JOURNAL OF MATERIALS SCIENCE 2 (1967) 507–512

Vitreous Carbon – A New Form of Carbon

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Received 19 June 1967

The carbonisation of certain cross-linked polymers under carefully controlled conditions yields a non-graphitising carbon which, on account of its high lustre and conchoidal fracture, has been called "vitreous carbon". Other properties distinguishing vitreous carbon from the more common forms of the element include high strength, hardness, and resistance to corrosion, with low porosity and permeability. It has advantages over other materials of construction in a wide range of laboratory, metallurgical, mechanical, and electrical applications.

1. Introduction

Carbon exists in many forms, but of these only two, diamond and graphite, can be completely characterised, and these are the true allotropes; both occur naturally. A wide range of artificial bulk carbons has been prepared for industrial use but these materials are basically graphitic in structure or may be graphitised readily; their properties (e.g. degree of graphitisation) can be controlled to some extent to suit particular applications. A new form of carbon has now been prepared [1] which, on account of its similarity to glass in both appearance and fracture, has been called *vitreous carbon*. Vitreous carbon exhibits many differences in properties from those of graphite and baked carbons and provides a useful addition to the range of carbon products already available.

2. Structure of Vitreous Carbon and Other Carbons

Each atom in the diamond lattice is joined by covalent links to four others surrounding it at the corners of a regular tetrahedron, with an interatomic distance of 1.54 Å. The hardness, high density, and high melting point have been attributed to the covalent bond. Graphite, on the other hand, consists of carbon atoms arranged as hexagons in flat parallel sheets: the distance between adjacent sheets (which are held together by van der Waal's forces) is approximately 3.35 Å, while that between atoms within a sheet (covalent bonds) is 1.42 Å. The layers may be packed so that half of the carbon atoms in one layer lie over the mid-points of the hexagons in the next layer, the atoms in the third layer being situated directly above those in the first layer. This is the *abab* arrangement or *hexagonal structure*. Another structure, in which the position of the third layer with respect to the second is the same as that of the second with respect to the first (*abcabc* arrangement or *rhombohedral structure*), occurs to the extent of a few per cent in most samples of graphite. The hexagonal structure, which is more stable, can be partially converted to the rhombohedral by grinding, but on heating to 2000 to 3000° C the change is reversed.

Diamond has a density of 3.52, whereas the true crystal density of graphite is 2.26. Graphite is the stable form of the element and diamond is converted to it on heating to 1800° C. Diamond is the hardest substance known and is represented by a figure of 10 on Mohs' hardness scale; on the other hand, graphite is soft and has a value of 1 on Mohs' scale. It flakes readily and will mark paper.

Industrial carbons and graphites are generally prepared by heating a mixture of ground coke and pitch in the absence of air to a maximum heat-treatment temperature of about 1200° C (baked carbons) or about 2500° C (graphites). The products are composite granular materials, the structures and properties of which are dependent upon those of the coke grains and the carbon residue resulting from the carbonisation of the pitch, and also upon the heat-treatment temperature. Crystallite growth during the high-temperature treatment increases with the degree of order in the original coke grain. Variations in these parameters account for the wide range of properties available in carbon products. Manufactured graphite exhibits very marked anisotropy in its mechanical properties, considerable variation being found in properties measured parallel and perpendicular to the "grain" or axis of extrusion.

Vitreous carbon is prepared by the thermal degradation of selected organic polymers. The properties of the chars are dependent on the maximum temperature of the heat-treatment, but a material which has proved satisfactory for a large variety of purposes has been prepared by limiting the maximum temperature to 1800° C. X-ray diffraction patterns of material fired to this temperature (fig. 1) are very diffuse and have been interpreted in terms of a "turbostratic" structure consisting mainly of graphite-like hexagonal layers in very small "packets", with no true graphitic orientation between the layers. It is possible that some even less well-ordered material may also be present. The "crystallite" size, estimated from the broadening of the (1 0.)* and (00.2) reflections, is only 50 Å (L_a) × 15 Å (L_c), compared with many hundreds of Ångströms for a typical electrode graphite; the interlayer spacing is approximately 3.5 Å, compared with 3.35 Å for a true graphite. After heat-treatment at 2750° C, the apparent size of "crystallites" increases only slightly, to $L_a \simeq$ 73 Å, $L_c \simeq$ 28 Å, with an interlayer spacing of 3.44 Å. (However, under certain conditions, superficial recrystallisation has been observed [2].)

