

HEAT CONDUCTION IN CARBON MATERIALS*

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A general review of available data on heat conduction in carbons and graphites is presented. The interpretation of these data is given in terms of scattering of lattice waves by other lattice waves and by crystalline boundaries and leads to predictions for the dependence of thermal conductivity on heat treatment temperature.

I. INTRODUCTION

Measurements of thermal conductivity of solid carbon materials have been reported within the last two years by Berman¹, Mizushima² and Tyler and Wilson³. Prior to 1952, the best data available were those of Powell and Schofield^{4, 5}.

This paper attempts to present all of the recently published data and to discuss predictions⁶ of the heat-conducting properties based on these data.

The data on graphite are presented in Section II; baked carbons are treated in Section III. The brief survey of the theory of heat flow in nonmetallic crystals given in Section IV serves as introduction to the

formulation of predictions in Section V. The conclusions are given in Section VI.

II. EXPERIMENTAL RESULTS ON GRAPHITE

The best starting point for the discussion of heat conduction in carbons is the thermal conductivity of single crystals of graphite. Single crystals are available only from natural graphites. Measurements on single crystals of graphite are difficult in the extreme, because of the peculiar mechanical properties of the material. A single crystal of graphite supports very little shear stress parallel to the graphitic planes, making it difficult to obtain good thermal contact.

Berman¹ reports measurements below room temperature on a single piece of natural graphite for heat flow directed along the graphitic planes and also perpendicular to the planes. His data, plotted against temperature in Fig. 1, show two significant features:

1. The thermal conductivity of natural graphite in either direction shows a maximum below room temperatures and falls off to very low values as the temperature decreases toward absolute zero.

2. Heat flows much more easily along the graphite planes than normal to them. The factor of three for Berman's sample may well be larger for a more nearly perfect crystal. As a result of this anisotropy of the single crystals most of the heat conducted through

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¹ R. Berman, Proc. Phys. Soc. (London) **A65**, 1029 (1952).

² S. Mizushima, Phys. Rev. **86**, 1040 (1952).

³ W. W. Tyler and A. C. Wilson, Jr., Phys. Rev. **89**, 870 (1953).

⁴ R. W. Powell, Proc. Phys. Soc. **49**, 419 (1937).

⁵ R. W. Powell and F. H. Schofield, Proc. Phys. Soc. **51**, 153 (1939).

⁶ A brief review of the picture of heat conduction in carbons and graphites has been published recently by S. Mrozowski in Phys. Rev. **86**, 250 (1952); see also a modified and improved version in J. Am. Ceramic Soc. **35**, 282 (1952).

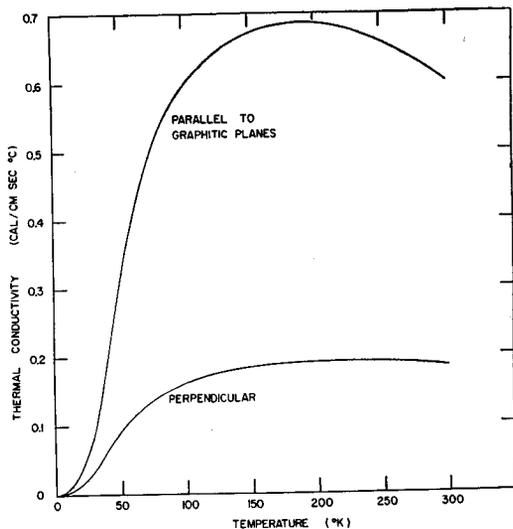


FIG. 1. Thermal conductivity of natural graphite according to Berman.¹

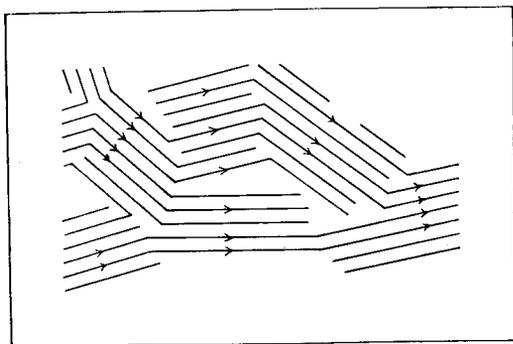


FIG. 2. Schematic arrangement of crystallites in polycrystalline graphite.

polycrystalline material is carried along the graphitic planes of the small crystallites.

