

Graphite As A High Temperature Material

The high temperature physical properties of graphite are reviewed and interpreted in the light of present day knowledge of the mechanisms affecting these properties. The thermal and mechanical behaviors only are discussed and, whenever possible, comparisons are made with other refractory materials. Possible further studies are indicated, including some carbide work.

by John E. Hove

AS long as the term *high temperature* implied only temperatures up to about 1000°C, the materials problems which arose could usually be handled by fairly conventional metal alloy types, such as the Co-Cr-Ni superalloys, for which there exists a great deal of technology. Perhaps this temperature can still be considered an upper limit for normal applications, but it is certainly true that the number of abnormal applications is increasing rapidly. The advent, in recent years, of ram-jet and rocket missiles and of high power nuclear reactor heat sources has raised a host of questions concerning the basic problem of what material to use in the temperature range up to 2000°C and higher. While there are, of course, many metals, in the second and third transition series, which melt at considerably higher temperatures than this, these metals are, at present, pretty well excluded from practical use by other considerations, such as recrystallization, chemical activity, or excessive plastic deformation. The behavior of metals, from the standpoint of dislocation theory, is just beginning to be understood and thus there is some hope for the future development of very high temperature metals, but the immediate problems would most logically appear to have solutions involving the nonmetals, such as the refractory ceramics and graphite. For this reason, there is presently a great deal of engineering and experimental research being performed on the latter materials, much of this research being exploratory in the sense of gathering new property data.

The situation, so far as graphite is concerned, is somewhat more fortunate than with the other refractory solids in the sense that a great deal is already known about its basic properties. This stems both from the fact that the carbon-carbon bond has been of interest to chemists for a long time (and graphite can be considered as a very large aromatic molecule, if desired) and the fact that its properties, both as a function of temperature and of radiation damage, are of critical importance to nuclear reactor designers. It is still true, of course, that such fundamental questions as why graphite remains solid to such a high temperature and why it has such a high thermal conductivity cannot entirely be answered at the present time. It is, nonetheless, meaningful and instructive to consider such problems in the light of existing knowledge. This is what the present paper will attempt to do.

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Before going on, it may be appropriate to classify graphite and justify its discussion before readers primarily interested in metals. Graphite is comparatively unique among materials in that there is always a property or group of properties which precludes calling it either a metal, a semiconductor, or a ceramic. It has the high electrical and thermal conductivities of a metal, but the artificial, polycrystalline types show a negative thermal coefficient of electrical resistivity, generally characteristic of semiconductors. On the other hand, semiconductors, by definition, show an ever increasing resistivity as the temperature is lowered, whereas graphite approaches a finite, and, indeed, a rather low resistivity in the region of 10°K and, furthermore, a good single crystal of graphite has a positive temperature coefficient, as for a metal.¹ On still another hand, its porosity and brittleness at lower temperatures would put graphite in the ceramic class although, unlike most ceramics, it is readily machinable and has a high resistance to thermal shock. All things considered, it is probably more nearly appropriate to call graphite a metal than anything else.

Although certainly outstanding in some ways, graphite has its peculiarities and, especially if the reader is unfamiliar with the data, it is probably valuable to review some representative property variations at high temperature. This review is meant to be mainly illustrative and no attempt has been made to be exhaustive.

Review of High Temperature Properties

At ordinary pressures, graphite does not melt, but sublimates directly into the gaseous phase at about 3700°C. Although the phase equilibrium diagram is still in some doubt, graphite will melt, at a slightly higher temperature, at pressures in excess of about 100 atm. The chief difficulty of using graphite in an oxidizing atmosphere is that the reaction rate becomes quite high at fairly low temperatures. If a threshold oxidation temperature² is defined as the temperature at which graphite loses 1 pct of its weight in 24 hr, the value in air is 450°, the value in steam is 700°, and the value in carbon dioxide is 900°C. Efforts are presently being made to raise this threshold temperature either by impregnation with a retardant of some type (sodium tungstate and phosphoric acid, for example) or by a suitable metal or oxide coating. It is probably fair to say that, to date, these attempts have not shown any outstanding success in all respects.

