential fields for metallurgical research was opened when means were developed to apply high temperatures to materials under very high pressures. The background for the subject was built over the years by the integrated efforts of many individuals, but the development of apparatus by General Electric Co. fired the imagination of researchers.

To those whose routine efforts are devoted to producing and marketing a metal product, there will be an understandable reserve about getting excited over this subject, since the high-pressure, high-temperature cells available to date are small. On the other hand, the Engineering Supervision Co. recently offered to provide considerably larger cells than those used to date. No technical barriers seem to bar the construction of larger cells when needed; therefore, there is little cause for concern on this particular point.

More important is the question of what can be accomplished by the use of combined temperature-pressure operations. Here researchers, now adequately equipped, are striving for answers. Their efforts will bear close observation, because the results might bring about a drastic change in materials as we now know them. The use of high-temperature, high-pressure apparatus in studies of materials is so vast as to appear limitless. Facing this scope of possibilities, can one honestly maintain doubtful reservations about the potential of this subject? Advances are being made already in developing basic knowledge which will, at a minimum, feed back to help understand and improve present processes.

Effects on melting temperatures

For practical purposes, the melting temperature of a metal has long been treated as a constant. For example, temperature calibrations are based sometimes on the melting point of a pure metal. In the future, it is likely that the question, "What is the

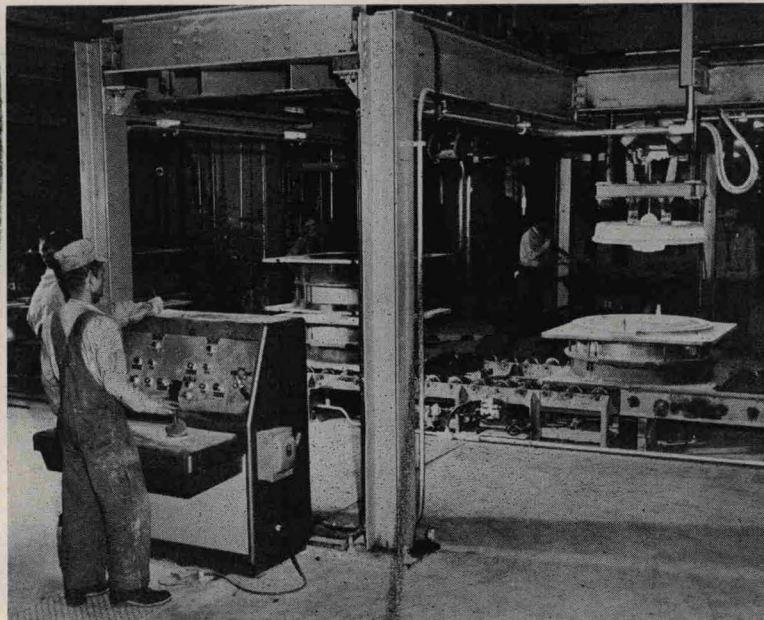
melting temperature of iron?" will be recognized by technologists as demanding the counter question, "At what pressure?". Recent work described by Strong⁽¹⁾ illustrates the point. Strong's work and others^(2, 3, 4, 5), has been used in Fig. 1 to show the relationship of melting temperatures versus pressure for several metals.

At this time, the Clapeyron-type equation, $dT/dP = T_m(\Delta V)/L$, is useful for predicting the effect of pressure on melting temperatures. The expression dT/dP is the change of melting temperature with a change of external pressure. If the proper units of T_m , the melting point at zero pressure, ΔV , the volume change on melting, and L , the latent heat of fusion, are substituted in the equation, fairly good estimates can be made. For those metals that expand on melting, an increase in pressure generally results in a higher melting temperature, since pressure tends to prevent expansion (and melting). This situation is overcome by increasing the temperature to the extent that melting can occur. In general, an opposite relationship exists for those metals that contract on melting; an increase in pressure lowers their melting temperature.

