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Graphite as a Structural Material

in Conditions of High Thermal Flux

A survey of existing knowledge and an
assessment of current research and development

- by -

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This report was prepared for the Materials Group of the Structures and Materials Panel, Advisory Group for Aeronautical Research and Development, N.A.T.O. In its original form it contained proposals relating to the action that AGARD might take in encouraging and promoting work on graphite at very high temperatures. These proposals, which were discussed at the Meeting of the Group held at Aachen in September, 1959, are here irrelevant and have been omitted from this present edition.

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SUMMARY

The state of fundamental knowledge on the subject of graphite and the graphitisation process is reviewed. The principle methods of manufacture may be considered to include (1) conventional graphitisation of a coke filler-binder mix, (2) the compaction at high pressure and temperatures of natural or artificial graphite particles without a binder, (3) pyrolytic graphites derived from gaseous deposition, and (4) conventional graphites impregnated by liquid or gas and re-graphitised. The present state of development of these processes is examined. The erosion of graphite by high velocity gases at high temperatures is due primarily to oxidation effects which occur preferentially at crystallite boundaries. Coatings of carbides and nitrides improve the resistance at temperatures below about 1700°C, but above this, pyrolytic coatings are more successful. The addition of vapourising compounds, iodides and fluorides, or the addition of carbides and nitrides to the graphite mix, are both beneficial, but of little value at very high temperatures. The development of new graphites, either the impregnated type, or those produced by pressure baking, may offer a margin of improvement, as the best surface structure at temperatures of 3000°C and above appears to be simply graphite. Additions may do little to improve the mechanism of erosion, but they may usefully lower the surface temperature. Considerations relating to thermal shock, creep and fabrication are surveyed. Some of the conclusions are; that graphite is of singular importance to high temperature technology; that commercial issues cannot be allowed to impede vigorous development towards more resistant forms; that much is to be gained by viewing graphite from a metals standpoint; that the fundamental theory of the basic crystal mechanics is undeveloped; that the present wide variability in properties should not be regarded overseriously; that non-destructive assessment by damping measurements needs development, that coatings and impregnants are of high priority, and that, of all factors, oxidation is the most serious limitation to use at the present time.

1. Introduction

1.1. The purpose of this report is to review the present state of graphite research and development in the light of the demands being made of this material by high-temperature technology, particularly where conditions of high thermal flux occur. On the basis of this review, an assessment is made of possible developments in the graphite field, and of the technological requirements likely to arise in the future.

This report is based upon discussions and visits in Europe and in the U.S.A., together with a reading of the published literature. The visits made were limited by the time available, and many quite important centres of graphite activity had to be omitted from the programme. This limitation was in part remedied by the opportunities for discussion afforded by the Buffalo Conference on Carbon, held in June 1959, which enabled contact to be made with representatives from a large number of interested organisations.

1.2. Previous Graphite Assessments

Two important previous assessments have been made. These are :

1. Staff Study in Graphite for Military Applications by J. R. Lane. Report No. MAB-43-SM, dated 9th May, 1957, and
2. Report of Steering Group on Graphite Research and Development. Office of the Assistant Secretary of Defense (R & E), Reference No. CME/235/1, dated 5th September, 1958.

The special difficulties of producing and specifying high-quality reproducible graphites are well summarised in these reports, and some of the conclusions reached are supported by this present survey.

This report will draw upon these two previous assessments, where necessary, but will go much further in its detailed examination of the scientific and technological factors involved. Consideration will first be given to the fundamental nature of graphite, and to the forms in which it is now available. This will be followed by an examination of the place of graphite in space and aeronautical technology, special reference being made to those properties which appear to be of most relevance. These sections lead up to the assessment itself and to the final proposals.

2. SURVEY OF PRESENT KNOWLEDGE AND INDUSTRIAL METHODS

The term graphite, strictly applied, describes a particular form of crystalline carbon structure. This form is found in nature in deposits, it can be developed as a by-product in processes such as the solidification of carbon-iron, or by the high-temperature treatment of carbonaceous materials. The products which result from the various commercial processes are not perfectly graphitic throughout. For example, a single

crystal of graphite has a theoretical density of 2.26, whereas most commercial products have a density somewhat less than 2.0. The reasons for the imperfections are several: actual voids may exist; carbon may not be wholly converted to graphite; the graphite crystals themselves may contain substructures and faults, and there may be impurities in the material. Many such departures from the perfect graphitic structure are attributable to the rather special way in which graphite is manufactured: indeed, this has no parallel in materials technology. Briefly, in the standard type of process, the particles of starting material, such as petroleum coke, or even natural (mineral) graphite, are bonded together by pitch or some other binder, the compact being carbonised by heating, and the whole subsequently subjected to prolonged heating at a temperature of around 2500°C to induce graphitisation of the carbon. A large number of variable factors exist in such a sequence, including the nature of the starting powders and their composition, the composition of the binder, the pressures and temperatures concerned, and so forth. Because the properties of the final products are so sensitive to variation in these factors, the actual details of production are often closely-protected secrets. It will be apparent that graphite cannot be given the kind of specification which can be drawn up for, say, an alloy, where, for a given composition and heat treatment sequence, consistent properties can be achieved by different manufacturers, although this does not mean that certain minimum properties cannot be expected. It is important to realise at the outset that the word graphite can be applied to materials of very different kinds, even though they may all be characterised by a high content of graphitic carbon. It would have been far better to refer to these as graphitic materials, but established usage makes this impossible.

We may note here that in industrial applications generally, carbon itself, in the non-graphitic form, has considerable uses - for example, as bricks in blast furnaces. It is, in fact, stronger than most graphites, and has a higher modulus, but its thermal conductivity is about one-twentieth, and its electrical conductivity about one-quarter of that of graphite. It begins to oxidize at a lower temperature than graphite - about 330°C compared with 450°C for an average graphite, although the actual difference can be much greater, as certain graphites have been developed with a higher threshold of serious oxidation - possibly as high as 650°C, although these details are hard to obtain from the manufacturers. It has very nearly the same coefficient of expansion as bulk polycrystalline graphite and the same specific heat.

Developments in graphite quality were, for a long time, promoted by its applications in electrical and chemical plants, and these industries still provide its largest market. More recently, high-purity graphite in fairly large quantities has been required in nuclear reactors, and this, too, has proved an excellent stimulus to new research and development. It has been more difficult to interest the industry in the high-temperature field because of the limited quantities involved and the small financial

returns which might be expected. This is a natural commercial reaction, but perhaps not as prudent as it might appear. The real rewards to the graphite industry of developments in nuclear engineering may yet prove, in the long run, to lie in the knowledge derived from those associated researches which such developments necessarily entailed. Many of these advances, indeed, stand to the credit of organisations outside the established graphite industry. It may well be that the requirements imposed by high-temperature technology will bear similar fruits, in the long term, in serving to stimulate the activities of diverse research groups and direct these into parallel, related channels. If an overall improvement in material quality should result, it might well bring great changes to the industry as a whole, and affect, eventually, applications in quite different fields.

2.1. Fundamental Structure

Graphite consists of layers of aromatic carbon rings, in which the carbon atoms are spaced at a distance of 1.45 \AA , and valence-bonded. The layers are separated by a distance of 3.348 \AA and bound by van der Waal's forces. In the usual (hexagonal) form, alternate layers are in identical alignment one above the other, so that the stacking sequence is ABABAB, the difference between the A and B positions being a relative shift of 2.46 \AA . The structure is illustrated in Figure 1, and is evidently hexagonal with a unit cell of 4 atoms, the cell dimensions being $a = 2.456 \text{ \AA}$ (cell width) and $c = 6.696 \text{ \AA}$. A simple way of visualising the stacking is to note that half the atoms are aligned in all the planes, the remaining atoms (that is, the other half) being disposed on the sites X or Y (Figure 1) on alternate planes. This structure does not account for all the X-ray diffraction lines that are exhibited by natural and artificial graphites, even in very pure materials. It has been shown that the observed anomalies are consistent with the existence of a rhombohedral form of graphite, given by the stacking sequence ABCABC, where the A and B planes are positioned as before, but with the C plane taking up a position given by a further shift of 2.46 \AA in the same direction as the displacement of B relative to A. This rhombohedral form usually occupies only a few per cent of the volume, but the amount is markedly increased by grinding. The rhombohedral form is unstable at high temperature, but much higher temperatures (say 3000°C) are required to revert it back to the hexagonal form in natural graphite, as compared with temperatures of, say, 1300°C for artificial graphite.

The other important crystal feature is that of twinning, which occurs about the $(11\bar{2}1)$ twin plane referred to the morphological axes (see Figure 2). The hexagonal layers are rotated, relatively, by $20^\circ 36'$, which is equivalent to an insertion of an extra hexagon (2.46 \AA wide) on every other plane. Twinning is a common feature and easily initiated.

We may note at this point that although the graphite structure is quite different in its bonding (and in its arrangement) from that of hexagonal metals, there are certain common geometrical features. Stacking faults in the hexagonal metals take the form of layers in the face-centred cubic sequence ABCABC as for rhombohedral graphite; twinning is very similar; vacancies and interstitials can exist, and are created by the same conditions - such as irradiation. There is evidence of dislocations - in fact, applying the concepts of metal dislocation theory, we would say that rhombohedrally-stacked layers are surrounded, in the hexagonal matrix, by partial dislocations. We shall return to these dislocation questions later.

Very recently, electron microscope studies in a number of different laboratories have established the existence of what appear to be rolled-up sheets, forming what are known as 'scrolls', about $1-5\mu$ in diameter. One view is, in fact, that these scrolls are responsible for the lubrication effect of graphite, in that they act as rollers between the surfaces. Whether this deduction is correct or not, the features certainly exist, and indeed their structure is identical with that of graphite whiskers, which are also composed of rolled-up sheets of layer planes (many layer planes thick) and are consequently hollow along their length. The strength of these whiskers has been investigated, although there are experimental difficulties - for example in gripping, which results in the cylinder being crushed - but tensile strength figures of about 3×10^6 psi have been obtained.

2.2. The Graphitisation Process

In converting a condensed polymeric organic solid, such as petroleum coke, into graphite, a sequence of structural changes is involved. The long-chain or aromatic molecules first polymerise into assemblies of cross-linked planar benzene-rings, surrounded, at their edges, by hydrogen or hydrocarbon groups. These groups can be driven off at sufficiently elevated temperatures (about 800°C) provided their escape from the aggregate is physically possible. In this intermediate stage, the aromatic layers are not ordered in the graphite sequence, but are stacked into parallel disorientated arrays of some kind, with considerable disorder at their boundaries; this structure has been termed turbostratic. The final process of graphitisation involves, then, the relative re-orientation of these planes into the graphitic arrangement, although boundaries and faults of various types must necessarily remain.

