

Review

Phenomena of catalytic graphitization

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In recent years the phenomena of catalytic graphitization have developed considerably. Four types of catalytic graphitization are known to produce G-, T_S -, A- and T_n -components. The review summarizes the use of elements, alloys and compounds as catalysts. The importance of catalyst particle size is stressed as well as the method of addition of the catalyst to the carbon. Extents of graphitization induced by catalysts are markedly dependent upon the existing degree of graphitization already present in the parent carbon. The effects of graphitization at different temperatures are summarized as well as the effects caused by the ambient atmosphere, for example by oxygen and nitrogen. Mechanisms of catalytic graphitization resulting in G-, T_S -, A- and T_n -components are outlined and changes in synthetic graphites caused by catalytic graphitization are presented.

1. Introduction

Graphites are materials of significant importance to a technological society [1]. Their high electrical conductivity, combined with their thermal and chemical resistance, enables them to be used as electrodes in steel making, as electrodes in the chemical industry, as refractory materials in chemical and high-temperature applications and in nuclear reactors [2].

Fig. 1 is a diagrammatic representation, showing stacking sequences, of constituent lamellar molecules, in isotropic, graphitizable, turbostratic and graphitic (graphite) carbons. The crystallographic order, already present in graphitizable carbons of heat-treatment temperature (HTT) 700 to 1300 K, is established as the lamellar nematic liquid crystals and mesophase of the carbonization process [3]. It is the approximately parallel stacking sequences of molecules in the initiating liquid crystal which is perfected towards hexagonal graphite at graphitization temperatures.

Some carbons, usually isotropic (see Fig. 1a) and prepared from parent materials which do not fuse, for example from thermosetting resin, copra

and wood, do not graphitize on heat treatment to graphitizing temperatures.

Graphite is made commercially by electrical resistive heating (to temperatures in excess of 3300 K) [1] which process forms a significant proportion of the total manufacturing costs. Any progress towards being able to make an acceptable graphite at temperatures below 3300 K is therefore of great interest. The phenomenon "catalytic graphitization" is well established since the inventions of Acheson [4]. Industrially, catalytic graphitization does not have extensive applications because of the undesirable characteristics of graphites containing significant amounts of residual catalyst material.

Several reviews of catalytic graphitization are available [5–8]. Traditionally, catalytic graphitization refers to the enhancement of the crystallinity of the carbon by the formation of graphitic material involving a chemical reaction between the ungraphitized carbon and the metal or inorganic compound which constitutes the graphitization catalyst. Recently, this rather limited view of catalytic graphitization has been extended