In well-graphitized carbon stock, the small crystallites of graphite are usually hooked together in a rather disorderly way. Fig. 2 attempts to illustrate the situation for such material by schematically showing several crystallites (or platelets⁷) composed of just a few graphite layers viewed edgewise. As pointed out above, one expects most of the heat to be carried along the planes as indicated by the arrows in Fig. 2. However, the planes which are not hooked at the junction of crystallites are relatively ineffec-

⁷ S. Mrozowski, This volume, page 31.

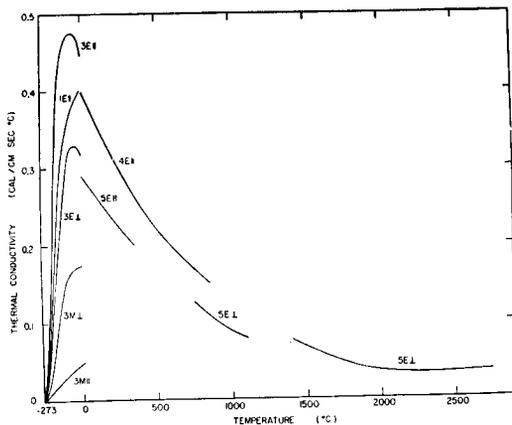


FIG. 3. Thermal conductivity of polycrystalline graphite. The numbers refer to references in the text. || means parallel to the axis, \perp perpendicular to the axis; E—extruded, M—molded material.

tive in carrying heat. It is also apparent that the arrangement of the coke particles and the crystallites within the particles determines the total length of path for the heat flow. Therefore, one expects for the thermal conductivity of polycrystalline graphites, values lower than for the single crystal in the parallel direction due to incomplete joining of the graphitic planes and to disorderly crystalline arrangement, in addition to the lowering due to the porous micro- and macro-structure of the material.

The published data on polycrystalline graphite are plotted versus temperature in Fig. 3. There is a pronounced maximum in the thermal conductivity (K) of polycrystalline graphites at or below room temperature⁸ and a slow decrease of K with increasing temperature above room temperature. This trend is in agreement with the behavior of natural graphite as far as the latter has been measured. The significance of such tempera-

⁸ Neither A. P. Crary (J. Appl. Phys. **4**, 332 (1933)) nor R. Buershaper (J. Appl. Phys. **15**, 452 (1944)) found a maximum in this region. Since their results are in such complete disagreement with all the more recent work, they are not included in this review.

ture dependence of thermal conductivity is discussed in Section IV.

The well-known anisotropy in physical properties for the transverse and longitudinal directions in extruded rods is not evident from the data of Powell and Schofield. An anisotropy in K for extruded rods is expected due to the alignment of the coke particles in the samples and to the alignment of the crystallites of graphite in the coke particles⁷. The first effect is principally due to the external shape of the original coke particles and their alignment in the extrusion process. One expects, therefore, varying degrees of anisotropy in K for extruded rods made under slightly different conditions or from different green mixes.

The scatter in thermal conductivity (K) as seen in Fig. 3 arises from a variety of sources. K depends on the density but not, however, in a unique manner. The value of K is affected by the shape and distribution of voids; furthermore, considerable amount of resistance to heat flow is localized at the junctions between particles. Both effects are controlled by such factors as the amount and type of binder material, the size and shape of coke particles, the conditions at extrusion or molding and the temperature to which the graphite was heat treated. One therefore expects a spread in K values from sample to sample because, due to lack of information, no good corrections to the data can be made for such structural differences.

III. EXPERIMENTAL RESULTS ON BAKED CARBONS

A number of determinations of the heat conductivity of baked carbons at room temperature have been made in the past with strongly differing results. They are all referred to in the paper by Powell and Schofield⁸. The scatter is certainly due to the same causes which were discussed in the previous section. Powell and Schofield have investigated the temperature dependence of K and have shown that K varies approxi-

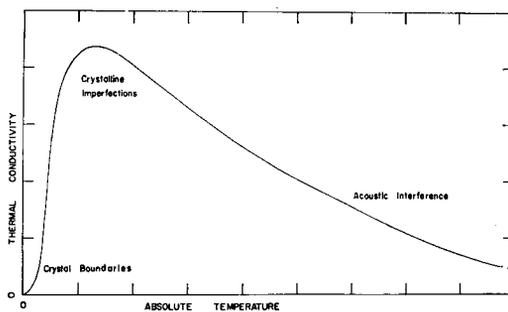


FIG. 4. Schematic temperature dependence of the lattice heat conductivity.

mately linearly with ambient temperature up to the heat-treatment temperature, whereas above this temperature K increases somewhat faster, the exact dependence on temperature in this higher range being not well established. Their curve for the range below heat-treatment temperature is given in Fig. 6 as a continuous line.