These main stages of graphite formation are not in serious question, and have been supported by most excellent X-ray diffraction studies. Two observations may however be made. Firstly, the sequence shows great variations in detail from one type of graphite to another, and, secondly the actual mechanisms, in so far as they involve detailed crystal geometry, have hardly been touched upon.

As evidence of the great variation that can arise in the graphitisation process we may simply consider, as examples, the structure of three graphitised particles, representing, respectively, carbon derived from the solid, liquid and gas phases; that is, hard coke (which is solid throughout the coking procedure - such as calcined phenolbenzaldehyde), soft coke (derived from liquid hydrocarbons, pitches and tars) and carbon black, derived from the incomplete combustion of a hydrocarbon gas or vapour.

Particles of soft coke are strongly oriented, with large scale ordering, and break up into distinctive flakes. Hard cokes have no such lamella structure, breaking up into equiaxed fragments. They are also more difficult to graphitise than the soft, presumably because of the effect that the cross-linking in their structure has on the growth mechanism. In neither case does graphitisation produce any great change in the particle shape, in contrast to the graphitisation of carbon black particles, which develop geometrical forms, the faces being parallel to the layer planes of the individual microcrystals making up the particle.

While, then, details differ for the different types of material, we are left with certain common features which certainly derive from the same basic processes. Figure 3 shows results for the crystallite growth in a carbon black and a petroleum coke.

In general, the linear dimensions start at perhaps 10-20 Å, but increase rapidly for temperatures over about 1000°C (which is the temperature at which a rapid evolution of hydrogen occurs). Growth therefore seems to be associated with the re-combination of edge atoms made available for bonding by the removal of their attached hydrogen or hydrocarbon groups. For carbon black, the dimensions parallel to the planes, L_a , may reach 100 Å or more depending on the particular material (i.e. about 40 rings), and that normal to the planes, L_c , may reach 50 Å or more (i.e. about 15 planes). This alignment occurs at first without any rotational adjustment, so that orientations about the plane normals are random. As the temperature is raised, pairs of neighbouring planes assume the graphite relation, the actual temperature at which this occurs depending again on the specific material - it can be over 2800°C although usually rotations begin at about 2000°C. There does seem to be some correlation with L_a in this respect, as nearest neighbour graphitic ordering appears to start when L_a reaches about 100 Å. It has also been possible to detect second neighbour ordering, and this has shown that in the early stages, groups in the ABA and AFC sequences are of equal probability. The retention of bands in the ABCABC sequence would, of course, result in rhombohedral stacking faults. For prolonged heating more and more layers orient themselves into the graphitic sequence.

The details of the crystallite growth processes vary markedly with the material, particularly in the matter of the actual crystallite

dimensions: for example, it will be seen from Figure 2 that the L_a value for petroleum coke can reach about 500 Å.

Recent research on the process in hard cokes suggests that the L_c and L_a growth speeds are initially low, and controlled by the filler composition. At the higher temperatures, growth occurs largely by increase in L_a .

The graphite structure is obviously anisotropic, and the coefficient of thermal expansion in the c-direction (normal to the layer planes) is about thirty times greater than in the a-direction. In cooling, after graphitisation, very great internal stresses can theoretically arise, and these could be large enough to break the bonds and form voids. It is argued that the restraints imposed on polycrystalline graphite in this respect are largely responsible for the inability to achieve the 'perfect' graphite density of 2.26, although, of course, the effect may be mitigated, or obscured, by the fact that the starting compacts already contain voids which may not be filled by the graphitisation treatment. This could lead to anomalies. However, it may be important to recognise in this connection that the idea of void-creation by anisotropic shrinkage is tenable only if no stress-relieving (recovery) mechanisms operate. In particular, if dislocations are accepted, then the necessary geometrical adaptations during cooling could be readily provided by dislocation generation and movement. It seems likely that some such adaptation does, in fact, take place.

Graphite also exists as a natural mineral, but here again there is a great variety in the forms it can take. Quite large and relatively pure pieces characterise the Ceylon graphites, whereas the Madagascar deposits are finer and, when separated, take the form of characteristically thin platelets. In other cases, the gross pieces have no obvious crystallographic form, and are termed (somewhat misleadingly) amorphous graphites: deposits of this type are found in Mexico, Korea and Northern China. These natural forms are used extensively in the industry, either as the main starting material or as additives. One obvious difference distinguishes the artificial graphites from those compounded of mineral particles. In the first case, the coke particles are graphitised together with the carbonised binder material; in the second case, as the primary particles are already graphitic, only the bonds are graphitised. This necessarily means that for the artificial graphites there is a greater possibility of achieving good bonding by the growth of interlocking boundary crystals. What might be called the compatibility of binder and particle material, in this matter of graphitisation, is an important practical consideration, although there is little fundamental understanding of the effect. This derives again from the inexactness of the theories of crystallite growth.

The conventional methods of graphite manufacture necessarily involve the creation of micropores in the material. Considerable research

has in more recent times been devoted to producing impermeable graphites, particularly for nuclear applications. It might be convenient to divide the pores into two broad types; those which arise at the particle boundaries in the baking processes, due to the loss of the volatile constituents, and those on a smaller scale which make up the misfit boundaries between adjoining crystallites of different relative orientation. While the former may (theoretically) be processed out, there is a limit to the latter contribution, set by the crystallite size. The larger the crystallites, and the greater the degree of preferred orientation, the less the microporosity. This has been confirmed by experiment: showing the crystallite boundary micropores to be about 3 to 8 Å in width. This compares with interparticle voids of, say, 10000 Å or more. (See Figs. 4 and 5).

To sum up: the processes of graphitisation have certain general features which can be recognised and measured, but in detail they depend greatly on the materials used and on the exact graphitising conditions. This variability has made it difficult to establish a proper quantitative theory. The reasons why some carbons graphitise far more readily than others is not understood. For example, an anthracene low temperature char graphitises much more readily than chars from simple benzene derivatives, but if the conditions are adjusted, graphitisable carbons can be prepared from benzene itself. Not only do the size of the crystallite parameters vary from one type of carbon to another, but so also do the spacings, as shown in Table 1.

It is possible to build up less and less defective graphite by polymerizing smaller aromatic molecules at progressively higher temperatures. X-ray studies show that the progress of polymer formation takes place more rapidly with some than with others: carbon polymer from polyvinyl chloride gives a density of 2.25, whereas from polyvinylidene chloride the density limit is 1.59 even after 3000°C heating.

It does seem that certain types of crystallite boundary are extremely stable, even at very high temperatures, so that if the initial structure is such that these types are developed, then further growth ceases. This is clearly true for lamp black particles where the crystallites grow to the maximum size consistent with the retention of layer-plane surfaces. Surface planes which contain edge-atoms of the layer planes are therefore of high-energy. Growth which involves their creation is therefore impeded unless the energy can be derived from, say, an internal stress field.

Franklin has proposed an index for the proportion of layers stacked in the graphitic sequence, based on X-ray measurement of the c-spacing. As the value for misoriented layers is 3.44 Å, and that for oriented layers is 3.35 Å, a proportion may be calculated if a mean intermediate spacing is measured. This method has been widely adopted, without reservations, as a means of following the development of the graphitic

structure, and is most useful, but quantitative deductions should be more carefully examined than is frequently the case.

A perfect fragment of natural graphite can be reduced to a turbostratic state by grinding, with reduction in L_a and L_c , and much the same is observed with artificial graphites. Thus grinding produces the reverse effect to graphitisation treatment. These effects are not interpreted in any dislocation terms at the present time, although it is in this direction that the most satisfactory theory may be developed.

2.3. Conventional Artificial Graphite

There are differences in detail between the manufacturing procedures of the various graphite companies; these differences arise from experience of certain materials and of the requirements of particular markets, being based very largely on empiricism. Information regarding these somewhat special techniques is not obtainable. There are no publications on the subject.

It is necessary, therefore, to generalise the processes of manufacture of graphite from particle binder mixes under the heading 'conventional artificial graphite' even though no single standard process exists.

Carbon artefacts are prepared from the products of the distillation of petroleum and coal. The hard cokes derived from petroleum residues or from the pitch of the coal-distillation process are crushed to powder form, calcined to remove the volatile constituents, and graded into powders with suitable particle size distributions. Lamp black, carbon black or natural graphite fines may, or may not, be blended in. A binder material is then added, this is usually ground pitch, in suitable proportions, and the whole mixed. The mixture is then pressed or extruded. These 'green' mixes are then baked at between 900 and 1300°C under non-oxidizing conditions, with the object of achieving the maximum carbon with the minimum of mechanical damage. The blocks of carbon so prepared are then packed into carbon powder and heated to not less than 2500°C by direct current heating, during which the process of graphitisation proper occurs.

2.4. Pyrolytic Graphites

Carbons can be produced by the thermal breakdown of gaseous compounds, such as benzene, methane and propane. The deposits of carbon which occur at elevated temperatures (from about 1000°C to 2000°C depending on the compound) can be highly oriented crystallographically, although the percentage of aromatic layers stacked in the graphite sequence may be very small. Thus turbostratic structures are formed, which may be subsequently graphitised by heating.

The process of deposition may be made continuous, by maintaining

a constant flow rate (and gas composition), but control of all the experimental variables, to the required degree, is not easy. For successful products, the conditions of deposition should be constant throughout, which means that the surface at which the hydrocarbons are being broken down and deposited should be held at constant temperature. As the deposit grows, it acts as a layer of low thermal conductivity between the wall and the deposition surface (usually being oriented so that the c-direction is normal to the growth face) and this upsets the thermal distribution. For sufficiently high deposition temperatures (say 2100°C), the deposits are essentially graphitic, at least for certain hydrocarbons, yielding very high densities of from 2.1 to 2.2. They are impermeable to helium at room temperature. The cross-sections of the deposits, when examined microscopically, reveal a cone-like growth from the base material. The nature of the deposit, is incidentally, affected by the nature of the substrate, ceramic bases being coated with a compact carbon, while metals and metal oxides give a powdery deposit.

The growth cones are not, as might be expected, crystallites, of a common orientation, although the parallelism of the layer planes with the growth surface remains strongly preferred. There is no evidence at the present time that disorientations within such cones are any less than those which occur between, say, adjacent cones.

The process of deposition is one which is amenable to straightforward reaction kinetics. Activation energies may thus be determined and this enables propositions to be made regarding the nature of the rate-determining step. For example, with benzene this step appears to be ring-cleavage (that is, C-C bond cleavage) whereas in methane it appears to be breakage of the C-H bond.

2.5. Natural Graphite

The incorporation of particles of natural mineral graphite in the mixes from which graphite products are manufactured is common practice, as has been noted above. There are, however, commercial products now available in which the natural flakes, from which impurities have been removed, are compacted under pressure at elevated temperatures without the use of a binder. The resulting material is highly oriented and is not (as far as it is known) as strong mechanically as the wholly artificial forms. However, the grades of graphite produced in this way have been largely developed to their present state for nuclear reactor applications and their full possibilities may not yet have been exploited. The density is high, about 2.1, but perhaps the most noteworthy of its characteristics is the highly consistent properties which can be achieved as between different samples. This question of reproducibility is one of the most troublesome in graphite applications, particularly with the larger pieces. It may be said that few companies subscribe to the view that a graphite of this type has serious structural possibilities, but it may well be worth examining.