Most commercial graphites are fabricated by impregnating a carbon flour (say of coke or lampblack particles) with some type of hydrocarbon

pitch and heating to temperatures usually in excess of 2500°C. In actual practice, this pitch impregnation may be repeated a number of times and the first impregnated material is subjected to a relatively low temperature, just sufficient to drive volatile components out of the pitch.³ Since single crystals of graphite are very highly anisotropic, the forming method by which the final specimens are obtained can introduce a fair amount of anisotropy. Thus, coke-type graphites, when molded or extruded, can have a strong directional dependence of some properties. On the other hand, lampblack-type graphites usually have little or no anisotropy because of the isotropic way in which the original carbon particle graphitizes. The end product of these commercial processes is a material made up of graphite particles (each composed of many single crystallites arranged with some degree of randomness) bonded together by nongraphitic carbon. The specific gravity of such graphites varies considerably, but is rarely higher than about 1.8, whereas a single crystal would have a theoretical value of 2.26. Mrozowski⁴ has given arguments to indicate that it may be impossible to obtain densities higher than about 2.1 by the method mentioned above, and that realizing the full theoretical density may require either high pressure or some deposition technique as a part of the fabrication process. It should also be mentioned that these densities are an average value for a given specimen and for, say, an extruded rod, the local density may vary appreciably over the radial dimension. In discussing the high temperature properties, it is also of some importance to realize that if the measurement temperature is higher than the heat treatment temperature of the specimen, additional graphitization may occur, causing an apparent irreversible change in the property. Apparently a fabrication temperature of 3000°C is sufficient to give practically complete graphitization and the application of higher temperatures does not cause significant change.

There is one use for graphite which is important enough to be mentioned, but which is generally outside the scope of this paper and will not be discussed in any detail. This involves its application as a high temperature lubricant. Although quite a bit of work has been done (and is being done) along this line, very little of this effort has been intended to increase the understanding of the lubricating mechanism, which is still in some doubt. Since a graphite crystal has a layer structure with rather weak bonding between layers, the general slipperiness of the material has usually been explained as due to the ease of sliding of one plane over another on a microscopic scale. A serious doubt as to this mechanism was raised by Savage,⁵ who made rather extensive tests at room temperature of the effect of various atmospheres on graphite friction wear. He found that the presence of water vapor (or, alternatively, of ammonia, acetone, benzene, or a few other substances) was essential to good lubrication. In either a vacuum, dry hydrogen, nitrogen, or carbon monoxide, wear was very rapid. Furthermore, the dust was approximately the same regardless of the type of graphite and was very hydrogen absorptive. From these tests Savage concluded, first, that the action of friction was primarily to chop off those crystallites which were not aligned in the plane of the surface (thus producing particles with highly reactive *free bonds*) and, second, that the water vapor forms a very thin, perhaps monomolecular, surface layer which is actually responsible for the lubricating qualities. In this interpretation, graphite shows little friction wear only because it is capable of holding a monolayer of water. Furthermore, this layer, in some unknown but fortunate way, is electrically conducting, thus enabling graphite to be used for sliding electrical contacts. There has, in turn, been a possible doubt raised about Savage's mechanism by some preliminary experiments by Carter.⁶ In these tests it was observed that graphite showed a negligible friction

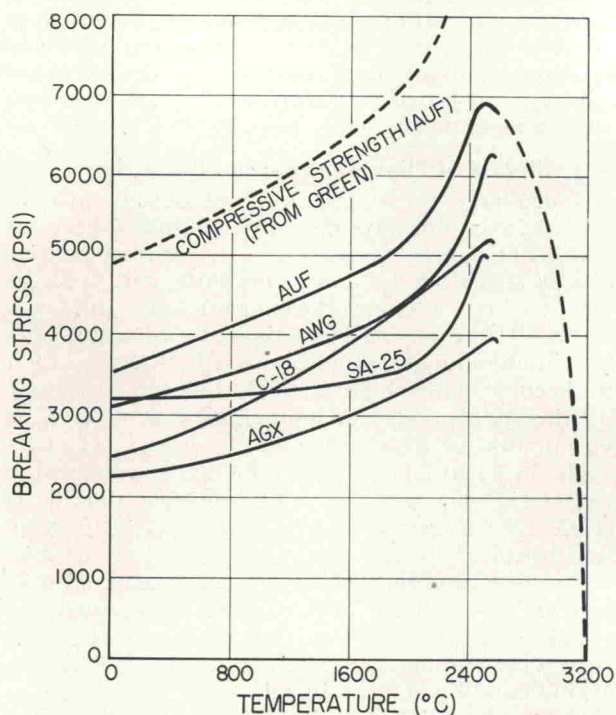


Fig. 1—Short time tensile strength of various grades of graphite.