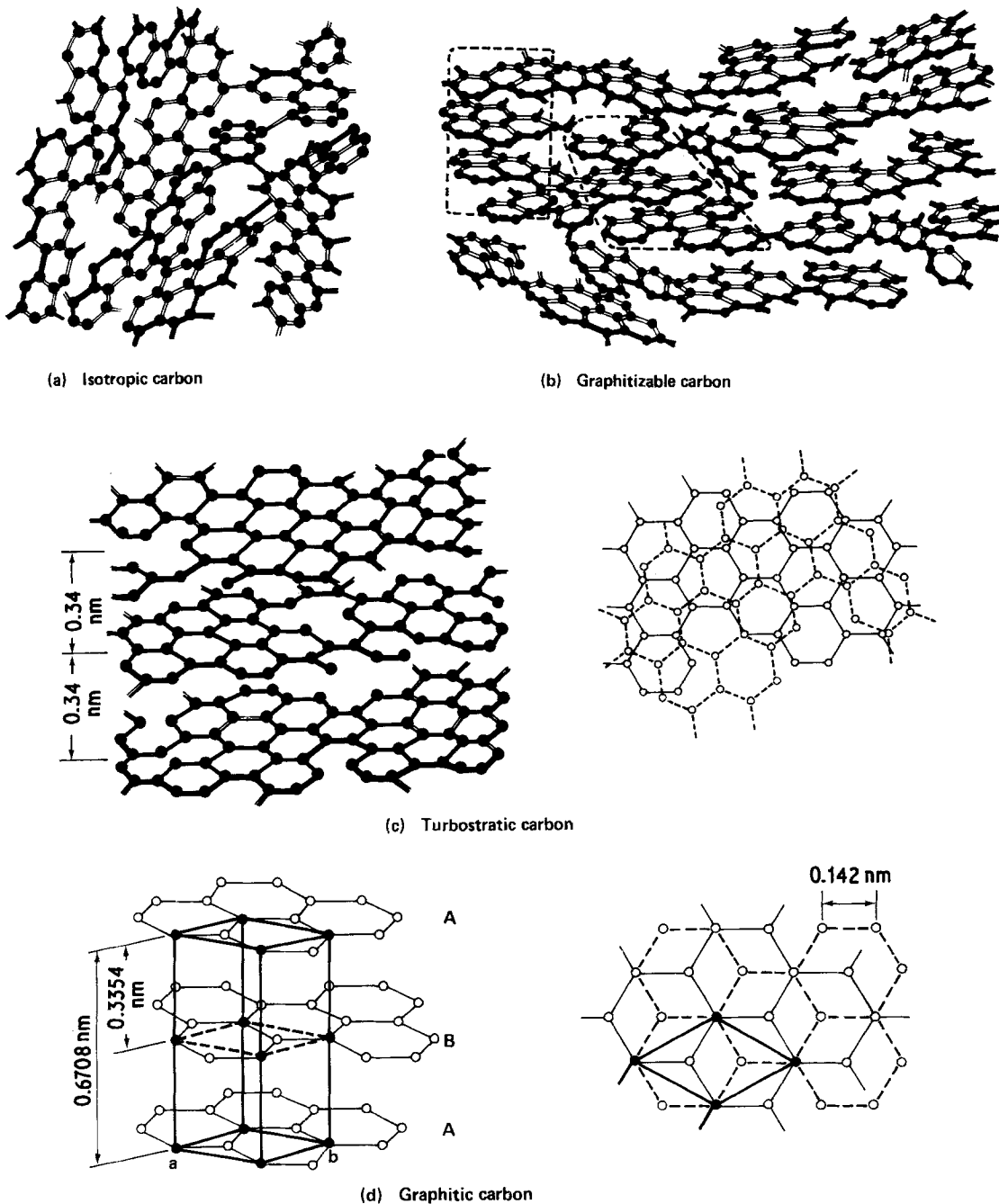


Figure 1 Diagrams of structures of (a) isotropic, (b) graphitizable (c) turbostratic and (d) graphitic carbons.

using new experimental techniques. This review summarizes the established aspects of catalytic graphitization and outlines these new catalytic effects.

2. Phenomena of catalytic graphitization

The processes of the catalytic graphitization of carbon have been studied extensively in recent

years, mainly by workers in Japan and Germany. The phenomena of catalytic graphitization are now known to be extensive and complicated. This review attempts to place these phenomena into four categories or processes and sets out methods of catalytic graphitization, of resultant structures and properties as well as considering industrial implications.

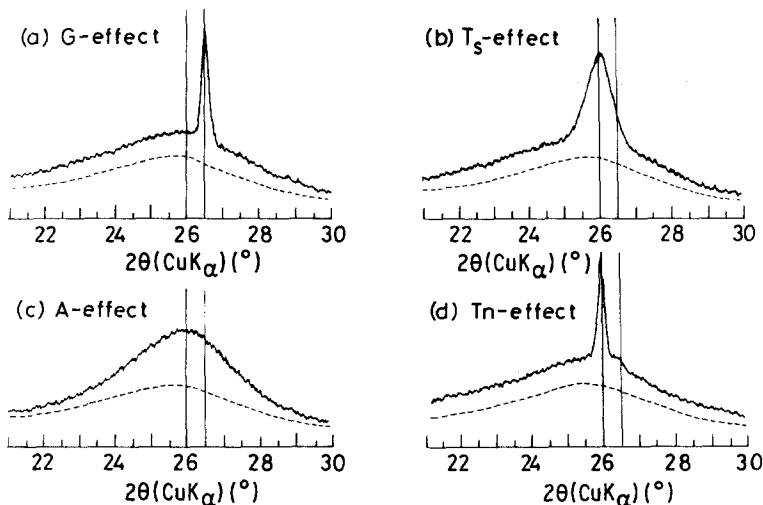


Figure 2 X-ray diffraction (002) profiles of carbon before (dotted line) and after (solid line) catalytic graphitization.