2.6. Coatings

Graphite is readily oxidized at high temperatures and for successful operation some form of protective coating is required, such as an impervious layer of carbide. A large number of research organisations are now engaged in examining methods of coating graphite, and, because of the commercial implications, few details can be ascertained. One method is based upon the vaporisation of halides (NbCl_5 , TaBr_5 , ZrBr_4 , for example) at temperatures in the region of 2000°C , at low pressure - a few cms. of mercury. The carbide coatings deposited (NbC , TaC , and ZrC in the above cases) bond well to the graphite, being locked into the porous structure, and they can be made in thicknesses of the order of 1 mm. They appear resistant to thermal cycling and by using the base carbon to form the carbide, the rate of growth is controlled by diffusion and is, therefore, largely insensitive to the vapour flow conditions.

At sufficiently high temperatures, above 1500°C , rapid oxidation of these carbides occurs, and silicon carbide (SiC) and boron carbide (B_4C) are much superior. These have been widely used as coatings, as well as silicon nitride (SiN) and boron nitride (BN) and combinations of these. Low oxidation rates at temperatures of about 2000°C can be achieved by such compounds. Boron nitride itself has a usefully low thermal conductivity.

2.7. Impregnation-filling

The term impregnation-filling is used here to distinguish the processes of ~~pre~~-filling from impregnations specifically designed to improve high temperature resistance - for example, cerium oxide additions. These will be discussed specially in Section 3. The porosity which inevitably exists in the conventional artificial graphites takes the form of interconnecting macropores, about 1μ in radius, forming a network between the original particles. The need for an impermeable graphite in reactor technology has concentrated attention on ways of filling these macropores, either by small particle additions to the original cokes, or by the addition of a nitro-substituted organic compound or by impregnation after baking or graphitising. The last of these processes appears to offer the best prospects for the future, and several successful methods have, in fact, now been evolved. In the case of the reactor grades, purity is important, and the pores must be filled with carbon: for other applications it may be possible to accept a finite level of impurity if the sealing off is made more effective.

Perhaps the most obvious course, as far as impregnation is concerned, is simply to coat with a binder-type material and re-bake. This does reduce the rate of gas diffusion, but the reactivity to an oxidising gas is not reduced, and may, in fact, increase.

Of the published methods of impregnation, perhaps the most important are those developed at the Royal Aircraft Establishment at Farnborough: they may be usefully distinguished as representing liquid and gas impregnation.

2.7.1. Liquid Impregnation

In this method, the graphite surface under treatment is impregnated with furfuryl alcohol ($C_5H_6O_2$) plus a suitable catalyst, so that polymerisation occurs, yielding a solid resin which is carbonized at $1000^\circ C$ to give about 50% carbon. During the carbonization the resin shrinks uniformly without becoming liquid. As the impermeability is unaffected by high-temperature treatment, the method may be applied to carbons which can subsequently be graphitised. Fine-grained materials appear most suited to this kind of treatment, and it is usual to carry out two impregnations. In the case of tubes, a common one for reactor applications, one impregnation is made from each side. Considerable improvements in mechanical properties result from this kind of treatment, such as strength and modulus: the effect is demonstrated by the diagram of Figure 6. The successful use of furfuryl alcohol has naturally led to its being considered as a binder material. Quite large section bars of graphite have been produced with such a binder, and the permeability of the product normal to the extrusion direction was fifty times lower than that of a conventional low-permeability graphite.

2.7.2. Gas Impregnation

The gas impregnation techniques are really based on the pyrolytic methods noted above. Normal pyrolytic deposits onto a graphite base are highly oriented and the differential thermal expansion between the coating and the base can give rise to cracking and to separation, although very thin adherent coatings have been successfully achieved. However, these difficulties are neatly avoided by the R.A.E. process. The rate of pyrolysis is a function of temperature, and by controlling matters so that such pyrolysis occurs only within the pores of the material, the sealing-up action occurs wholly internally, and no surface-coating problems arise. With a nitrogen-benzene vapour atmosphere, the transition from surface to internal deposition occurs between $750^\circ C$ and $800^\circ C$. The weight can increase by about 9% without any dimensional changes, and permeabilities of 1.5×10^{-9} cm/sec can be achieved.

2.7.3. Development work on impermeable graphites

A number of organisations in the U.S.A. and Britain are engaged in development work on impermeable graphites, some of these in association with research programmes on the high-temperature protection of conventional graphite surfaces.

The Royal Aircraft Establishment process has been taken up by the Hawker Siddeley Nuclear Power Company, and a plant with a capacity of 400 tons per annum of furfuryl-impregnated graphite is expected to be in operation by about mid-1960. The oxidation rate of the finally graphitised product is about one-twentieth of the original graphite, but at relatively low temperatures (550°C): its high temperature performance is not yet published.

2.8. Dislocations

Some special reference should be made to the question of dislocation theory in relation to the graphitic structure. A number of electron microscope observations have now been made which are thought to provide direct evidence of dislocations. On the theoretical side, a number of possible dislocation forms have been examined. On the whole, this work is viewed with some scepticism, and often, perhaps, for the wrong reasons. Dislocations are features of the microstructure which have provided the only sensible explanation of many phenomena in metals, they have been detected in mica, alumina and diamond and appear quite logically to represent the minimum possible local distortion that can be introduced into a regular, continuous lattice. It is difficult, in fact, to imagine that the graphite structure is so perfect as to be dislocation-free.

However, it appears unlikely that the screw dislocation parallel to the c-direction is physically possible. Indentations on the layer planes recover elastically, which would not be the case if screw dislocations could be punched through. Conversely, edge and screw dislocations on the layer planes appear eminently reasonable, particularly as they can account for the twinning features, and can be reconciled with stacking faults. There are special difficulties, of course, with graphite which distinguish it from the case of metals, and these would well repay special study. A number of experiments drawn from the field of metal physics suggest themselves in this connection.

We may expect considerable developments in the dislocation theory of graphite behaviour over the next few years.

3. THE PLACE OF GRAPHITE IN HIGH-TEMPERATURE AERONAUTICAL AND SPACE TECHNOLOGY

The very high-speed propulsion of machines into and through space depends, at the present time, and in the foreseeable future, on rocketry. Greater thrust can be achieved by a simple scaling-up, or, more efficiently, by new fuels operating at higher temperatures. To utilise these fuels, temperature-resistant materials are required in the rocket nozzles, and, of the various possibilities, graphite is the most outstanding.

The kinetic heating associated with vehicle re-entry imposes even more severe conditions involving very rapid heating to high temperatures

in an oxidising atmosphere. The duration of heating may be fairly long, particularly with manned vehicles. Nose cones and leading edges in graphite are therefore being attempted and tested.

The heat energy, if it cannot be satisfactorily conducted away by the missile structure, must be dissipated by radiation, by mass flow or by energy-absorbing transformations. The conversion of the solid to the liquid and the vapour phases involves the absorption of the related latent heat, and thus the ablation capacity of a material (heat absorbed per unit mass lost) obviously depends on these quantities. Graphite shows no liquid phase, and sublimates from the solid to the gaseous form with a usefully high energy of sublimation (about 170 kcal/mole).

An assessment of graphite must therefore cover its resistance to high temperature and high velocity surface attack, its thermal properties, its emission properties, its strength and its general compatibility with other materials.

3.1. Erosion

In the conditions of the rocket nozzle, graphite is eroded by the burning gases. This is particularly severe with the newer high-temperature fuels, such as those containing aluminium. Opinion on the exact mechanism of this erosion, and the factors influencing it, is divided. A microscopic study of certain graphites, which have been widely used in nozzles, after exposure to rocket conditions, has resulted in the conclusion that the attack occurs preferentially at the interfaces of the original particles - that is, in the binder material. Another view is that the presence of metallic particles may seriously accelerate the wear by abrasive action. Yet another is that the effect is worse with the metallic propellants simply because they operate at higher temperatures, and for no other reason. Silicon carbide and silicon carbide-silicon boride coatings certainly bring improvements at the lower temperatures but are of negligible benefit above 2000°C. In fact the non-uniformity of the attack (once the carbide coating has been eroded through locally) results in a distortion of the nozzle profile which is more deleterious than that brought about by a more uniform wear. Silicon carbide coated graphites fail by the conversion of the silicon carbide to silicon dioxide which liquifies at 1600°C and is driven off by the gas stream.

It cannot be pretended that enough experimental facts are known about this subject at the present time. However, it may be useful to attempt a closer consideration of the questions.

As with all chemical kinetics, the rate of attack, other things being equal, will increase with temperature. The temperature factor alone, however, cannot explain the wear rate, and we may discard this explanation at the outset. The constituents of the fuels are, however,

of great importance, as has been demonstrated by experiments in which magnesium and aluminium fuels were used in similar nozzles at very nearly the same temperature. Only the aluminium-containing fuel eroded the graphite to any serious extent, and this suggests that the important factor is a chemical reaction between some constituent, such as Al_2O_3 , and the graphite.

Fundamental studies are clearly required for a proper assessment, and we shall here draw upon certain results recently presented on work which is still in progress (Hennig, 1959). The nature of the chemical attack on graphite surfaces in reactions with CO_2 , O_2 , O_3 , and O , at temperatures below $1000^\circ C$ has been studied by optical and electron microscopy. Hennig finds that metallic particles of Fe, Au, Ag, and W do not act individually in catalysing the reactions but only when aggregated into larger colloidal particles of about 200 \AA diameter. The attack is not on the basal plane but only on the edges of the steps, and then only in certain preferred directions, so that a sort of channeling results. If vacancies are present, however (as produced by irradiation for example), then the layer planes are attacked at once and pitting results - presumably this accords with the previous observation, the attack being at the edges of the vacancy clusters. Whatever the detailed interpretation of these and other related effects may be, it is clear that the crystallographic nature of the surface, and the constituents of the gases, are of fundamental importance. The most beneficial surface structure appears to be that presented by the layer plane face, at least for the case of O_2 - in fact, chemisorbed O_2 protects the layer planes. On the other hand, O_3 attacks the layer planes direct. The presence of chlorine, bromine and carbon monoxide affects the nature of the attack, and slows it down. Grinding, on the other hand, accelerates chemisorption, whereas subsequent annealing retards it.

It is very likely that the binder material (or, more properly, the boundaries) offers sites for preferred attack by O_2 , because such boundaries may have a locally more disoriented structure, with a higher concentration of faults and vacancies, and with exposed layer edges. An aspect of this dependence has been demonstrated by natural graphite (micron size), moulded without a binder up to densities of 2.0. Heat treatment at temperatures up to $3000^\circ C$ results in a gradual decrease in the reactivity (at a given temperature) to carbon dioxide - the factor is about 30. The activation energy remains the same (42 kcal/mole), so there is no question of a differing mechanism, the result being due to the reduction in the extent of the vulnerable material by processes of growth and boundary diffusion, and with the consequent dissolution of stress concentrations built up in the moulding process.