In view of the low density, only two-thirds of the theoretical density of graphite, any structure based even remotely on that of graphite would be expected to be associated with a high porosity; yet the porosity is exceptionally low (table I) and the density in helium is the same as in water, showing that any pores present must be inaccessible to helium molecules. The most likely explanation is that the structure differs from that of graphite to a much greater extent than is suggested by the above interpretation of the X-ray data. The hardness and high strength of vitreous carbon (section 3.1) suggest that the structure may include some tetrahedral cross-links between the hexagonal layers. This is considered likely in view of the presence of such cross-links in the start material and the isotropy of properties irrespective of the method of fabrication of the polymer precursor.

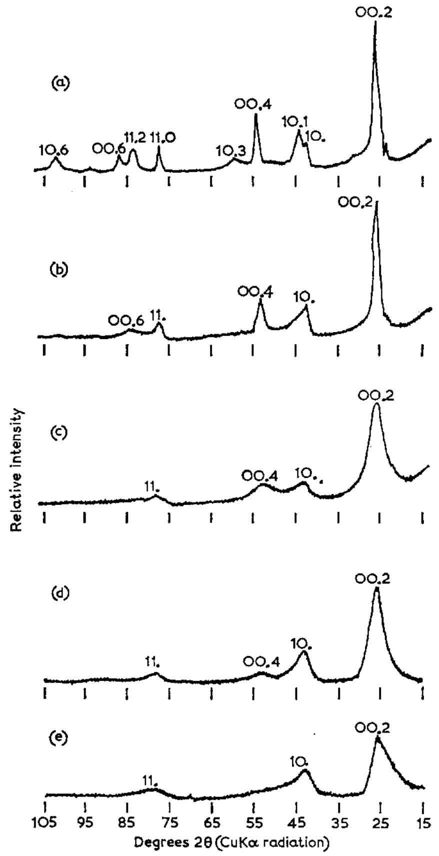

Figure 1 X-ray diffraction patterns of petroleum coke and vitreous carbon: (a) petroleum coke, 3250° C; (b) petroleum coke, 2200° C; (c) petroleum coke, 1200° C; (d) vitreous carbon, 2750° C; (e) vitreous carbon, 1800° C.

3. Properties of Vitreous Carbon

3.1. Physical Properties

Typical physical properties of bulk carbons are given in table I.

One of the most striking differences between vitreous carbon and conventional graphites is its extremely low permeability to gases. The value for vitreous carbon, obtained by a mass spectrometric method using helium, is about 13 orders of magnitude less than that of an electrode graphite and 9 orders less than that of Morganite EY9; it is comparable to that of hard glasses. The very low porosity of vitreous carbon to water and to helium is surprising in

*i.e. (1 0.0) and (1 0.1) unresolved

TABLE I Typical physical properties of carbon products.

Property		Baked carbon	Electrode graphite	Morganite EY9	Vitreous carbon
Apparent density (g/cm^3)		1.57	1.55	1.7	1.47
Porosity (%)		20 to 30	20 to 30	17	<0.05
Permeability to gases (cm^2/sec)		—	>20 (air)	0.015 (air)	$<2.5 \times 10^{-11}$ (helium)
Transverse strength (lb/in.^{2})*	With grain	1100	1000	5800	10 000 to 30 000
	Across grain	800	700	1900	
Compression strength (lb/in.^{2})	With grain	3800	2900	7400	10 000
	Across grain	—	—	3300	
Young's modulus (10^6 lb/in.^{2})	With grain	1.2	0.6	1.9	3 to 4
	Across grain	—	—	0.7	
Electrical resistivity (10^{-4} ohm cm)	With grain	50	9	19	30 to 80
	Across grain	75	11	39	
Thermal conductivity (cal/cm sec ° C)	With grain	0.017	0.22	0.14	0.01 to 0.02
	Across grain	—	0.17	0.11	
Coefficient of thermal expansion ($\times 10^{-6}$/° C)	With grain	—	2.2	1.8	2.2 (0 to 100° C)
	Across grain	—	3.6	4.0	3.2 (100 to 1000° C)

*1 lb/in.^{2} = 7×10^{-2} kg/cm^2

TABLE II Typical impurity levels of vitreous carbon.

Impurity (as oxide)	Quantity (ppm)
Calcium	40
Iron	40
Aluminium	20
Silicon	80
Titanium	<5
Strontium	<5
Barium	5
Sodium	5
Magnesium	<5
Ash	200

view of the low value of the density (viz. 1.47) compared with that of the other carbons (1.55 to 1.7), and the expulsion of large volumes of volatile products during the carbonisation process. It is worthy of note that polymers containing quantities of bromine up to 2 wt %, when subjected to the vitreous carbon process, still retained substantially the whole of the bromine even after heat-treatment to 1800° C.