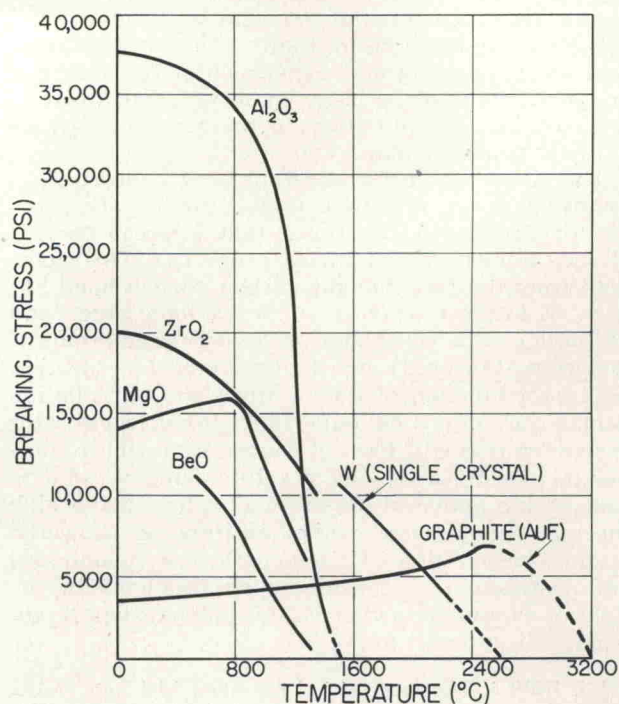


Fig. 2—Short time tensile strength of various high temperature materials.

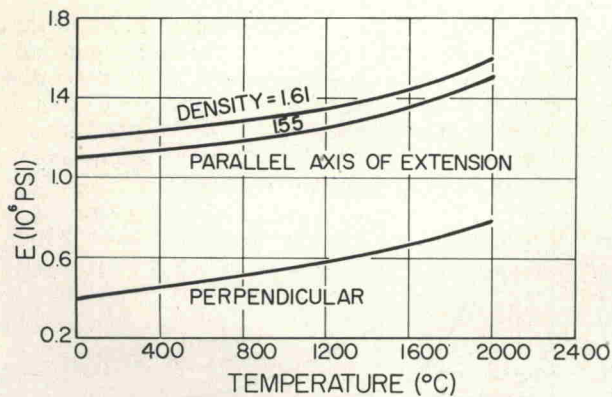


Fig. 3—Temperature variation of Young's modulus for AUF graphite.

wear in very dry helium at about 660°C, in apparent contradiction to what would be expected from Savage's scheme. While further work is clearly indicated, this result suggests that the high temperature may allow enough intergrain plastic flow to permit the crystallites to rotate into the surface plane, presenting a smooth surface. It is possible that the effect of water vapor is to loosen the interparticle binding and thus accomplish the same end. This is an interesting and important field of research which deserves more effort.

The mechanical properties of graphite show some interesting behaviors at high temperatures. As might be expected, they depend to a large extent both on the type of carbon used initially and on the method of fabrication. Fig. 1 shows the now rather familiar variation of the short time breaking stress with temperature for a variety of graphites.⁷ The National Carbon Co. designation of the various grades is used. The type AUF and the type AWG are nominally the same graphite, a rather homogeneous fine grade, except that the AUF is extruded and the AWG is molded. As can be seen, this introduces a fair difference in the tensile strength. The SA-25 is a lampblack graphite which shows practically no preferred orientation. Since both the AUF and AWG data are taken in the best direction, it is seen that the averaged strength of the isotropic SA-25 is less than either one of them. The remaining two grades of graphite are coarse grained types. It is to be noted that all the specimens show a considerable increase in the tensile strength with increasing temperature. The short time compression strength behavior is also shown in Fig. 1 and has the same type of variation with temperature. Although, at low temperatures, graphite is not a particularly strong material, it is relatively strong at high temperatures. In Fig. 2, several materials are compared with AUF graphite for the short time tensile strength. From these curves, it appears that above 1600°C the graphite shows considerable superiority, except for the tungsten single crystal, a case of perhaps only academic interest. If this graph were replotted on a strength to weight basis, graphite would, of course, show marked superiority in this temperature range because of its low density. Unfortunately, the writer was not able to locate enough data on the transition metal carbides to make a comparison in the high temperature range. A value of the tensile strength at 1200°C of between 9000 and 15,000 psi for ZrC and TiC has been reported,⁸ but apparently there are no reported values at higher temperatures. These

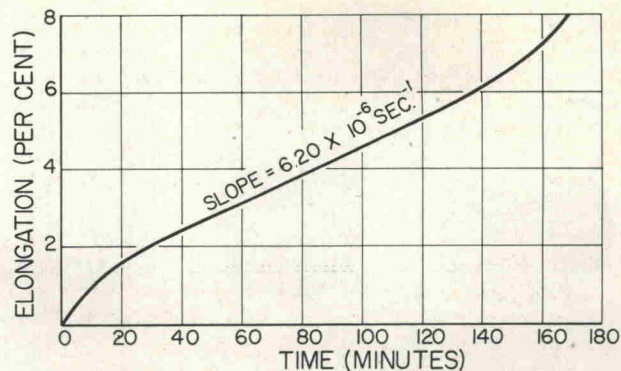


Fig. 4—Creep curve for AUF graphite. Stress is 4500 psi; temperature, 2500°C.

materials, along with graphite, are of great interest because of their good resistance to thermal shock due, in turn, to a combination of their high thermal conductivity and strength and their low thermal expansion coefficient.