The chemical considerations alone are still inadequate, however, in judging the behaviour when the erosion is superimposed upon conditions

of thermal shock. Differential expansions in the surface may readily result in the development of microfeatures which are susceptible to attack: the creation of surface steps by slip for example. We are here in a field where the crystal mechanics of graphite are relevant, and it may be said, at this point, that this part of the fundamental theory is still in its infancy. We shall take up the question again later in considering the limitations of our present fundamental knowledge. The actual surface chemistry of graphite is indeed, much better developed, and paramagnetic resonance techniques have enabled a number of theoretical possibilities to be examined. The details of this work would lead into special technicalities which cannot be pursued in a report of this kind, but it should be recorded that these researches are of high importance, and of great relevance to the high-temperature field. As with all properties, the rate of attack and its nature varies greatly between graphites of different origin and pre-treatment. This is consistent with the view that such attack is strongly related to the microstructural detail.

Graphite has a good resistance to thermal shock, and it is found that a coarse-grained graphite is better in this respect than the finer grades which usually have better strength characteristics. Decreasing the amount of filler component decreases the thermal shock resistance, so that it would appear that the boundary material is largely responsible for absorbing the anisotropic thermal stresses.

The degree of oxidation-pitting that occurs is dependent on the local concentration of impurity in the graphite, being worse for titanium, vanadium and calcium than with iron and other impurities, at least up to about 1000°C. Va (giving Va_2O_5) plus Na F is a particularly serious catalyst, and the attack (say 2.5 p.p.m. of each) is worse than the sum of the individual rates of each separately. The purity of the graphite is therefore important.

The rate of reaction of carbon with gases is influenced also by the porosity and the amount of internal surface material, and by the diffusivity of the gaseous reactants. At low temperatures the dominant reaction is simply that of chemical attack at all surfaces, internal and external, and the slower the rate the lower the concentration gradients. This would apply to the phenomena discussed above. As the temperature increases, the reactivity rate increases, the diffusion of the gas through the pores becomes a controlling factor, the effective rate decreases, and the overall activation energy (as measured) decreases. For even higher temperatures, the mass transfer through the boundary gas layer becomes important, this layer decreasing in thickness with increasing gas velocity. It is therefore to be expected that porosity is of importance as a rate-determining factor in oxidation, but this is not significant for temperatures below about 600°C or so.

Returning to the nature of the burning of graphite, it has been observed that very special surface features are developed. All the layers of the steps which are attacked do not burn off at the same rate, and, as a result, a sort of undercutting occurs because of the fact that some planes burn more slowly - these are spaced at about 0.5μ with a very regular periodicity even in the most perfect graphite crystals obtainable: again these experiments are at temperatures below 1000°C .

In measurements made at very high temperatures (2400°C) with gas velocities in the region 20 - 60 metres/sec in gases containing about 50% H_2O , there is some evidence that the rate is proportional to the square root of the velocity. The latest series of measurements indicate that the rate of reaction is in the region 3.5 to 5.0×10^{-3} gm/cm² sec. at gas velocities of about 50 metres/sec., this rate decreasing with graphite density. Some experimental results on carbons are presented in Figures 7 and 8. These have been selected in order to demonstrate the character of the velocity and temperature dependence observed. Measurements of this type on graphite itself are more difficult because of its higher thermal conductivity, but the difference between graphitized carbons and the carbons illustrated by the figures appears to be small, at least at temperatures of about 2000°C , being about 10% better as far as carbon consumption is concerned. On the other hand, there is experimental evidence available which shows that pyrolytically deposited carbons have a significantly lower rate of reactivity than either commercial carbons or graphite, by a factor of about 3. In combustion tests of this kind small incandescent grains have been observed in the combustion gases, and these appear to be eroded by the burn-up of the interparticle bonds. Incidentally, it is curious that the degree of parallel stacking appears to increase with oxidation; the effect being partly reversed when the oxygen is removed. No very convincing explanation of the effect has been deduced.

There is an almost total lack of correlation between reactivity and many of the bulk measurements: resistivity, ash content, degree of crystallinity, so that only direct measurements have any real value.

Pyrolytically-coated graphites have shown about the best resistance to erosion so far obtained, but at the very extreme temperatures, about 3000°C , they simply flake off if there is not a proper thermal matching to the undersurface.

Impregnation can be beneficial in a quite different way, in offering a means of energy extraction by vaporisation: for example, impregnation with ammonium iodide can hold down the surface temperature for several minutes at a quite high rate of heating. Materials with higher boiling points are, however, required. Impregnation with metals appears unlikely to be of great value. Firstly, the rapid differential thermal expansion at the start of the combustion could result in the fragmentation of the

surface layers, and secondly the metal may well be swept out in the liquid phase, giving little benefit where it is most needed. For a reasonable quantity of such coolant to be introduced, a fair pore size is required, so that the metal can be absorbed in the graphite structure - at least in the boundaries.

Rare earth additions have been experimented with, such as cerium oxide and aluminium fluoride, but for operation above 2000°C no really noteworthy advance has been achieved. One difficulty in drawing conclusions from the test results is that they differ greatly with the exact test conditions, so that materials which appear to show improvement in one jet torch are disappointing (and even worse than unimpregnated graphite) when tested in another. The possibilities of impregnation are, however, scantily investigated as yet, and some real advantages may yet be attained by such means.

The actual admixture of carbides to the graphite mixes has also been investigated, with promising results. Combinations of graphite with B_4C and SiC have resisted temperatures around 1600°C for some 80 mins without failure by burning. No improvement has been achieved to date by metallic impregnation - for example with copper.

The actual sublimation of carbon itself, in the graphite form, is the most obvious mechanism to use to advantage. The difficulty is to arrange that such erosion is truly atomic, and not, as it most certainly is at present, in the form of particles. Burning must also, of course, be prevented.

3.2. Thermal Shock

The graphite structure is very anisotropic thermally and consequently, in the aggregate, very high local stresses can be created under conditions of rapid heating, such as in rocketry and re-entry. In detail, the requirements of the two applications differ. In the nozzle, a relatively short-term retention of profile is required, while for re-entry, surface loss is to be expected, and the insulation and survival of the main structure become the important factors. In order to take advantage of the lower conductivity in the c-direction, the graphites must possess a high degree of preferred orientation, with the layer planes lying normal to the heat flow. Whether or not this structure characterises the whole component is a question of detail design - the best theoretical material for combining resistance to shock with surface properties is undoubtedly one in which the degree of ordering changes gradually from the preferred orientation of the surface to a completely random structure internally.

As was noted earlier, in section 3.1., graphite has a good resistance to thermal shock, particularly the coarser grained materials. These are, however, not the best from other points of view, such as erosion and strength.

The problems that thermal shock resistance raises are not special to graphite. For high temperature technology this resistance is required in addition to mechanical strength, and, at times, to thermal resistivity. Very often one factor can be raised only at the expense of another, and in general it appears wisest to design for assemblies of different materials, each dealing with a separate factor, such as surface attack, insulation, strength, and so on. The art of design, in this connection, is to take advantage of the thermal anisotropy of graphite in creating an assembly with the minimum thermal stresses, and this aspect of the matter is one which should be given closer attention - it involves close collaboration between both the materials and design engineers.

One quite fundamental thermal problem at the present time concerns the fact that the bulk expansion of polycrystallite graphite is about one third of that of a single crystal. This is essentially equivalent to a restraint in the c-direction expansion, but exactly what occurs is not known.

3.3. Strength and Creep Resistance

It is a well known experimental fact that the ultimate tensile and compressive strengths of most graphites increase with temperature up to about 2500°C, to a value about twice that at room temperature (tensile) and then decrease. This effect is probably due to secondary factors, such as stress concentration relief, or even graphitisation, and does not represent a true strength increase in the perfect graphitic structure as such. There are, in fact, other substances, such as ceramic oxides, which show the same sort of effect. (Certain experiments show that this increase does not occur in tests in vacuo - but further critical experiments are required before deductions may be drawn). Recent experiments on highly-oriented pyrolytic graphites have shown that the strength of these materials (some ten times greater than commercial graphites in the a-direction) does increase, approximately linearly, with temperature. This really undermines the stress-concentration relief explanation of the strength increase, although possibly not completely: work on single crystals would be valuable in this connection. There is a strong orientation-dependence, and the strengths are different when measured parallel or perpendicular to the direction of preferred grain alignment: in extruded material this direction is that of the extrusion, whereas in moulded material it is perpendicular to the direction of the moulding pressure. Graphite is less ductile, but stronger, in tension parallel to the grain as compared with tension perpendicular to the grain. Elongation increases with temperature, from negligible amounts < 0.5% below 2000°C up to, say, 5% at 2500°C, and up to 15-20% at 2800°C. No elongation has been detected on test pieces fractured at room temperature. Large density decreases can occur - up to about 15% at the higher temperatures, showing that voids are being created, and pores opened up. The 0.2%

proof stress is about 80% of the ultimate tensile strength at 2500°C, and about 65% of the strength at 2800°C.

At 2800°C, the strength of graphite is about 3000 p.s.i., or 250 kg.cm⁻². Increasing the rate of strain at these high temperatures decreases the ductility.

The strength of graphite is compared with a number of refractories in Figure 9. Its superiority at temperatures above about 1500°C is apparent. As the temperature increases, graphite also shows an increase in elastic modulus, which is not well understood: there is a belief that this may be due to the effects of differential expansion in locking-in some of the crystallites, but the theory needs more precise scientific formulation. Single crystal work is required here also. There is a parallel in this case with the effect of neutron irradiation which also causes an increase in modulus, with an increased c-spacing. The real answer probably resides again in a proper dislocation approach, the increased modulus probably reflecting the reduction in the dislocation contribution due to latticebending restraints.

Graphite exhibits creep at elevated temperatures, the general behaviour being very similar to that observed in metals, and capable, therefore, of expression in terms of primary, steady state and tertiary creep. However, this is not universally accepted, and results have also been expressed in terms of a simple logarithmic creep.

In viewing the mechanical behaviour of graphite at high temperatures it is useful to apply the same general framework as that adopted for metals; similarities and differences may then be distinguished. Firstly, in fitting creep functions to the graphite curves, exactly the same dilemma arises as with metals, namely, that a variety of functions can satisfy the experimental data. In particular, it is possible to select a transient creep function of such a form that the postulate of a steady state creep is unnecessary, even though the curves show an apparently extended linear region. We shall not press these questions, because they are common to the whole field of creep, and discussion of empirical fitting in this respect has always been singularly profitless. One of the most important examinations of the creep behaviour is that which adopts the analytical methods applied to the behaviour of metals, particularly in the matter of the deduction of activation energies. This work, carried out at The Jet Propulsion Laboratories, and the more general approach which it represents, we regard as the most penetrating contribution yet made to the creep question. Scatter in the results with graphite, is, of course, more serious than with metals, and uni-specimen techniques have therefore been adopted by Jaffe et al, with stepwise increments in temperature being applied during the test.