2.1. The G-effect

Graphitic carbon (the G-component, Fig. 1d), with a d_{002} -spacing of approximately 335.4 pm and a crystallite height, $L_c > 50$ nm can form within a less-crystalline parent carbon on heating with a graphitization catalyst which is usually present in appreciable quantity. The X-ray diffraction pattern of such graphitized material is a composite of a broad profile from the parent carbon and a sharp profile from the G-component ($2\theta = 26.5^\circ$), see Fig. 2a. This is a multi-phase or heterogeneous graphitization. Graphite which is found in cast iron [9] or kish graphite of the iron melt [10] is of this type. Fig. 3a shows a high-resolution phase-contrast transmission electron micrograph of fringe-images from the lattice of a G-component graphite.

2.2. The T_S -effect

If the catalyst is finely divided (e.g. 20 nm nickel particles) and heated with a non-graphitizing parent carbon the more ordered, turbostratic T_S -component (not the three-dimensionally ordered graphitic structure, Fig. 1c) is formed. Values of d_{002} and L_c vary from 338 to 342 pm and from 6 to 20 nm, respectively, dependent upon the catalyst used and calculated from the broadened profile at around $2\theta = 26^\circ$, using $\text{CuK}\alpha$. This turbostratic structure is stable and remains unchanged on heating to 3300 K at a pressure of 0.1 MPa [11, 12] or to 2300 K at 0.5 GPa [13]. Fig. 2b is the composite X-ray diffraction profile of the parent carbon and T_S -component ($2\theta \sim 26^\circ$). A phase-contrast micrograph of the T_S -component is shown in Fig. 3b [14–17].

2.3. The A-effect

A more homogeneous catalytic graphitization can occur if the parent carbon is heated with a very finely divided catalyst such as vaporized metal or by elemental substitution in the carbon crystallite. Fig. 2c shows the single sharpened profile of the d_{002} diffraction resulting from so treating a phenolic resin carbon. A phase-contrast micrograph of this A-component is shown in Fig. 3c [16].

2.4. The T_n -effect

A non-graphitizing carbon heated to graphitization temperatures gives a complicated (002) X-ray diffraction profile in which a broad profile has, superimposed over it, two small but sharp peaks situated at 26° (T_n -component) and 26.5° (G-component) [18–21]. If a non-graphitizing carbon is heated with a suitable catalyst, for example charcoal with calcium vapour, the peak of the T_n -component becomes quite pronounced at a temperature above 1700 K, see Fig. 2d. This T_n -component, with a d_{002} of 342.8 pm and L_c of 90 nm [22, 23], is turbostratic, as is the T_S -component, and shows interference bands at intervals of 20 to 30 layers. A sharp peak situated at 26° becomes pronounced also on grinding a non-graphitizing carbon [24], but it is not known if this component gives interference bands of the type seen in Fig. 2d.

3. Conditions of catalytic graphitization

3.1. Elements of catalysts

Ishikawa and co-workers [25, 26] attempted unsuccessfully to categorize the efficiency of