There is a question as to the extent that these relationships hold at higher pressures and temperatures, not yet attainable in present apparatus. It is known for bismuth, that the melting temperature decreases with increasing pressure to a point where the metal transforms into a new solid phase. This new phase has a melting temperature curve which then increases with pressure. The melting temperature curve for rubidium increases with pressure to a maximum and then decreases, but this is unusual, as Strong⁽¹⁾ has indicated. For other metals, melting temperatures have been found to increase or decrease as expected up to the limits of present apparatus. Will these relationships continue; will phase transformations occur; and what are the ultimate results of pressure application to metals? These are interesting questions for conjecture, but what can be done with the knowledge already at hand on the effects of pressure on melting temperature of metals?

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Right, view of operations . . . wheel at left has just been poured. Crane at left removes the cope, while crane at right removes a previously-poured wheel.



Left, a close-up view of the pouring tank and cover.

Applied to steel mills

Application of the pressure-pouring process to the casting of semi-rolled shapes has been the subject of considerable investigation by Griffin's metallurgists, even prior to U.S. Steel's interest in the technique. The objective has been the elimination of high-cost primary rolling mills and soaking pits.

Many types of steel have been used in Griffin's experiments; they have varied in carbon content from 0.10 to 1 pct, and have included stainless types and boron steels. Perhaps the greatest interest has been in casting slabs, and Griffin has cast slabs measuring 5x37.5 in. x 15 ft from low-carbon steels. Stainless steel slabs also have been cast, and tube rounds up to 6 in. in diam have been cast without segregation. With reference to billets, experimental work has shown the possibility of casting 3x3 in. x 30 ft shapes from 150-ton heats in 40 min. Thus, pouring is rapid and stripping can also be accomplished with considerable speed.

These semis have been characterized by good surface finish, practically eliminating the necessity of scarfing and other surface treatment. One problem is that of center-line shrinkage; in practice it will probably necessitate a sealing of the ends of the cast shape in order to prevent oxidation stringers from forming. Because of this shrinkage, finished rolled shapes can not be cast. However, it appears likely that subsequent rolling can produce steel products of a quality equivalent to present commercial practice.

The difference between pressure pouring and present techniques appears to lie both in capital costs for steel-mill equipment and in production costs encountered in soaking pit, rolling, and scarfing operations. A further saving would result from increased yield of usable metal, resulting from an elimination of hot tops and cropped ends of semi-rolled shapes.

U.S. Steel's pilot-plant work in the next two years should answer the question of whether pressure pouring can be applied commercially to steelmaking.

So far as is known, no industrial use has been made of the information that melting temperatures of metals may vary with pressure. The author's opinion is that, in time, uses will develop as the facts become better known and people dwell on possible applications.

Melting temperature information is of importance in gaining new information about the solid and liquid states of metals. It increases our scientific understanding of metals, and, in turn, this information should feed back to promote better industrial processes.

One scientific area may be cited in which melting temperature versus pressure data are important. In Strong's article⁽¹⁾, he shows how geophysical information of the Earth's structure is being advanced. Previously, data on the melting temperatures of iron were extrapolated to build theories on the core structure of the Earth. New high-pressure data have shown there was considerable error in the extrapolations. Because of the limits of present pressure apparatus, extrapolation is still necessary, but accuracy has been improved, and old formulae can be revised to match more realistic values. Much more work is needed, but significant progress has resulted from the recent high-pressure, high-temperature work.

Melting temperature data are valuable to researchers involved in high-pressure studies. Strong⁽¹⁾ has pointed out that thermocouples might be used in high-pressure apparatus at temperatures higher than the *melting points* of the thermocouple metals! As another example, a platinum heating element or structure in a high-pressure device might be retained in the solid state at 3700°F, although we usually think of platinum as a liquid at about 3225°F. Molten germanium at the relatively low temperature of 1000°F might be brought into contact with another material, if desired. Usually, a temperature of about 1650°F is considered necessary to melt germanium. Aluminum and germanium have the same melting temperature at about 325,000 psi. Thus, limitations of commonly expressed constants for melting point can be removed to some extent from research activity.