The results show that the value obtained for the activation energy does depend on the method of analysis adopted, somewhat higher values being obtained from steady-state creep rates than when the 'time to a fixed strain' is used in the calculations. There is also a difference when measurements are confined to a single specimen - the so-called unisp specimen technique. Little significant difference is apparent in the energies deduced from creep stressing parallel and perpendicular to the grain direction. The values deduced range from about 140 to 220 kcal/mole, although for a given method of analysis, the values fall within a much narrower band. Details of all the conclusions which may be drawn cannot be entered into here, and it must suffice to say that the approach appears to be as valid as it is for the case of metals, and that more recent work suggests that two energies are involved, one around 200 kcal/mole, and the other much lower - possibly near to 100 kcal/mole.

Apart from these energy discrepancies, for which there are certain fairly plausible explanations, the results conform very well to the pattern of behaviour in metals. They show that the degree of preferred orientation affects the energy of the creep process, and also confirm that the creep rate increases continuously with temperature - the tensile strength increase with temperature is not, therefore, reflected in an increased creep resistance, and thus the strength phenomenon is associated wholly with the fracture mechanism. On the other hand, the dependence of the creep rate on the stress is less critical than with metals. The density decreases during creep, because of pore volume increase.

Certain evidence is now available showing that below room temperature the fracture (in a transverse bend test) propagates predominantly through the binder, whereas at high temperatures the crystallites may be fractured. The graphite strength also increases if tests are conducted in vacuo.

When graphite is unloaded it exhibits a strain-recovery with time, which can be relatively large. For example, unloading after about 10% creep at elevated temperatures can result in about 3% recovery. In this, graphite behaves more like a polymer than a metal, where the strain recovered is much smaller. However, it should be noted that, on reloading, a true softening-recovery (annealing) effect can be observed and the similarity with metals is again apparent. This is a question on which further experimental evidence is required. High temperature pre-treatment of graphite, even for short times of a few minutes, lowers the creep rate of materials subsequently tested at a lower temperature. This, it is generally agreed, is due to graphitisation effects, although repeated temperature cycling of this kind has not, as far as is known, been attempted in substantiation.

The plastic behaviour of graphite is certainly a function of strain history, and differs in its nature with orientation. This effect has

been quoted in criticism of the activation energy derivations based, for example, on uni-specimen measurements. In fact, the same criticisms may be made of the method in its application to metals.

The derivation of creep rates by the drawing of tangents is useless, as the apparent steady state depends on the time of test - again this is exactly the metal problem. If the logarithm of the creep rate is plotted against the logarithm of the stress (for a fixed time), then a straight line with a slope of almost exactly 2.0 is obtained, with small differences between the cases of stressing parallel and perpendicular to the grain direction.

To sum up: enough work has now been done to show that the exact value for the energy does depend upon the method of evaluation, but this is a problem common to materials generally. It also shows that the energies fall into two main groups: high energies around 200 kcal/mole, approximating to the quoted energy of self-diffusion (although in graphite this is a function of the actual diffusion step - a distinction not always appreciated) and low energies near to 100 kcal/mole. It may be that these will be shown to be consequences of elemental processes occurring within the layer planes, or across adjoining layer planes, but the theory is as yet too little advanced to allow any more specific speculation.

Finally, in the field of mechanical property evaluation, some note must be made of the methods of test adopted at the Armour Research Foundation, involving the compression of rings of graphite. This technique avoids grips, it has advantages in machining and in enclosing the specimen, in concentrating the effects in the fracture zone and in providing information direct by the very nature of the fracture. It can, of course, only be used with brittle materials. Further, it can be applied to dynamic measurements, such as modulus and damping. The method is one which has very advantageous features for high temperature measurements on brittle materials, and on graphite in particular.

Impregnation has a very beneficial effect on the mechanical properties, as noted in the relevant section. Much more, however, needs to be known of its effect on creep.

4. SPECIAL TEST FACILITIES

The imposition of the type of service conditions expected in graphite applications requires large-scale and expensive test equipment. Plasma jets (arc torches) can impose shock heating to high temperatures, but atmospheric control is also required, and prolonged running, at least for re-entry simulation. The position has been reached where the vehicle itself is probably the only realistic test facility and consequently unless there is very close co-operation between those working in the materials sciences and the service testing groups, then

the best advantage will not be taken of the data that such tests may provide. Plasma jet tests on reasonably large cones (3 or 4 inches diameter) show that there is certainly a greater pitting of the graphite in air, as compared with that when water vapour is present. The great difficulty really is that graphite burns, and no use can therefore be made of the high sublimation energy. Plastics have shown up rather better as re-entry materials, and both these and graphite are far superior to the refractories, which simply melt.

The arc image furnace is a very useful small-scale laboratory equipment, and also enables reflectance and emissivity measurements to be made. Temperatures of about 3000°C are possible, but not with supersonic air flow, because of convection cooling. At 3500°C, graphite has a diffuse reflectance of about 2.0% and an emissivity of 98%.

5. FABRICATION

The high-purity graphites of nuclear grade are abrasives and the life of the cutting tools used in shaping graphite components is short, although better life is naturally achieved with tungsten carbide tips. The thorough removal of dust and swarf is required, and all the bearings, slide ways, lead screws and the like must be enclosed. The cutting can be carried out fairly fast - up to 100 in/min. Otherwise little special equipment is required.

Handling of the components has to be particularly controlled, as mechanical damage can easily occur.

The parts for rockets and missiles must be machined at the present time, as the dimensional accuracy required, for large components, is not possible by direct preparation in the form of, say, mouldings. Interference or force fits are possible, and large graphite inserts may be joined by shrink fitting.

Blocks of graphite may be bonded to each other by using a conventional binder or a substance such as furfuryl alcohol, and re-graphitising. Otherwise, graphite may be brazed using a copper-silver eutectic alloy, in vacuo, at a temperature of 950°C, or by zirconium or titanium heated in vacuo to about 1850°C. By such means graphite-graphite or graphite-metal bonds are possible. It is important that niobium has been joined to graphite by such means, as this metal may well figure in high temperature structures as the backing material for graphite.

The joints obtained appear as strong as the original graphite. There remains the possibility of the direct fabrication of large-scale components (such as rocket nozzles) by pyrolytic forming. Whether the necessary degree of control of the manufacturing variables would make this an economic possibility is not yet known.

6. SUMMARY OF BASIC GRAPHITE DATA

Figures for the bulk properties must be regarded as typical only, as the actual values obtained vary greatly with different graphites.

DENSITY	2.26	Single Crystal
	2.17 +	Pyrolytic
	1.90	Impregnated
	1.80	Conventional artificial
FUNDAMENTAL STRUCTURE	Hexagonal (usually) plus rhombohedral	
	1.42 Å	C-C spacing
	3.35 Å	Layer spacing
	Twins on (11 $\bar{2}$ 1)	
HEAT OF SUBLIMATION	170 kcal/mole	
POROSITY (VOLUME)	5 - 20% Conventional graphite	
THERMAL CONDUCTIVITY (cal/cm.sec. °C)	0.6 a-direction 0°C natural graphite	
	0.17 c-direction 0°C natural graphite	
	0.25 - 0.40 conventional 0°C	
	~ 0.1 at 2000°C	
	~ 0.05 at 3000°C.	
SPECIFIC HEAT (cal/mole °C)	5 - 6 at 1500°C - 3000°C	
	8 at 3500°C.	
THERMAL EXPANSION (°C ⁻¹)	1.5 x 10 ⁻⁶	a-direction
	26 x 10 ⁻⁶	c-direction
	4 x 10 ⁻⁶	conventional
	all average values up to 1000°C	
	10 x 10 ⁻⁶ at 3000°C.	
ELECTRICAL RESISTIVITY (ohm. cm ² /cm.)	1 - 2000 x 10 ⁻⁶ conventional	
	100 - 4000 x 10 ⁻⁶ pyrolytic	
	(very variable, but can be very high ~0.5 normal to growth)	
THERMOELECTRIC POWER (μV/°C)	50 at 0°C against Pt.	
TENSILE STRENGTH (p.s.i.)	4000 at 2500°C	
	3000 at 2800°C	

CREEP RATES (sec^{-1}).	10^{-4} at 3000°C for 2000 p.s.i.
	10^{-6} at 2400°C for 2000 p.s.i.
	10^{-5} at 2800°C for 1600 p.s.i.
DUCTILITY	0 at 1500°C
	0.05 at 2500°C
	0.1 at 2700°C
	0.2 at 3000°C

7. ASSESSMENT OF THE PRESENT GRAPHITE SITUATION

From the foregoing, it will be evident that an adequate assessment of the future of graphite can be made only when the very special problems it raises have been justly appreciated. We shall attempt to summarise, in the following paragraphs, the main conclusions to be drawn from the present survey.

(a) Graphite is undoubtedly a material of great importance to high-temperature technology.

(b) The industrial researches on graphite cover an extremely wide field. Many of these researches are of outstanding scientific quality, and there is a lively sense of experimental development which is not at all tied down by traditional practice, as might be thought. Many quite new ventures, which could be revolutionary, are in the pilot plant stage. There is, however, little sense of urgency in the manner in which the high-temperature resistance question is approached. The reasons for this are plainly commercial, and even externally-supported research and development contracts are accepted with little evident enthusiasm, as the fear remains that with the onset of an emergency the special knowledge acquired may be distributed to competitors.

(c) We must recognise at the outset two things about the graphite industry. Firstly, the product is one in which competitive superiority is based upon individual manufacturing techniques, and secrecy surrounds the technical details. Secondly, until quite recent times, little serious academic work outside the industry was carried out on graphite, partly due to the fact that such work necessarily involves equipment of a special kind. The industry, has, then, over the years, cornered most of the available knowledge and skills and is mainly concerned with organising its very great resources in directions of most commercial profit, as is natural.

(d) There is no doubt that the proper and most effective place for any graphite development is within the framework of the existing industry, but the needs of high-temperature technology, particularly in

matters of defence, cannot be set aside simply because they raise awkward commercial issues within that industry. If a proper response cannot be stimulated, then projects must be put in hand in other organisations. This would be a less satisfactory result, because of the excellent experimental facilities for such work which the industry possesses. Indeed, from a commercial point of view, the industry has, in fact, everything to gain by realising the extent to which a successful high-temperature graphite would be exploited by future technology. While much development work on subjects of direct concern to the high temperature question is certainly going on at the present time, it is on too small a scale in relation to its potential importance.