The Young's modulus for AUF graphite is shown in Fig. 3 as a function of temperature.⁷ It may be noted that there is relatively little effect of density but a large effect of orientation. As for the tensile strength, there is an appreciable increase of the modulus, at least up to 2000°C, as the temperature increases. The experimental values were obtained by photographically observing the lowest natural frequency of a cantilever beam, and it was found that support losses were so great as to negate attempts to get internal damping factors. As far as the writer is aware, there have been no published efforts to obtain internal friction relaxation data (although Currie et al. report room temperature damping factors as obtained from resonance peak widths⁹).

Although normally considered a brittle material, graphite begins to show an appreciable creep rate above 2000°C. Actually, even at room temperature, the stress-strain plot is not linear, the strain at rupture typically being about 40 pct greater than the calculated elastic strain.³ Fig. 4 shows a creep curve obtained for AUF graphite at 2500°C and a 4500 psi load. The tertiary stage, in this case, probably has a contribution from loss of material due to sublimation as well as necking. Similar data have been obtained for temperatures from 2100° to 2900°C and for a variety of stresses, enabling a family of creep rate vs stress curves to be drawn. Malmstrom et al. have applied elementary rate theory to these data and obtained an activation energy for the plastic flow process of 226 kcal per mole. However, the writer has reexamined these data in the light of a recent, rather careful determination of the self-diffusion,⁹ which yielded about 170 kcal per mole. In obtaining a slope, Malmstrom, Keen, and Green weighted their highest temperature value (2900°C) rather heavily; since the creep rates at this temperature were determined for two stresses only, this point probably has an appreciable error. Considering this, a value of 170 kcal for the creep process fits their results actually somewhat better than 226 kcal, and it is probably fair to say that a self-diffusion mechanism forms the basis for the creep process in graphite. Whether or not this is something analogous to grain boundary flow, as observed in metals, is another and still un-

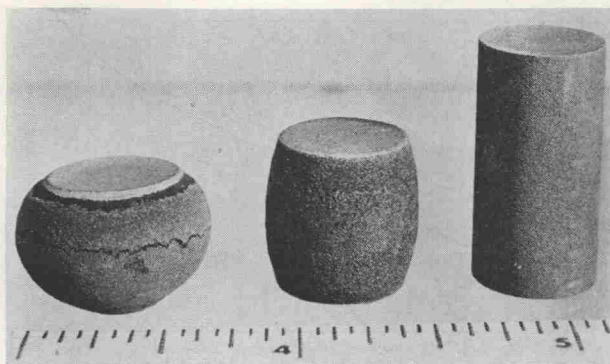


Fig. 5—Specimens compressed slowly at temperatures of 2600° and 2400°C (from left) as compared to untested specimen (right).

answered question. Fig. 5 illustrates the creep process in graphite under a slowly applied compression load.

Of all the thermal properties of potential high temperature materials, the thermal conductivity is certainly one of the most important. Depending on the use, it should be either very high or very low. Above room temperature, graphite has one of the highest thermal conductivities of any structural material. This is illustrated in Fig. 6, where a comparison is made with several ceramics and a representative superalloy range. As can be seen, BeO is the only material comparable to graphite and both of these materials have values comparable to good metals, such as copper, at room temperature. These high conductivities contribute to the good resistance to thermal shock of these two, although BeO is much poorer than graphite in that respect. Presumably this is because BeO has a higher bulk thermal expansion (by about a factor of 2) and a higher modulus of elasticity (by about a factor of 50) than graphite.² As a matter of purely side interest, there is also shown, in Fig. 6, an enlarged high temperature region for the data on alumina and magnesia. The solid lines are the published data of Kingery,¹⁰ while the dashed lines represent unpublished data obtained recently by J. D. McClelland of Atomic International. The reversal in the order of the two solids is probably not too serious a discrepancy since, even though the densities of the samples were about the same, there are several factors which could cause changes in the absolute magnitude by these comparatively small amounts. The more interesting factor is that McClelland did not obtain the minima which characterized Kingery's curves.