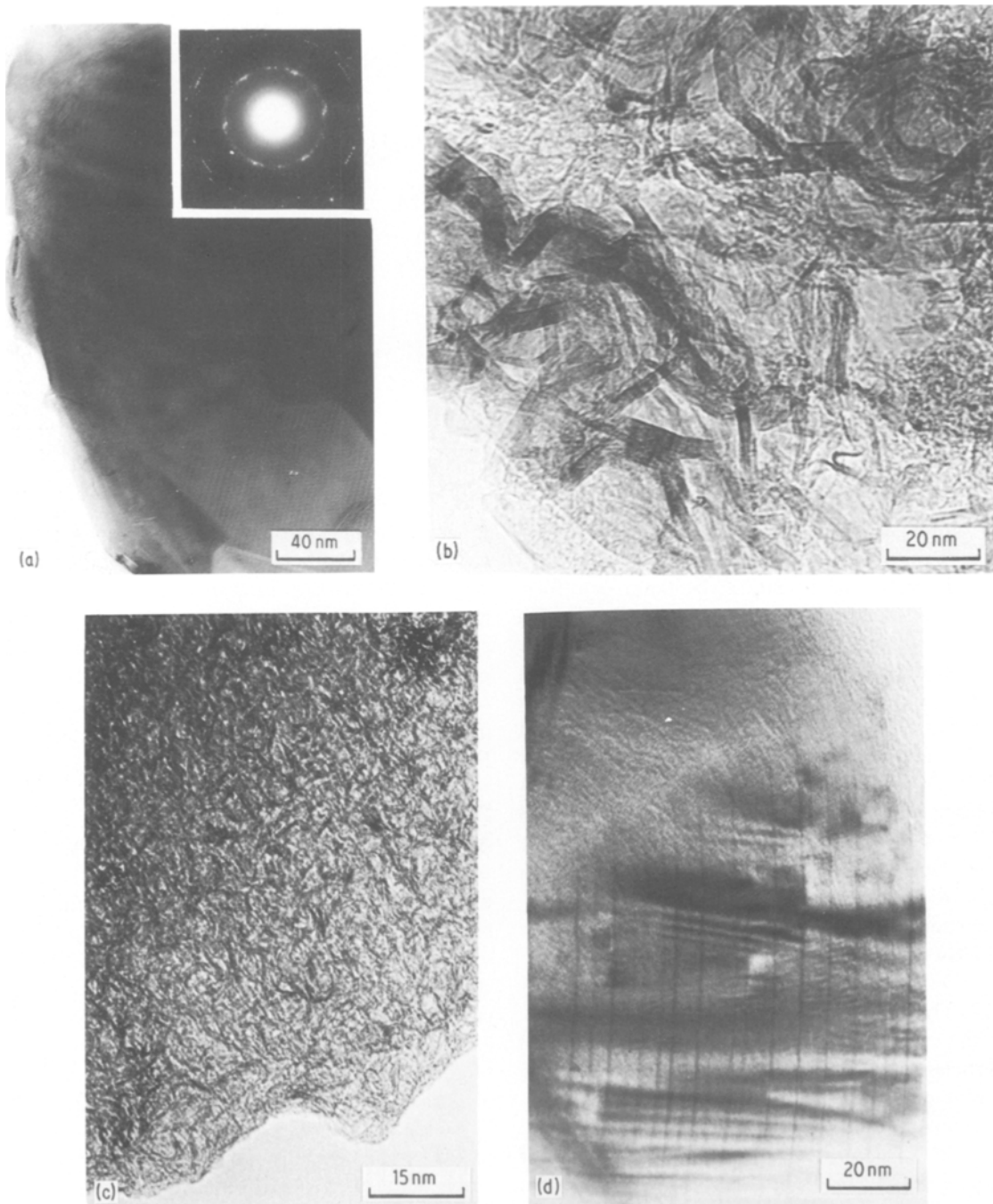


Figure 3 High-resolution phase-contrast electron micrographs of: (a) the G-component, PF carbon, 30 wt% Ni, with HTT of 2100 K, 0 min soak [16]; (b) the T_S-component, PF carbon, 1 wt% Ni, with HTT of 1700 K, 0 min soak [16]; (c) the A-component, PF carbon, no additive, with HTT of 2100 K, 1 h soak [16]; (d) the T_n-component, charcoal catalyzed by calcium vapour, with HTT of 2100 K, 1 h soak [22].

elements as catalysts using the periodic table. Their failure in this may be due to: (a) the use not only of metals but also of oxides and carbonates; (b) the use of a graphitizing carbon which is not so susceptible to catalytic graphi-

tization as non-graphitizing carbons; (c) the use of only 0.5 to 3 wt% of catalyst, amounts often too small to produce detectable changes. Weisweiler *et al.* [27], in a more systematic examination, heated a glassy non-graphitizing