Another use of melting temperature data is in the design of new high-pressure cells. For example, liquid germanium could be confined under pressure, and, by cooling it below its freezing temperature, very high pressures could be produced. As Hall⁽²⁾ has mentioned, the behavior of germanium is such that it is an excellent standard for very high-pressure calibration work.

Effects on phase changes and shifts

Several outstanding effects of pressure on phase changes of metals have been found. Butuzov⁽³⁾ has presented the phase diagram of bismuth with pressure as a factor as shown in Fig. 2. Such data are useful in the calibration of high-pressure, high-temperature devices. Methods are being developed to determine the crystal structures of the bismuth phases. These phase changes are reversible; therefore, X-ray diffraction data must be obtained while the metal is under pressure. The uses of a diamond cell for such studies has possibilities.

Hall⁽⁵⁾ has reported that a hitherto unknown form of tin has been produced at high temperature and high pressure. No doubt other new phases in metals will be found in the future.

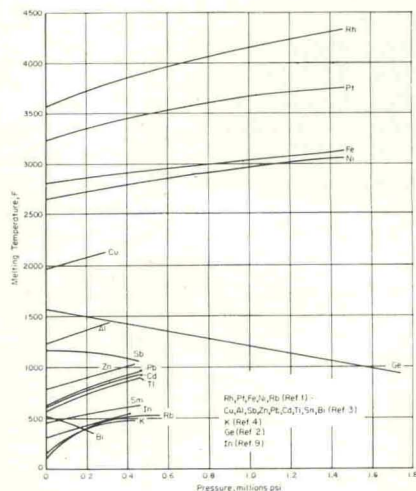


Fig. 1—Melting temperatures of several metals at various pressures.

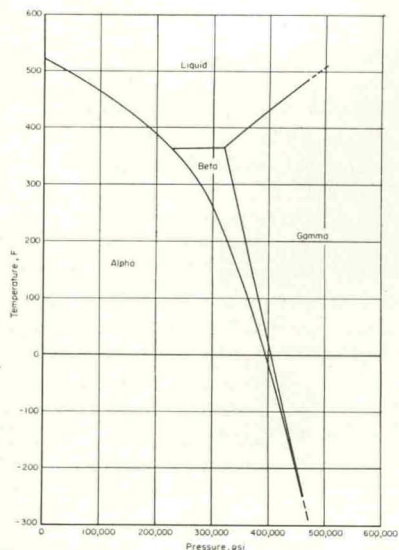


Fig. 2 Phase diagram of bismuth (Ref. 3).

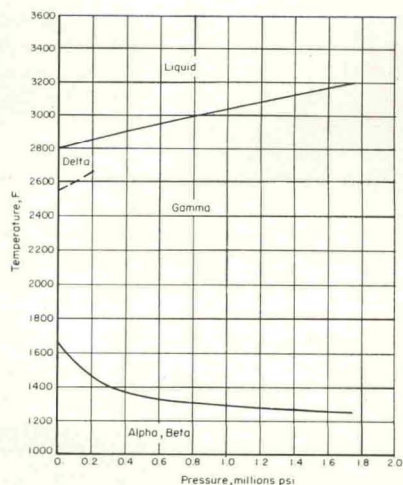


Fig. 3—Effect of pressure on phases of iron (Ref. 1).

Before high-pressure, high-temperature data were available, calculations were made on the transformation of α to γ iron under high pressure. The calculated values were used to help explain the history of meteorites. Laboratory data, such as that given by Strong⁽¹⁾, reveal that the theoretical values do not check with the measured values (Fig. 3). From this information, theory can be revised and a better understanding of meteorites obtained. Possibly, the information on meteorites will assist in solving re-entry missile problems.