(e) The greatest single handicap to the utilisation of graphite at the present time is its chemical reactivity, at high temperatures, particularly its heavy rate of oxidation. Studies of the resistance of possible coating materials are therefore of prime importance, together with studies concerned with the fundamental mechanisms of surface reactions.

(f) The service users, for their part, must be prepared to provide technical details of their current and future test conditions, and give the industry a chance to develop materials with the optimum characteristics. Collaboration is in certain cases very close indeed, with a good exchange of information, but this is not universal. Some manufacturers feel that they are all too little informed of the conditions and the results of tests and that as a consequence their expert knowledge is not used to full advantage. How substantial this criticism is cannot be assessed in a report of this nature as it raises issues which are outside the terms of reference of the co-ordinator. In any case it may well be that much of the information which the manufacturers require, such as exact gas compositions, velocities and temperatures, is not known, although those concerned are well aware of its importance.

(g) The most profitable material for immediate development appears to be a very pure impregnated graphite, with a randomly oriented structure, subjected to surface treatment by coating, or by the development of a preferred surface structure, or by the impregnation of a vaporising constituent, or by combinations of these and other methods.

(h) The most profitable material for a longer term development appears to be one based upon high-pressure compacting without a binder, together with a surface treatment of some form. A project of this type is in hand.

(i) The present state of fundamental knowledge is inadequate, particularly in the field of graphite physics. The basic processes of deformation are not known. The fundamental features of the microstructure have not been established. The nature of possible dislocations, and their contribution to the bulk properties, are in doubt, and indeed the whole question of the existence of such dislocations is still in the discussion stage.

(j) Everything is to be gained by approaching graphite from the standpoint of metals knowledge and experience, even though this approach must necessarily be modified in a number of important respects. The situation in the fundamental field is remarkably similar to that which existed in metals twenty years ago. The same arguments are going on about creep, its formulation and interpretation, about the nature of deformation processes generally, about annealing, recovery, grain growth and the like. Laborious mechanistic models are proposed, as they were with metals, whereas many of the effects would probably fall into place very readily were a proper theoretical basis established. Fundamental studies on the behaviour of graphite single crystals are badly needed, and this is generally appreciated. The difficulties of growing reasonably large crystals are, however, very great, and there is no immediate prospect of success in this direction. The fundamental chemistry questions are already adequately covered, although it would be of benefit if these were extended to even higher temperatures, and high rates of gas flow. The real controlling factor in erosion is still not known.

(k) Graphite cannot be assessed merely in isolation, as it were, divorced from advances and developments in those other materials which have applications in the field. It is one of the several materials from which successful heat-resistant composite assemblies must be constructed, and, as such, questions of compatibility, bonding and so forth, necessarily arise. Unless these are introduced into the overall design considerations, then the real significance of any graphite improvements will not be properly assessed.

(l) Variability in the properties of graphite as between supposedly identical pieces is serious at the present time, but need not cause special concern. This is a matter which is occupying much of the industry's attention, and all the evidence available shows that improvements can be made, particularly by densification and impregnation.

(m) The question of the development of graphites based on very pure starting materials is of relevance to the high-temperature issue, but here again, the industry is devoting considerable resources to an examination of the possibility, and developments may be awaited. It may be that the evident expensiveness of these materials will ultimately blunt the interest of the industry, but this is a question which may be faced when the facts are known. If development work does cease because of the apparently unrealistic cost of the products, then the matter ought at once to be reviewed again.

(n) The creep deformation of graphite does not give rise to serious concern at the present time, but researches ought to be encouraged in studies which might be expected to yield a more creep-resistant form, for example, by added elements, which may form interstitials between the layer planes, or fine (refractory) particles which may act similarly

to the precipitated-phases in precipitation-hardened alloys. Again, the metals background offers a number of speculative possibilities of a fairly fundamental kind which should be followed up.

(o) Better methods of non-destructive assessment are required, but it is unlikely that these would have any immediate beneficial effect on the selection of high-temperature graphites. The real importance of such tests lies in the increased understanding which measurements in the fields of internal friction and stress propagation may bring. Work on damping, in particular, is to be encouraged.

(p) Great advances in graphite quality have been made in recent years. We may expect that much improvement may yet be achieved, but with increasing difficulty. The remarkable strength of graphite at high temperatures, and its low density, make it a unique material, and justifies every possible effort being made in developing its oxidation resistance.

(q) The recommendations of the Steering Group on Graphite Research and Development (CMT 235/1) cover fourteen separate programmes of work, which we have considered in detail. The following fields of research recommended for support by that Group, are, in our view, now adequately covered:

Pressure baking of large graphite pieces; extrusion and moulding to shape; graphite whiskers; control of porosity; control of anisotropy; catalysis by impurities of oxidation; new methods of making uniform graphite.

The following fields of research recommended for support, are, in our view, not adequately covered:

Coatings and impregnants; oxidation-resistant additives; fundamental crystal structure; improved interplanar bonding; high-temperature reactivity. In particular, a much greater effort is required in the fundamental research relating to all these topics.

8. ACKNOWLEDGEMENTS

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TABLE I

Carbon Type	After carbonization at 1400°C			After graphitising at 2600°C		
	c	L _c	L _a	c	L _c	L _a
A	3.46	45	58	3.36	2900	220
B	3.60	16	47	3.39	220	54
C	3.52	30	53	3.38	159	72
D	3.47	46	60	3.38	220	75

The quantity c is here the interlayer spacing. L_c and L_a are the crystallite dimensions in the directions c and a respectively. All the carbons are prepared from benzene carbonized in a stream of helium, under different operating conditions. These carbons show different physical appearances as well as differences in the quantities noted in the table. Note the considerable c -growth in the A carbon on graphitisation, giving needle-like crystallites.

- ATOMS ALIGNED IN A & B PLANES.
- ◇ A PLANE SITES ONLY.
- B PLANE SITES ONLY.