Because of the large scale use of graphite as moderators in nuclear reactors, there has been considerable interest in the effect of neutron radiation damage on the thermal conductivity.^{3,4,11} While a thorough account of radiation damage is outside the present scope of this paper, it might be of interest to show a representative effect at low temperatures. There is no publishable data at high temperatures. Fig. 7 shows the thermal conductivity of a reactor grade graphite somewhat similar to AWG or AUF, but with larger grains. The total neutron flux received by each specimen is given in units of megawatt-days, where 1 megawatt-day is roughly 2×10^{17} fast neutrons per sq cm. At room temperature, the conductivity is reduced by a factor of almost 20 by

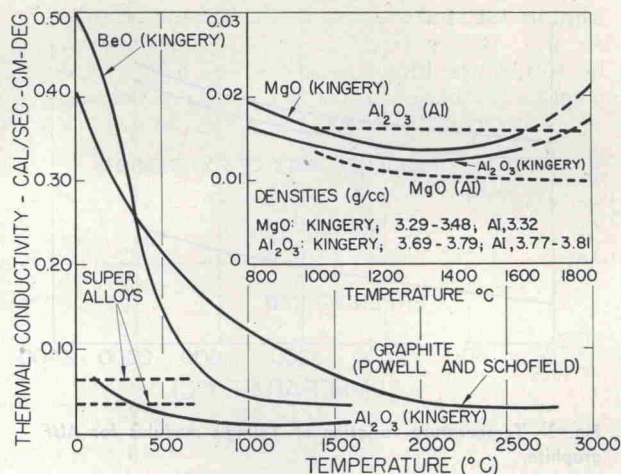


Fig. 6—Thermal conductivity of various materials.

460 megawatt-days, which is not a particularly heavy neutron dose. As will be described later, graphite conducts heat by traveling vibration waves, and the effect of neutron bombardment is to introduce lattice defects which scatter these thermal waves and thus decrease the conductivity. Similar data do not appear to have been taken for BeO, but quartz crystals have been irradiated and a large decrease near the maximum of the thermal conductivity again found.¹²

The thermal expansion of graphite single crystals is extremely anisotropic. Fig. 8 shows the fractional changes in the unit cell dimensions as found by X-ray diffraction techniques.¹³ Note that the *a*-axis data have been expanded by a factor of 10 to make the variation more readily apparent. The *a*-axis actually shrinks until about 400°C is reached, whereupon it begins to expand. No measurements have been made below room temperature. The most obvious explanation of this shrinkage is a form of Poisson's ratio effect where the very high expansion in the *c*-direction causes the basal plane to contract, either through a shear strain component or by interaction at the boundaries. In some ways this is not a very satisfactory interpretation and the matter cannot yet be considered as completely settled.

The connection between the crystal expansion and the expansion of a bulk graphite is not very direct. The lampblack graphites are almost isotropic and, at 800°C, the expansion is not too far from one third the *c*-axis expansion, a ratio which would be expected if crystallites capable of appreciable expansion in one direction only were arranged in a random fashion. The difficulty chiefly lies with the oriented graphites where, almost without exception, the sum of the expansion coefficients in three mutually perpendicular directions is much less (by factors of 2 to 5) than the single crystal coefficient.⁸ There is, of course, the porosity factor; that is, in a bulk material there are internal voids into which the grains may expand. This certainly contributes to the relative smallness of the bulk expansion, but it has also been observed⁸ that there is a decrease of some 35 pct in the volume expansion coefficient when a sample, graphitized at 3000°, is compared with one graphitized at 2000°C. The change in density between two such samples is at most a few percent, not enough to account for the difference in expansion. (The density change is in the wrong direction anyhow.) Furthermore, there was no detectable change between the X-ray dif-

fraction thermal expansion coefficient of these two samples. It has been suggested (Mrozowski¹) that the single graphite crystallites are aligned in nearly closed rings, with edge binding between the adjacent crystals. These rings would then act as partial constraints, the material inside the ring expanding radially into a center void and not contributing to the bulk expansion. There are some attractive points to this picture, the main one being that it introduces a complex relationship between the thermal expansion and the fabrication process, a relation which is apparently needed. On the other hand, it is necessary for the crystallites to expand somewhere, and if such rings force them to expand inward, it would certainly appear that there should be a density decrease comparable to the volume expansion decrease, a conclusion which is at odds with the data. It is, of course, possible to postulate that the higher temperature heat treatments shrink the overall specimen, but redistribute the void spacing in such a way as to decrease the effective expansion, but this explanation appears to become somewhat vague and of a definite ad hoc nature. At the present time, the only definite conclusion is that the problem of interpreting the low bulk expansion of graphite is strongly dependent on knowing the precise structure of the specimen, a factor which is still not well understood, although considerable work is being done.