Mizushima² investigated the dependence of K on crystallite size (strictly speaking on the size in the a -direction, that is, the diameter of turbostratic crystallites of carbon) for a definite type of carbon (made from a pitch coke) at room temperature. His results are included in Fig. 6.

IV. HEAT FLOW IN NON-METALLIC CRYSTALS

Metals and non-metals have distinctly different heat-conducting properties. Metals exhibit a thermal conductivity which is almost independent of temperature. Non-metallic crystals show a thermal conductivity (K) whose temperature dependence is indicated by the solid curve in Fig. 4, which has a maximum K at intermediate temperature and decreases to small values for very low and very high temperatures⁹. Occasionally for a non-metallic crystal the maximum is found to be higher than the value for a good metallic conductor, but over most of the temperature range non-

⁹ The general dependence of K on Temperature is discussed in a recent review by J. L. Olsen and H. M. Rosenberg, *Advances in Physics* **2**, 28 (1953).

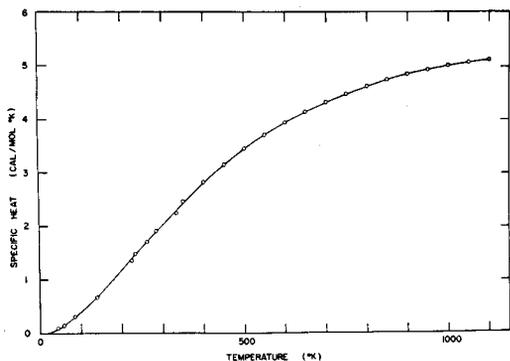


FIG. 5. Specific heat of graphite according to Magnus.¹⁰

metals have lower thermal conductivities than good metallic conductors.

The general temperature-dependence curve shown in Fig. 4 is basic for the interpretation of the thermal conductivity of baked carbons. It is expected to have the shape indicated for the following reasons:

For an electrically insulating crystal, heat energy in the form of lattice vibrations is carried by vibrational or acoustic waves through the crystalline lattice. Resistance to the flow of heat is due to the scattering of these acoustic waves. Vibrational waves in a perfect, non-metallic crystal are scattered by two rather distinct mechanisms, namely, by the temperature motion of the atoms (i.e., other vibrational waves) and by the boundaries of the crystal.

As was originally shown by Debye, the thermal conductivity of non-metallic crystals is

$$K = \frac{1}{3} Cvl, \quad (1)$$

where C is the specific heat per unit volume of the crystal, v is the speed of the acoustic waves transporting the heat and l is the mean free path of the acoustic waves concerned.

The specific heat observed for graphite by Magnus¹⁰ is shown in Fig. 5. For all substances, the atomic specific heat due to lattice vibrations varies as T^3 at very low

temperatures and is independent of T at high temperatures. Recently Gurney has shown¹¹ that the two-dimensional structure of graphite leads to a T^2 variation at moderately low temperatures; this is not inconsistent with the data of Magnus. With the temperature variations of the C factor as given in Fig. 5 and assuming the velocity of the acoustical waves to be almost independent of temperature, one can derive the shape of the curve in Fig. 4 from the relation (1) by considering the scattering of waves by the two mechanisms just mentioned—namely, temperature motion of the atoms and crystalline boundaries. For convenience let us divide the curve into three regions and consider separately the low temperature region, the high temperature region and the temperature region near the maximum in K .

The decrease of K at high temperatures is due to a combination of a slowly increasing specific heat factor and a strongly decreasing l factor. The decrease in the mean free path, l , with increasing temperature is caused by an increase in the number of excited lattice waves and in their amplitudes, and as a result of that a vibrational wave travels a shorter distance before finding atoms which are sufficiently displaced by temperature motion to scatter the wave concerned. As Debye has shown $l \propto 1/T$ for very high temperatures (above the Debye temperature θ); the atomic heat is almost constant for $T > \theta$ and the result is a decreasing thermal conductivity with increasing temperature.