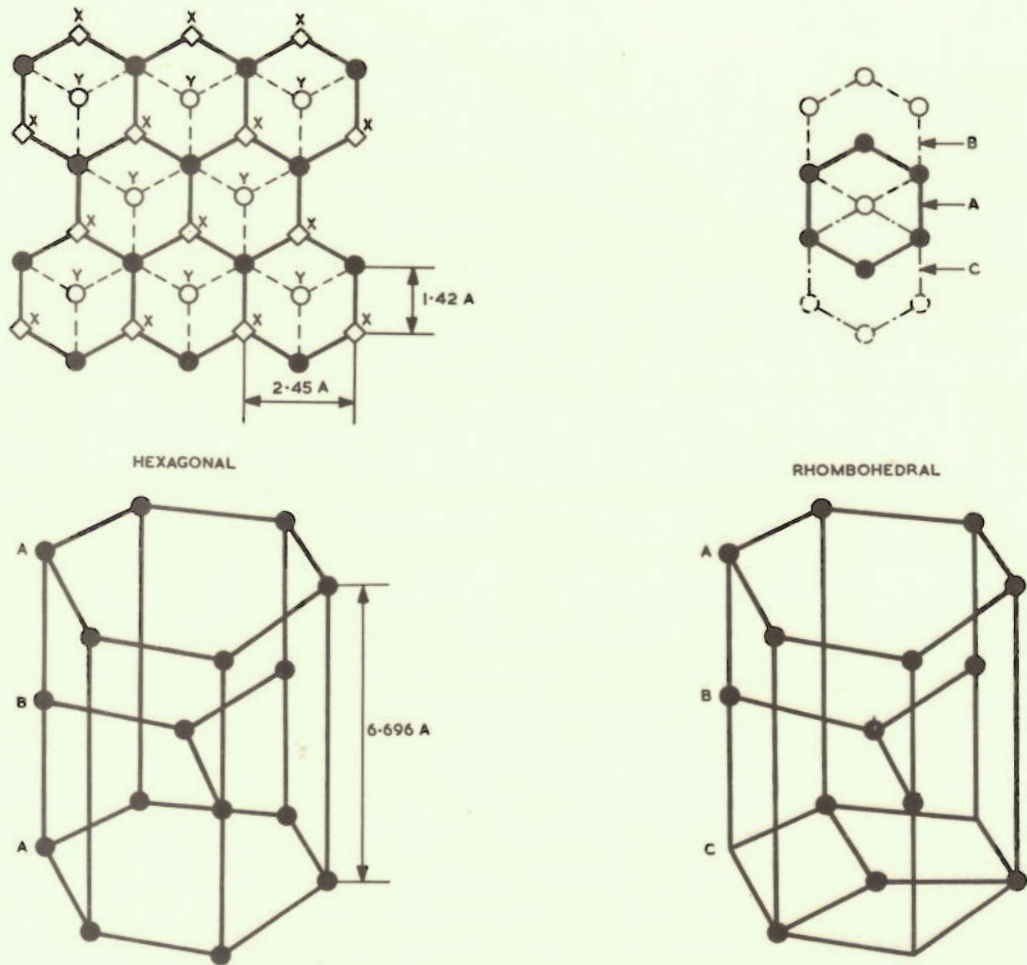


Fig.1 The crystallographic structure of graphite

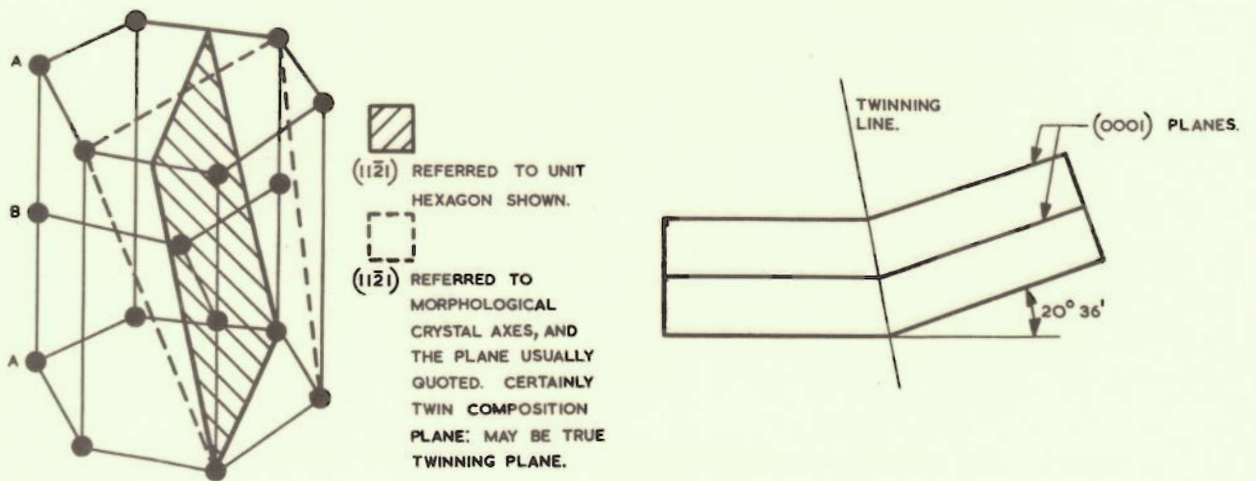
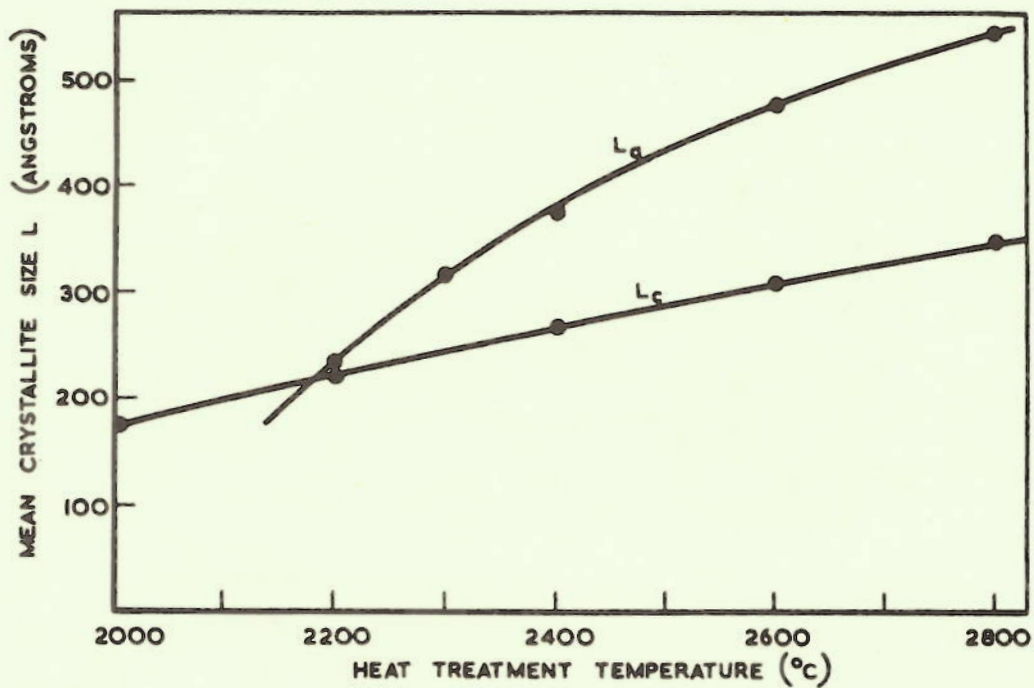
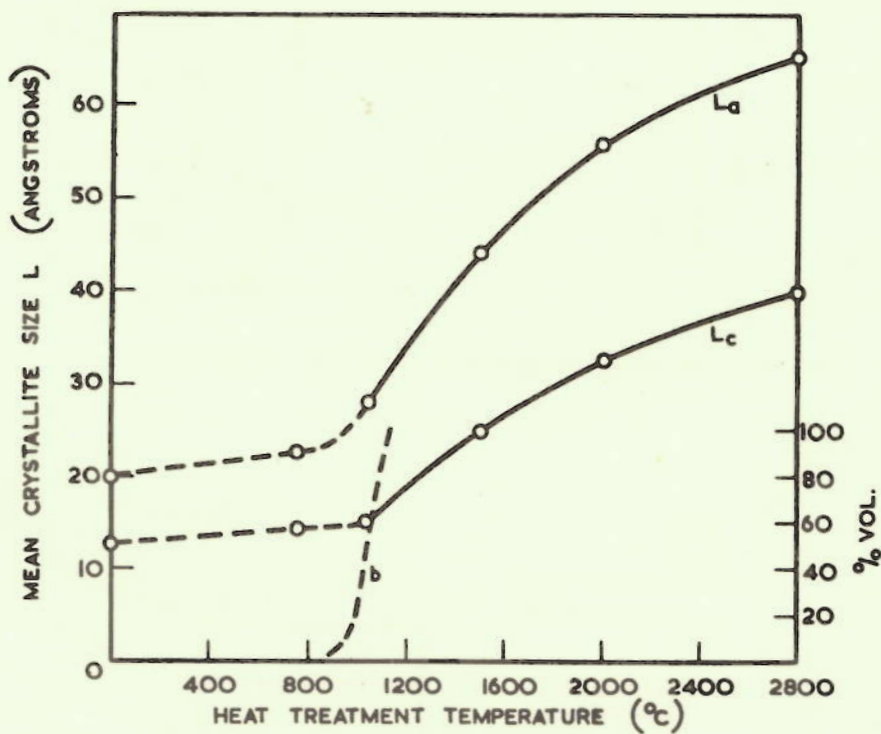


Fig.2 The twinning characteristics of graphite



(a)



(b)

Fig.3 (a) Growth of crystallites in a petroleum coke (after Bowman)
 (b) Growth of crystallites in a carbon black (after Warren)

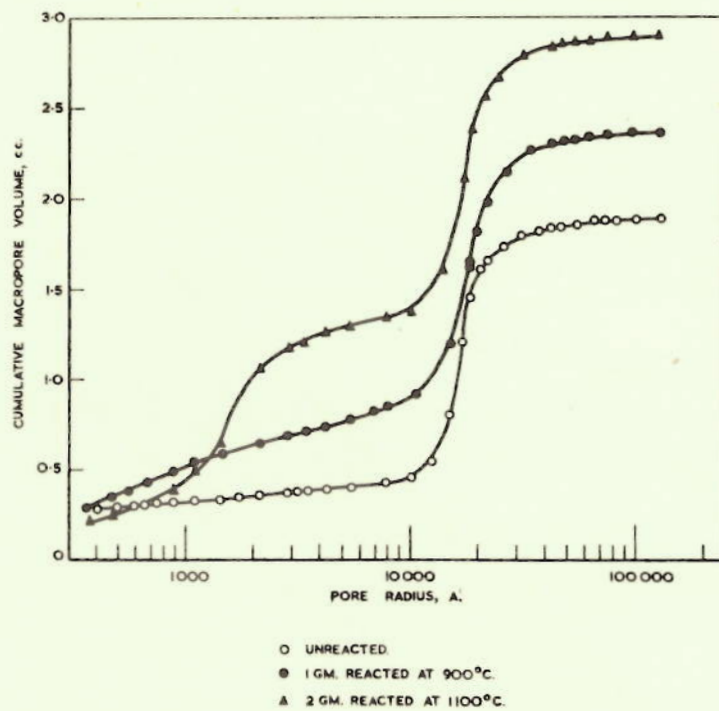


Fig.4 Change in macropore volume of graphitized carbon rods upon gasification (after Walker)

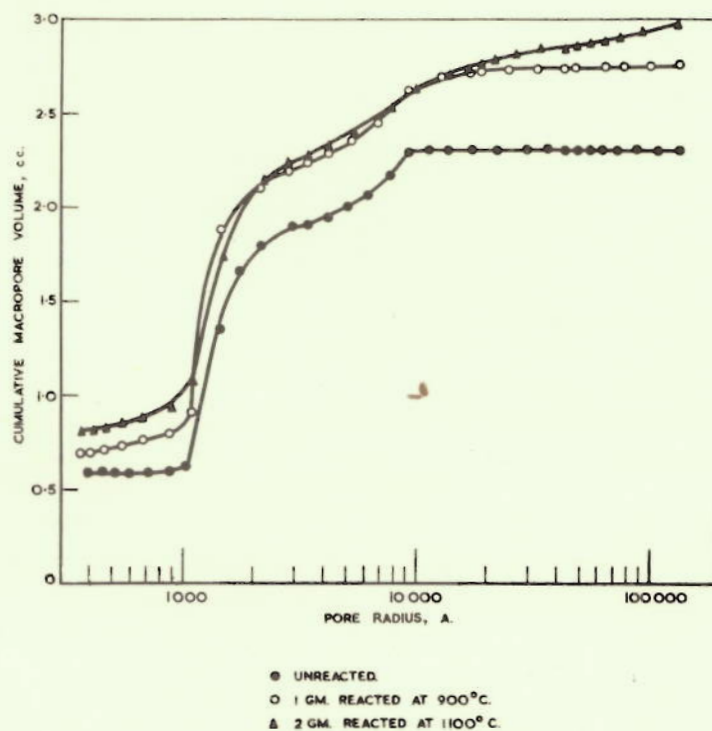


Fig.5 Change in macropore volume of lamp black rods upon gasification (after Walker)

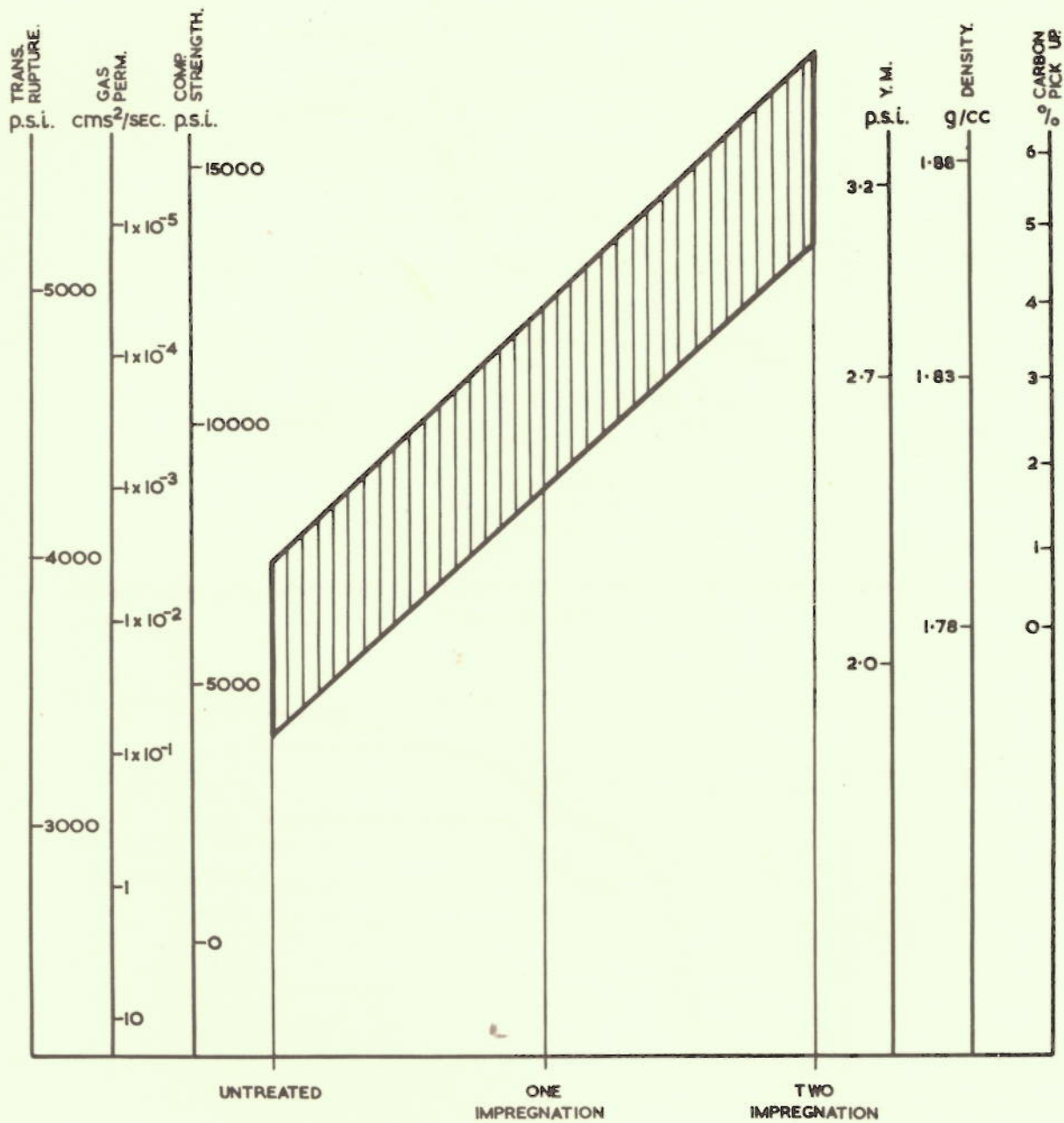


Fig. 6 The improvement of properties by furfuryl alcohol impregnation.
(Hawker Siddeley Nuclear Power Company results)