Interpretation of Properties

In interpreting the high temperature behavior of the mechanical properties of graphite, the polycrystalline nature of the material is of paramount importance. A graphite crystal by itself would be almost useless in any application involving strain, since it has almost no resistance to shear stresses trying to make one plane slide over another. This situation arises because of the crystal structure; the carbon atoms form hexagonal layers which are very loosely stacked on one another. Each atom is held by three neighbors in the same layer by strong trigonal bonds; the remaining bonding electron is shared by the entire layer and is almost the sole contributor to the electrical and magnetic behavior. The result of this is that the interplane binding force is a weakly metallic one which allows the nearest neighbors in two adjacent planes to be about three times as far apart as the nearest neighbors in a plane. Each plane is therefore very resistant to direct tension or compression but two planes may be slid over each other easily. For this reason it is rather unlikely that dislocations play any major role in graphite, although there is some crystal growth evidence that screw dislocations normal to these basal planes do exist.¹⁴ If anything, such dislocations would tend to increase the resistance to shear of a graphite crystal since they would tie several layers together. In a polycrystalline graphite, the various crystals are grouped in a more or less random fashion so that, in bulk tension or compression, it is always necessary at least partially to compress or stretch a high portion of the basal layers giving, thereby, a considerable strength to the structure. In a graphite with any degree of orientation, this would, of course, explain qualitatively why the tensile strength is the greatest in the direction parallel to most of the basal planes.

Since small strains probably involve a great deal of direct or indirect compression or expansion perpendicular to these basal planes, this would also

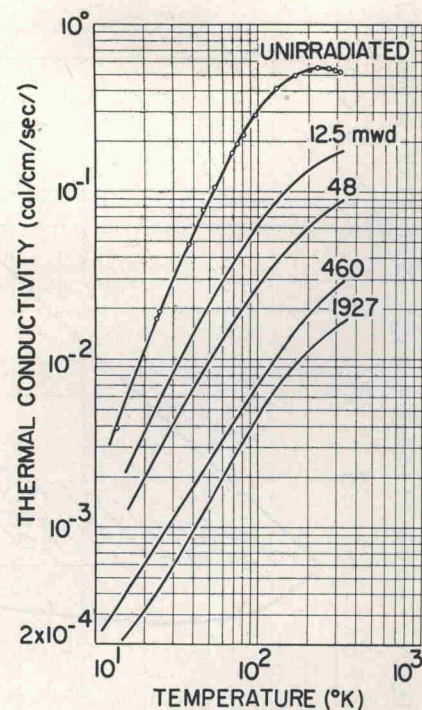


Fig. 7—Effect of neutron irradiation on the low temperature thermal conductivity of graphite.

explain the low Young's modulus. In this connection, it might be reiterated that, even at room temperature, graphite shows a very small elastic strain, the stress-strain curve becoming nonlinear at quite low stresses.⁸ The increase of short time tensile strength with temperature is not particularly mysterious; a similar behavior can be noted for some ceramics, as for MgO in Fig. 2. The most obvious explanation is that internal stresses, brought about by thermal contraction during some final stage of the fabrication process, are alleviated more and more at higher temperatures due to plastic flow. Such flow would also diminish the effect of microcracks which would otherwise develop into fracture surfaces. The increase of Young's modulus with temperature is a little harder to explain. It is possible that, if this property is predominantly influenced by strain in the c-direction of the crystallites, as suggested above, then thermal expansion effects will tend to lock the crystals together more firmly and hence make the material somewhat stiffer. It might be pointed out that one effect of neutron irradiation is also to increase the Young's modulus, which could be due to the radiation-induced expansion of the crystals, which is quite large. In fact, the parallel between damage effects and thermal effects is reasonably close. Thus, using the data presented herein, the fractional thermal change in modulus is about six times the fractional thermal change in c-spacing between 0° and 2000°C. Using some representative data for neutron irradiations of 100 megawatt-days,^{15,16} the fractional increase in modulus due to damage is about seven times the corresponding radiation change in c-spacing. Hence, when normalized to the same change in the X-ray c-spacing, both neutron damage and thermal effects give about the same change in Young's modulus, strongly indicating that expansion of the crystallite normal to the basal planes has a major effect on the elasticity of graphite. In the damage case, as in the thermal, the bulk expansion of graphite is much less than the c-spacing would indicate.