The α to γ transformation temperature of iron is lowered by high pressure, as expected. (Alpha to gamma involves a contraction, which should be favored by pressure.) This effect will be studied intensely in the future because of the basic importance of this transformation to the steel industry. Efforts are now under way on such studies with the objective of developing steels with better properties. One good possibility is that the use of high pressure during heat treatment of steels should result in finer-grained steels with better properties. This is based on the principle that less grain growth should occur at the lower transformation temperatures possible with high pressure.

Hall⁽²⁾ has mentioned a heat treatment of steel under high pressure. The steel is raised to the transformation temperature, and pressure is applied suddenly to freeze the new structure. Exceptional ductility and through hardening are claimed.

In addition to forcing materials into new phases (e.g., the reversible phases of bismuth) and the lowering of transformation temperatures, high pressure can be expected to cause shifts in composition from those limits now established on constitution diagrams. Thus, high pressure adds to the present two-dimension binary diagrams, but it certainly complicates the presentation of ternary and higher diagrams.

Phase shifts may offer opportunities, for example, in increasing the solubility of one metal in another. This could result in enhanced precipitation hardening of certain alloy systems and added corrosion resistance. Compositions of alloys may be shifted, resulting in an alloy that is less brittle than its counterpart of like composition made at low pressure.

High pressure may be a means of producing alloys containing a volatile constituent, an otherwise difficult and sometimes impossible accomplishment.

Effects on structural features

Casual observation with the aid of a microscope reveals that there are sizeable flaws in most materials. Such flaws may or may not be harmless. Voids or fissures, difficult to avoid in ordinary processing, might be closed or removed by use of high-pressure devices.

A tendency toward disorder of atom arrangements is produced in general when the temperature of a metal is raised. Disorder to some extent can be considered a natural condition in metals. There is an effort to make specimens of a more orderly structure; tiny metal whiskers are examples. These are in the form of very fine fibers and are considered to contain few dislocations. High pressure may be a means of providing an ordered structure in a body of large dimensions, in that pressure might assist in moving atoms toward ordered positions. It is possible that elevated temperatures to provide atom mobility would be necessary. One approach would

be to allow metals to solidify very slowly under high pressure. A thin section of a metal with a perfectly ordered structure might have high-strength properties, no ductility at room temperature, and unusual toughness characteristics.

The conventional preparation of non-ductile metal compounds, such as tungsten carbide, must result in far-from-perfect crystals. Flaws are apt to result from the cooling stresses set up in the non-ductile crystals. The values obtained from property measurements on such imperfect crystals are likely to be lower than those obtained on sound crystals. High-pressure apparatus might be used to prepare sound crystals of compounds. For example, the crystals could be subjected to high pressure, heated intensely, cooled, and then returned to atmospheric pressure.

Complete removal of voids from bodies made from metal powders is most difficult. The use of high pressure should nearly eliminate voids. There is the possibility of encapsulating powders in an evacuated container and subjecting the assembly to very high pressure and the necessary temperature for maximum densification.

For a considerable time, the effect of pressure on semiconductors has been of interest. Lattice spacing has an influence on semiconductor energy bands. Long⁽³⁾ noted that the density and mobility of electrons may decrease with pressure. The resistivity and Hall coefficient may rise with increasing pressure. For one p-type silicon crystal, Ryabinin⁽⁴⁾, et al., reported that the electrical resistance was reduced with increasing pressure.

Vereshchagin and Zubova⁽⁵⁾ noted that pressure-induced viscous flow of materials, including metals, is affected only by the number of external electrons present in the atom. They reported that the critical shear stress, which is inversely proportional to compressibility, is independent of type of crystal lattice and total number of electrons per atom.

Reaction rates and diffusion

New studies can be made on the reactions of metals with other substances under high pressure. It will be interesting to learn of the extent to which such reactions can be prevented or forced to proceed or reverse. The relative volumes of the reactants and products are expected to permit an estimate of the influence of high pressure on such reactions.

Diffusion rates are very likely to be influenced by high pressure. In the case of self-diffusion, there are indications that pressure has a retarding effect. This seems reasonable because pressure should crowd the structure and thus make self-diffusion more difficult.

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