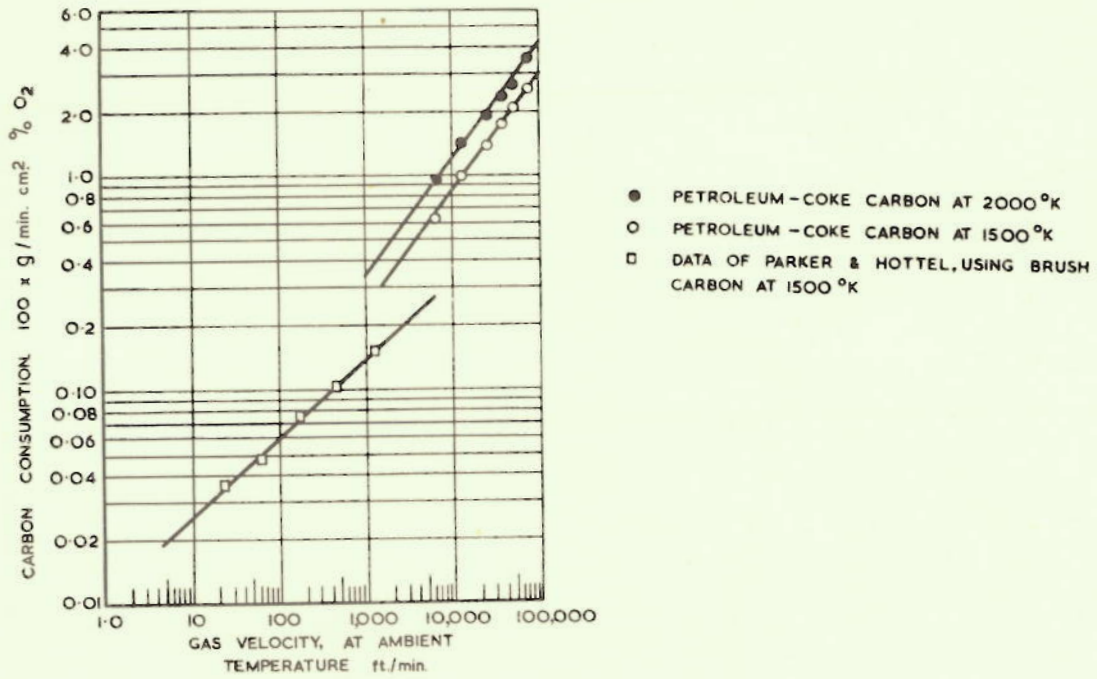


Fig. 7 The dependence of carbon consumption on gas velocity (after Day, Walker and Wright)

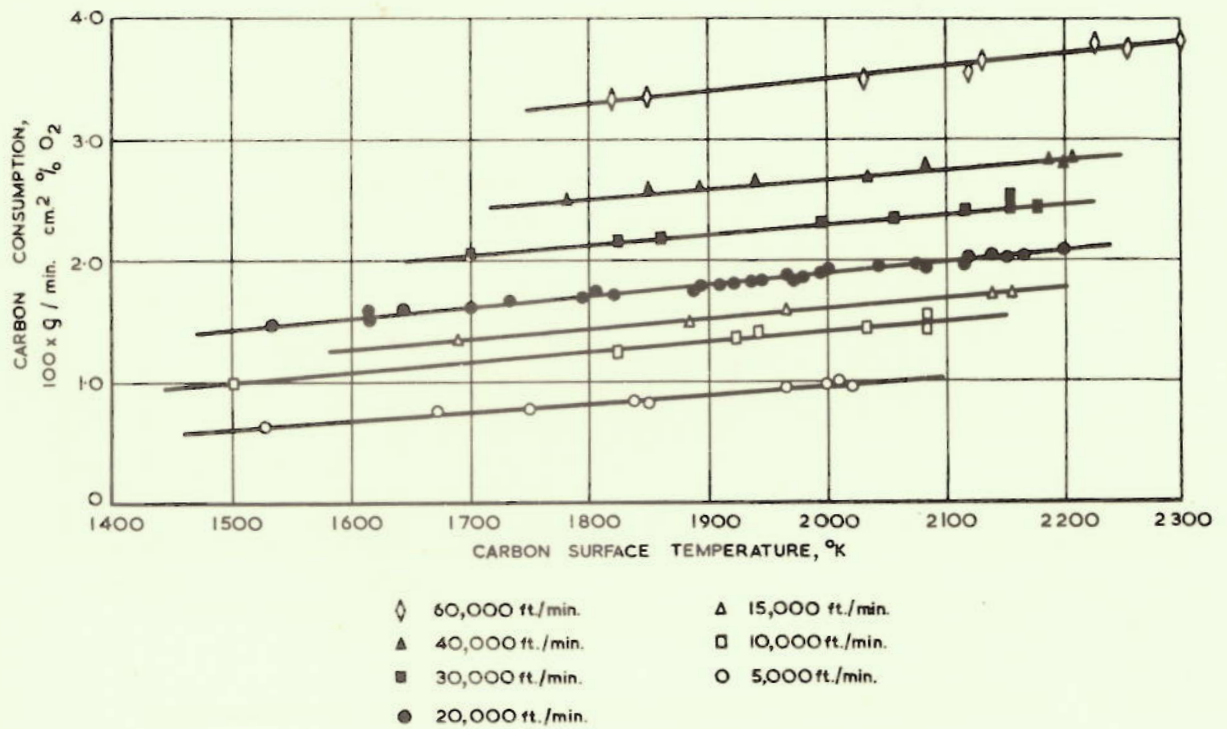


Fig. 8 Effect of temperature and linear inlet velocity on petroleum-coke (after Day, Walker and Wright)

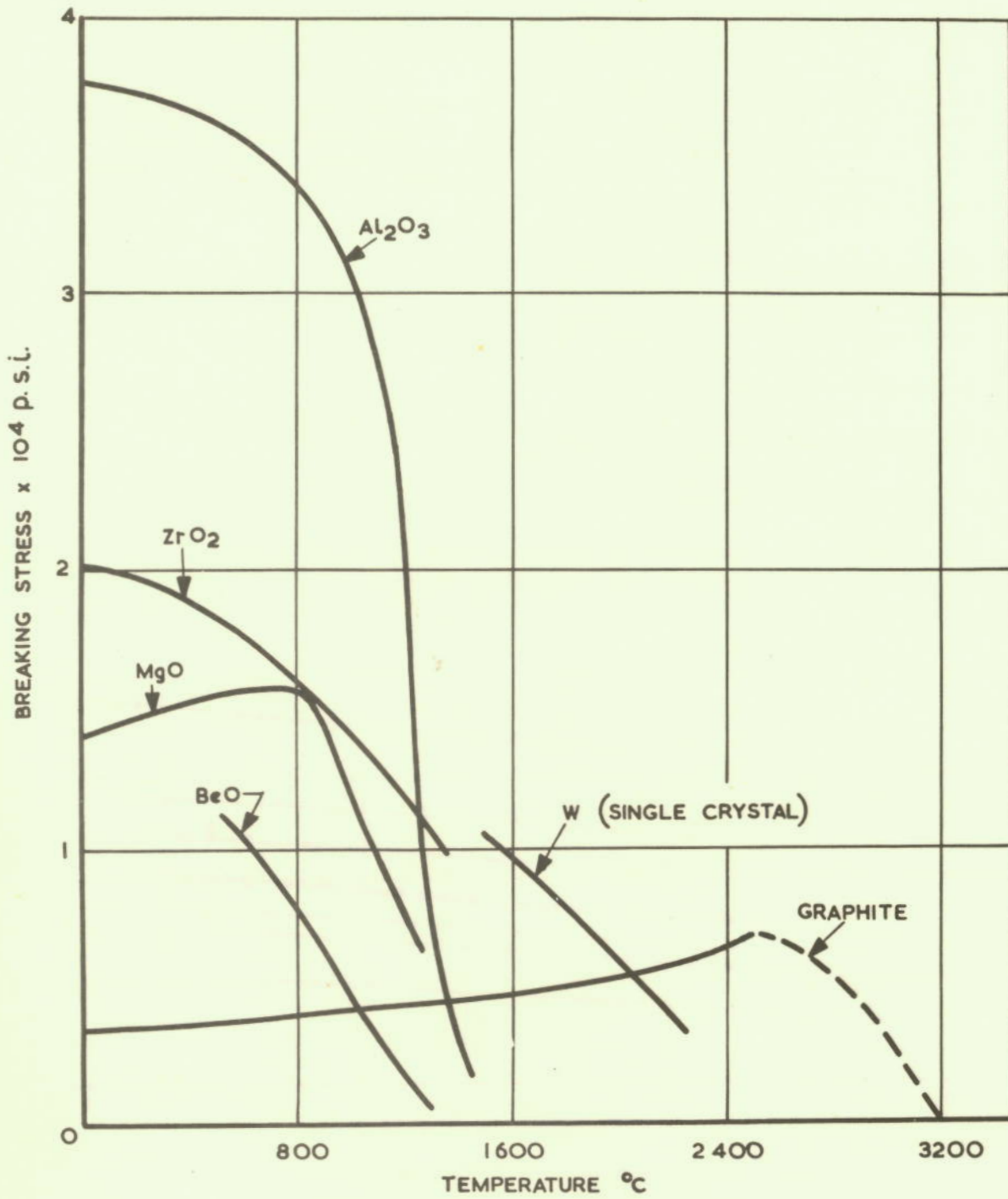


Fig.9 Short-time breaking strength of graphite compared with other high temperature materials. (After Hove).