Unlike metals, crystalline graphite conducts heat by thermally excited lattice waves rather than by

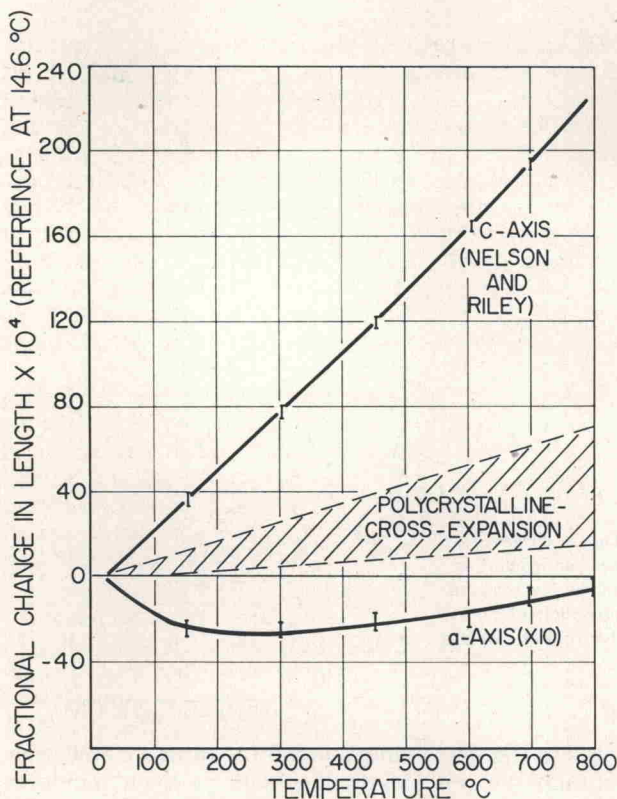


Fig. 8—Graphite thermal expansion.

electron transport.¹¹ A finite thermal conductivity thus arises because of processes within the material which scatter these waves or, in some other way, cause them to lose some of their energy. At very low temperatures, internal boundary surfaces are chiefly responsible for this scattering. At somewhat higher temperatures, as the predominant wave lengths get smaller, impurities and other internal defects become important; while at high temperatures, the direct interchange of energy between different modes is the primary effect. This last can be thought of as inelastic collisions between waves and arises because the modes are no longer harmonic at high temperatures, becoming less so as the temperature increases. The large decrease in the conductivity above room temperature is caused by this. Generally speaking, the stiffer the bond between atoms, the less will be the amplitude of vibration and the interaction between modes. Since graphite conducts heat almost entirely along basal planes, in which the bonding is very stiff, the exchange of energy between modes is small until very high temperatures are reached. The small mass of the atoms helps in this respect also. Therefore, there is comparatively little to impede the lattice waves and the conductivity remains high to quite elevated temperatures. BeO is similar to graphite in some of these respects except that, because of the different crystal structure, there are more modes which can interact with each other, which may be the reason that the conductivity falls off faster. In the cases of alumina and magnesia, the heavier atoms involved are probably the chief reason for the lower conductivity.

It may be worthwhile to expand this discussion of the thermal conductivity from the standpoint of the vibration characteristics of crystal lattices. Thus it is usually assumed that the conductivity falls off, at

high temperatures, either as an exponential or a linear function of the Debye temperature divided by the temperature.¹⁷ The justification for this lies in theoretical calculations on a simple cubic lattice and, for simple structures, a reasonably accurate Debye temperature can thus be obtained. The difficulty is, of course, that any crystal has three Debye temperatures; in nearly isotropic substances, one of these is for longitudinal waves and the other two are for transverse waves. For such isotropic materials, these three values are not greatly different and an averaged value can be used. For solids which are far from isotropy, these three values can differ widely and then the problem is encountered that the modes which are of importance to thermal conductivity may not be those which are important for specific heat. This latter difficulty occurs in graphite, where the three Debye temperatures are approximately 800°, 1600°, and 2500°K.¹⁸ The two higher polarization modes are probably responsible for heat conduction, while the lowest makes up most of the specific heat. A reverse situation apparently arises in alumina, where there is a very low temperature Debye value of 200°, but the high temperature specific heat demands a value of 940°K, which would thus be an average of the two high Debye temperatures.¹⁹ Magnesia has the single published value²⁰ of 945°K, which probably can be used as a single averaged temperature, since MgO is a particularly simple lattice. It is a good correlation that the high temperature thermal conductivities of alumina and magnesia are nearly the same,²⁰ in view of their similar Debye temperatures, and are considerably less than graphite or BeO (which has a Debye temperature of about 1200°K). It is still true, however, that considerable confusion exists about the mechanism of high temperature conductivity, and the subject demands a great deal more study.