At low temperatures, with the less vigorous vibrations of the atoms, an acoustic wave can travel much farther without being scattered by other vibrations. When this distance becomes very large, the wave will be scattered mainly by the boundary of the crystal and by lattice imperfections. The mean free path l becomes, under these conditions, of the order of the linear dimension of the crystal (or the average distance

¹⁰ A. Magnus, Ann. Physik 70, 303 (1923).

¹¹ R. W. Gurney, Phys. Rev. 88, 465 (1952).

between imperfections) and practically independent of temperature for a particular crystal. Therefore, the thermal conductivity at low temperatures will have the same temperature dependence as the specific heat.

The maximum in K occurs at a temperature when the two scattering mechanisms are about equally effective, that is, when l_T due to temperature vibrations (predominant at high temperatures) is about equal to l_B due to boundary scattering (predominant at low temperatures).

The shape of the curve around the maximum and the value of the maximum are controlled by several factors. If the resistance due to both boundary and lattice scattering is low, crystalline imperfections—dislocations, impurities and the like—may be the principal resistance to heat flow and thereby depress K values at low temperatures and flatten out the maximum.

The similarity of the shapes of the curves in Fig. 1 and Fig. 4 shows that all of the heat in crystalline graphite is conducted by atomic vibrations. Graphite has so few conduction electrons that they apparently do not contribute appreciably to either the specific heat or the thermal conductivity in the temperature range below 2400°C. The increase in K above this temperature⁵ may be due to a contribution of free electrons to the heat conductivity, since more and more free carriers are present in graphite as the temperature is increased.

V. HEAT FLOW IN POLYCRYSTALLINE CARBONS

If one assumes that the scattering by lattice vibrations is similar in all crystallites of carbon irrespective of their size (l_T the same for all types of carbons), the maximum in K versus T (where $l_T \sim l_B$) is expected to occur at higher temperatures as the crystallite size decreases, since l_B is of the order of crystallite dimensions (that is, about equal to the diameter of the crystal). The location of the peak in K (see Fig. 3) has been shown to be in fair, but not very con-

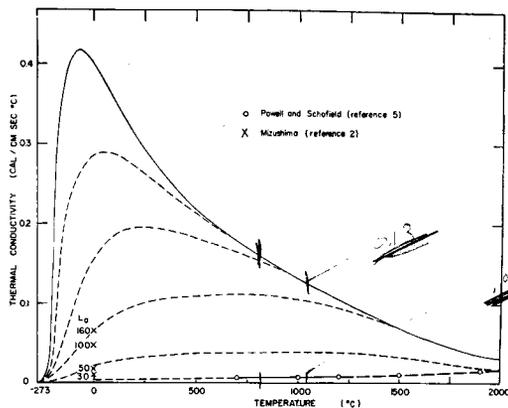


FIG. 6. Expected temperature dependence of the thermal conductivity of polycrystalline carbons as a function of crystallite size. Case of absence of intercrystalline resistances. Data for baked carbons taken from Powell and Schofield⁵ (O) and from Mizushima² (X).

vincing, agreement with the relative sizes of crystallites as determined for several types of polycrystalline graphites by X-ray diffraction^{1, 3}

Mrozowski⁶ pointed out that carbons present an excellent opportunity for an investigation of the changes occurring in heat conduction as a result of a decrease in crystallite size through the whole range from a single crystal down to almost amorphous material and gave a schematic picture of what is to be expected. The expected dependence of K on T is presented in Figs. 6 and 7 by dashed lines, where each dashed line is intended to correspond to a sample of the same carbon material, but heat treated to a different temperature. The curves for the larger crystallite sizes have shapes similar to that of well-graphitized stock (upper solid curve) with a reasonably-well-defined maximum in K near room temperature. For smaller crystallite sizes, the K values at low temperatures are lowered very markedly and the peak in K moves to higher temperature and becomes poorly defined.