Vitreous carbon is much stronger than any of the other carbons or graphites quoted. Its electrical and thermal conductivities resemble those of baked carbons but are considerably lower than those of the graphites. It has a hardness value of 6 to 7 on Mohs' scale; on using the Vickers' diamond identation equipment, the indentation almost disappears as soon as the pressure is relieved, suggesting that the material retains some of its elastic properties after treatment at 1800° C. Plastic properties are very marked in intermediate stages, and chars prepared at 100° C will readily deform under the influence of a load if heated to higher temperatures.

3.2. Chemical Properties

Vitreous carbon as normally prepared has an ash content up to a maximum of 200 ppm. Table II shows a typical analysis of the ash. The impurities are likely to be derived from the raw materials rather than through pick-up during the course of processing. Polymers which give a carbon yielding an ash of less than 10 ppm have been synthesised. Little in the way of gaseous impurities is retained in the carbon and the presence of hydrogen has been found barely discernible by proton resonance techniques.

Most forms of carbon are inert to a wide range of chemical reagents, but vitreous carbon, on account of its low permeability, negligible porosity, and a low specific surface, tends to be even more inert. Fig. 2 compares typical rates of oxidation of various carbon products [1, 3, 4] by dry air. The measured values of the rates of

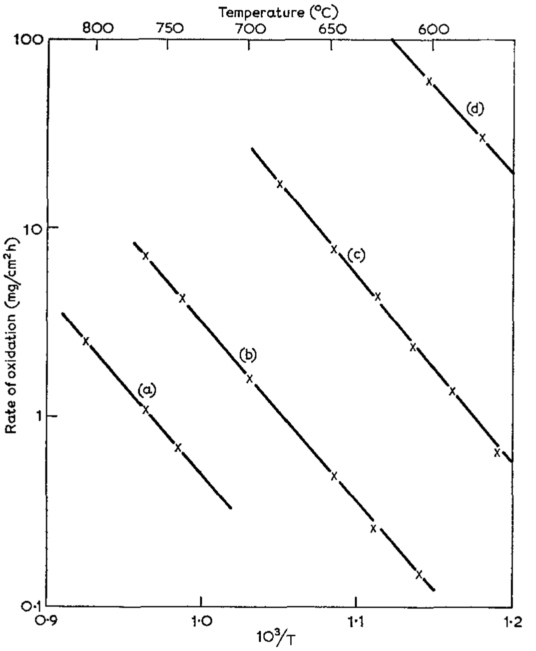

Figure 2 Oxidation rates of various carbons in dry air: (a) vitreous carbon, 20 ppm impurities; (b) vitreous carbon, 200 ppm impurities; (c) close-grained graphite; (d) baked carbon.

TABLE III Rates of reaction of vitreous carbon.

Reagent	Temperature (° C)	Weight loss rate (g/cm² h) (apparent surface)
Steam	570 to 580	0.05
Carbon dioxide	1000	0.1 to 0.5×10^{-3}
Carbon dioxide	2500	0.8
10% oxygen, 90% argon	2500	1.8
10% hydrogen, 90% argon	2500	0.07
Fused potassium bisulphate	500	2.4×10^{-4}
Fused boric oxide	580	$<5 \times 10^{-6}$
Fused caustic soda	320	$<5 \times 10^{-6}$

attack by some other reagents are shown in table III.

Fusions with calcium fluoride and alkali peroxides have a relatively small effect on vitreous carbon. Its behaviour in hydrochloric, hydrofluoric, nitric, sulphuric, and chromic acids, and in mixtures of nitric acid and oxidising agents, is better than that of the non-vitreous carbons.

Reactions with elements which give lamellar compounds with graphites are of interest. Vitreous carbon is highly resistant to attack by chlorine and bromine but disintegrates in the presence of alkali metals. With carbide-forming elements, diffusion may occur; for example, a layer of βSiC approximately 6 μm thick was formed on the surface of a crucible used for melting silicon. With non-carbide-forming elements including germanium, silver, gallium, phosphorus, arsenic, tellurium, zinc, tin, lead, etc., the rates of attack are very small.

4. Fabrication

Unlike the conventional carbons and graphites, vitreous carbon cannot yet be prepared in sections thicker than $\frac{1}{4}$ to $\frac{5}{16}$ in. Since its origin is a polymer, the techniques of forming the shape are generally those applicable to the plastics industry, and piece parts are usually formed before firing. The elimination of gaseous products during carbonisation is effected without disruption of the body; shrinkage is uniform and isotropic and dimensional accuracy of ±0.005 in./in. is obtainable. Machining of fully processed material is best carried out by diamond-grinding or ultrasonic techniques; there is little tendency for the material to break away as do graphites, and surfaces acceptable for hydrodynamic air bearings have been produced.

5. Applications

5.1. Laboratory

The following articles have been made: beakers, basins, boats, crucibles, closed and open end tubes, cone and butt joints, glass/carbon seals, burette taps, fritted filters, and susceptors.