Potential Studies

A few concluding remarks might be made regarding what can be done to change or improve graphite. As is now well known, both graphite and BN (which has almost identically the graphite lattice) have been transformed into the cubic phase by appropriate application of heat and pressure and, in the case of BN, a material has actually been created which does not exist naturally. Some of the previous unsuccessful attempts to change graphite to diamond have resulted in theoretically dense graphite. Since this is a material which may have many desirable properties, several groups are presently engaged in a study of its fabrication and behavior although, as far as the writer knows, no measurements of the high temperature properties of such a sample have been made. From a theoretical speculative standpoint, it is wondered why no strictly metallic, close-packed structure of carbon exists. The electronic configuration of carbon might well permit such a phase. It is a relatively simple matter to investigate theoretically, using a high speed computing machine, but nobody seems to have done so as yet. Such a phase, even if metastable, could possess some interesting properties although, like diamond, there is a strong possibility that it might transform to graphite at high temperatures because of the favorable entropy factor. The same speculative curiosity would apply to silicon and germanium also. For the latter materials, which have a diamond structure, it is also wondered whether they might have a metastable graphite-like phase.

If so, this would be of more than passing interest, since both silicon and germanium have heats of fusion which are abnormally high fractions of their cohesive energy. For example, if silicon had the normal entropy of fusion of about 2 cal per degree, it would have a melting temperature of nearly 5000°C. Therefore, if silicon could have a graphite structure with nearly the same heat of fusion, it might well become a very respectable refractory although, because of its heavier mass, it would probably not compete with graphite's thermal conductivity. Actually, graphite appears to be a rather unique material which is difficult to surpass for many high temperature uses.

Nothing has been said so far in the present paper about the reaction between carbon and the transition metals to form the so-called hard metal carbides, principally because the scope of this subject is so large as to require a separate paper. However, in the light of a recent interesting talk by Duwez²¹ on the need for research into the hard metals, the writer would like to add just a few comments, which would apply to the nitrides also.

In some ways, the physics of the hard metals is simpler to study than that of the parent metals, mainly because of their simple crystal structures. The most stable of these compounds all form NaCl lattices, with the metal-metal distances just slightly greater than the parent metal crystals. Their electrical conductivities are about the same, often better, than the parent metals and they form superconductors with some of the highest known transition temperatures. Because of the lack of any large difference in the electronic conductivity between the compound and the parent metal, which is true over a wide range of materials, it is tempting to speculate that there may be very little bonding in the usual sense between metal and nonmetal, and that the small nonmetal atoms primarily contribute a high vibrational entropy to the lattice. The usual arguments against this,²² and for a strong metal nonmetal bond, are 1) the preference for the NaCl lattice regardless of the parent metal lattice, 2) the high melting point despite a slightly increased metal-metal distance, and 3) the brittle nature of the compounds. Possible answers to these arguments involve 1) the fact that in a NaCl lattice, the metal atoms form the closest geometrical packing and do not leave any linear holes in the structure to provide easy diffusion paths for the small nonmetal atoms, 2) the fact that the melting temperature is strongly dependent on the lattice entropy as well as energy (it is amazing to the writer that this point does not seem to have been appreciated), and 3) the fact that materials may well be brittle in the polycrystalline state but not as a good single crystal (as witness graphite, for example).

If the metal nonmetal binding actually were small, then the materials become very interesting

from a theoretical standpoint, since they offer the chance to study a number of different metals, all having the same structure. Measurements which would be of great interest in these materials include the electrical resistivity as a function of temperature, the magnetic effects (particularly the Hall coefficient), the electronic specific heat, the X-ray temperature diffuse scattering, and the heats of fusion and vaporization. Just as important as getting good measurements is the fact that good materials must be available; single crystals would be preferable, but otherwise as pure and dense polycrystals as possible.

In the above discussion, the writer certainly does not necessarily mean to imply that there is little or no bonding between the metal and the nonmetal atoms. However, it does seem apparent that at the present time there is little basis for any decision as to the binding and that the arguments which have been advanced in favor of a strong bond are not difficult to refute.

It is certainly true that the solid state physicist has a long way to go to understand his trade. Nonetheless, it is still of great value for the physicist and metallurgist to abstract qualitative ideas from the theory and occasionally to try to apply them to some of the practical problems. Even if, as will probably be the case, such ideas do not wholly solve any of the problems, this will represent a slight chipping away at nature and should, it is hoped, eventually benefit everybody.

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