A region of considerable practical and theoretical interest is the high temperature region (up to 2000°C for the present discus-

sion). If there were little or no resistance in the connections between crystallites, then as Mrozowski points out⁶ one expects K to be independent of crystallite size in this high temperature region. This behavior is shown schematically in Fig. 6 by the dashed curves joining the curve for well-graphitized stock. For this case, all the values of K coincide because the mean free path l_T is so short that the scattering at the boundaries can be neglected. Suppose, on the other hand, that the intercrystalline regions add resistance to the flow of heat from one crystallite to the next. The high temperature K values will then be lower the smaller the crystallites are, because of the larger number of boundaries per unit length of sample. This intercrystalline resistance effect is indicated schematically in the high temperature portion on Fig. 7 by the dashed curves being successively lower as the crystallite size is decreased. Available data are too meager to permit a statement concerning the existence of such an intercrystalline resistance. One has, however, to keep in mind that intercrystalline resistances might well be strongly temperature dependent and might become negligible at high temperatures, thus leading to a case resembling

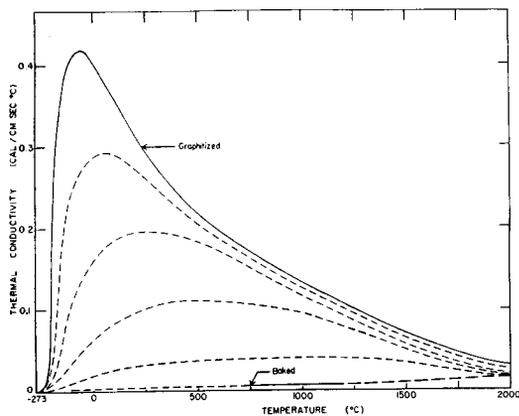


FIG. 7. Expected temperature dependence of thermal conductivity of polycrystalline carbons as a function of crystallite size. Case of presence of intercrystalline resistances at high temperatures.

Fig. 6. In fact, at low temperatures Tyler and Wilson³ found that K for polycrystalline graphites varies somewhat more rapidly with temperature than the atomic heat does; they suggest that the source of this discrepancy may be in the existence of temperature-dependent resistance to the heat flow across crystallite contacts.

So long as a sample is not heated beyond its previous heat treatment, its thermal conductivity will repeat itself for similar excursions in temperature. But heating to temperatures high enough to enlarge the crystallites within the sample will cause the thermal conductivity to shift up to a higher dashed curve on Figs. 6 and 7 along which K will again be repetitive. The changes in K expected to occur during the heat treatment are indicated on Fig. 6 and 7 by a heavy broken line.

For baked carbons in the range from room temperature to about 1000°C K is linear with T , which is consistent with the approximate linear dependence of C . For such small crystallite sizes the maximum of K is expected to shift to quite high temperatures, well above the heat-treatment limit, and so to be beyond observation. For the baked carbons a proportionality of K with the crystallite size is also expected; Mizushima's data² do not show the proportionality too well and thus are not as convincing a demonstration of the type of relationship between these two quantities as one would like to have.

VI. CONCLUDING REMARKS

In conclusion the following seems to be worth emphasizing:

A. The measurements on natural graphite indicate that most of the heat conducted through graphitic material actually flows along the graphitic planes. This feature predicts anisotropy in thermal conductivity of polycrystalline material similar to the anisotropy observed in its electrical resistivity.

B. The few data that are available show sufficient variation in the property of heat conduction from sample to sample to indicate real differences in the thermal conductivity of polycrystalline graphite due to crystalline arrangement, binder type and content, and base material. It remains for more systematic experimental study to clarify the extent of these differences well enough to allow satisfactory prediction in specific cases.

C. The general shape of the temperature dependence of the thermal conductivity of polycrystalline graphite shows that almost all of the heat is conducted by the lattice. Assuming this to be true in general for all carbons, predictions of the thermal con-

ductivity of polycrystalline carbons with intermediate crystallite sizes can be made. The predicted curves are given in Figs. 6 and 7. Experimental data to check these predictions are scarce and more satisfactory experimental support is needed before one can make a choice between the two cases. However, one can say in general that the recent data on thermal conductivity tend to support a unified explanation for the conduction of heat in solid carbons and graphites. It is expected that more systematic data, when available, will support the general predictions as sketched in Fig. 6 or 7 and will improve our understanding of the mechanism of heat conduction in carbon materials.