The extreme chemical inertness, impermeability, and non-porosity make vitreous carbon a useful material for crucibles. It has significant advantages over nickel, iron, platinum, tantalum, and other metals, for example in fusions and acid-leaching operations. Similarly, it has advantages over glass and silica, since it can be used in contact with alkalis and hydrofluoric acid. It is of great interest in the field of high-purity materials owing to its non-ionic and non-porous character, and has been used extensively for the processing of semiconductor and fluoride laser materials. Other uses include growth of alkali halide optical crystals, zone refining of metals and chemicals, and various analytical operations.

The similarity of the coefficient of thermal expansion of vitreous carbon to that of some borosilicate glasses has enabled interchangeable glass and carbon tube-joints to be made. Such joints permit the electrical properties and the corrosion resistance of the carbon to be utilised in standard forms of chemical equipment. In addition, burette taps having the same cone angle as normal glass taps have been made and these have an advantage over PTFE* inasmuch as there is no tendency to flow. The fritted filter is an interesting development and is particularly valuable in filtering from hydrofluoric acid or strong alkali solutions.

Glass/carbon seals have been made in several ways, these include direct compression seals and glass/metal/carbon bonds. They have been found to be tight to hydrogen.

RF susceptors of vitreous carbon form a useful item of vacuum furniture owing to the electrical properties and ease of outgassing of the material, and both nichrome and aluminium films have been made by evaporation of the metals from vitreous carbon crucibles.

5.2. Metallurgical and Chemical Engineering

An important characteristic of vitreous carbon is that it is not wetted by a wide range of metals, including aluminium, zinc, silver, copper, gallium, tin, lead, and precious metals; it has already found application in the processing of many of these metals and their alloys, for instance in the form of dip pipes for the dehydrogenation of molten aluminium with chlorine gas. Apparatus for direct casting and for floats, launders, distributors, filters, and Telegas probes is under investigation.

Thermometer pockets have been made for general use and these may well have a universal applicability. Dip pipes for corrosive liquids and jets for use in the manufacture of PTFE have also performed satisfactorily.

Encapsulated nuclear fuel elements, viz. uranium and thorium carbides enclosed within a vitreous carbon skin, have good fission-product retention properties, but shrinkage occurs on neutron irradiation.

5.3. Mechanical and Electrical

Various applications utilise the resistance of vitreous carbon to erosion. Mandrels and other equipment for glass-working have proved very successful as also have process jigs for glass/metal seals.

Coefficients of friction of vitreous carbon against a number of fibres, both natural and man-made, have been found to be almost identical to those of glass; the carbon may find use for spinning guides, thus avoiding static problems associated with non-conductors. In addition to the making of furnace tubes and bursting discs, other future developments may include steam, fuel and rocket nozzles, and floats for flow gauges. Type characters for teleprinters and typewriters are at present being evaluated. The smoothness of surface and chemical inertness of the material have been utilised in valves and artery tubes for artificial hearts.

Vitreous carbon brushes have been found satisfactory for carbon track potentiometers. Their main characteristics are low electrical resistance and noise, smooth surface, and resistance to erosion. Lightning protectors for telephone circuits have proved to be very durable under arduous test conditions, and welding rods for spot-welding aluminium outlast corresponding items made from graphite electroplated with copper.

Thin films of nickel and gold have been produced by electroplating onto a vitreous carbon electrode and since the carbon is non-porous the films are readily stripped.

6. Summary

Vitreous carbon is a new material which combines some of the properties of glass and silica with some of those of normal industrial carbons. For constructional purposes, it has significant advantages over silica and glass in its resistance to corrosion, and over other carbons in its impermeability and its resistance to both corrosion and erosion. It is more resistant to oxidation than other carbons and can be used safely in air at temperatures 100 to 200° C higher than graphite. Under non-oxidising conditions, it may be heated up to 2500° C without undergoing phase changes; in this respect, it is superior to glass, silica, and many non-graphitised carbons. Vitreous carbon is intermediate between glasses and carbons in respect of both thermal and electrical conductivity and can be described as a conductive ceramic.

Acknowledgements

The authors are indebted to all those colleagues

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*polytetrafluoroethylene

who have contributed to the development of vitreous carbon; to Mr G. V. Smith for carrying out the X-ray diffraction analysis; to John Wiley and Co for permission to reproduce X-ray diffraction data on petroleum cokes and physical properties of industrial carbons, from *The Encyclopedia of Chemical Technology* by Kirk-Othmer; and to Morganite Carbon Ltd of Battersea, London, for data on EY 9 graphite. Thanks are due to The Plessey Co Ltd, and to Vitreous Carbons Ltd of Evenwood, Co Durham, for permission to publish.

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