TABLE I Elements acting as a graphitization catalyst

Ia	IIa											IIIa	IVa	Va	VIa
Li	Be											B	C	N	O
[25] [26]	[65]											[27] [28] [52]			[68] [69] [70]
Na	Mg											Al	Si	P	S
	[27] [28]	IIIb	IVb	Vb	VIb	VIIb	VIII		Ib	IIb		[28] [65]	[28] [81]		[83]
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
	[28]		[28] [33] [61]	[28] [61] [85]	[27] [28] [34]	[28]	[27] [28] [60]	[27] [28]	[27] [28] [34]	[28] [50]			[28]		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
			[34] [61] [90]		[27] [28] [34]					[25] [26]					
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
	[25] [26]			[33]	[28] [33] [34]	[34]			[27] [33]	[25] [26]					

*The numbers in the Table are reference numbers

carbon crucible containing metals to temperatures about 100 to 200 K above the melting point of the metal. Some metals reacted with the carbon crucible to exhibit catalytic effects. However, Weisweiler *et al.* noted that Al and Si did not exhibit catalytic activity. This is because the reaction temperature was too low and carbides and nitrides were formed during heating.

Ōya and Ōtani [28] examined the catalytic effects of 22 metals on both non-graphitizing (phenol-formaldehyde: 10 wt% catalyst) and graphitizing (3.5 dimethyl-phenol-formaldehyde: 20 wt% catalyst) carbons, using optical microscopy and X-ray diffraction techniques to detect changes. Reaction temperatures were 3100 K or 3300 K at which graphitization had occurred or the metal had vaporized from the system. Ōya and Ōtani noted that the ability of transition metals to graphitize catalytically corresponded with their ability to synthesize diamond. See also [29, 30]. The Group Ib elements were an exception. Group IIb metals cannot react with carbon because of completed *d*-electron shells. Group VIII metals have a *d*-shell occupied by 6 to 10 electrons. The energy levels of such configurations change little on acceptance of electrons from carbon (carbon in metals is a positive ion [31, 32]). Group IVb to

VIIb metals have 2 to 5 electrons in the *d*-shell. They form strong chemical bonds with carbon to form metal carbides. Hence elements of Groups IVb to VIIb and VIII are graphitization catalysts. Known graphitization catalysts are listed in Table I in the form of the periodic table [33, 34, 35].

Borides of rare-earth elements are reported to be effective graphitization catalysts [36]. Boron is a very efficient catalyst and as such, mechanistically, it should not be grouped in Table I.

The co-ordination of catalytic graphitization with diamond formation can also include the efficiency of catalytic cracking of hydrocarbon gases onto surfaces of transitional metals [37].

There is no available theory to explain the catalytic graphitization by non-transition metal elements. Ōya and Ōtani [28] point out that the majority of graphitization catalysts have an atomic number of less than 40 and a first ionization potential of between 6 and 8 eV.

3.2. Alloys as catalysts

Alloys, as graphitization catalysts, behave differently from constituent elements. The lower melting point (eutectic) of alloys contributes to lower graphitization temperatures [38]. The solubility of carbon in ferro-silicon alloys is

lower than in constituent elements [39]. For ferro-silicon alloys, the optimization of catalytic ability occurs with 25 wt% of Si in the alloy [40]. Although, in alloys of increasing Si-content, the rate of nucleation of G-component graphite increases, the rate of diffusion of carbon in the catalyst decreases, so diminishing catalytic activity. Ōya and Ōtani [41] observed that with ferro-silicon alloys containing more than 33 wt% Si, the ferro-silicon separates into FeSi and Si at treatment temperatures. The addition of a small quantity of Si (1 to 3 wt% Si) can suppress Fe₃C formation in cast iron [42] as well as suppressing the growth of large single crystals of graphite from an iron melt [43].

When aluminium and titanium are present together, the conversion of coke into the G-component graphite is more complete than when aluminium alone is used, although the mechanism is not obvious [44]. A fibrous carbon was obtained from the decomposition of acetylene gas on nichrome wire (Ni-Cr alloys) [45] but this study was not extended to a comparison using Ni and Cr wires.

3.3. Compounds as catalysts

The catalytic activity of a compound is sometimes different from the activity of the constituent metal or other compounds containing the same metal. Both CaCO₃ and Ca(OH)₂ produce G-component graphite at their recrystallization temperatures under high pressure, but CaF₂ does not [46]. The former two calcium compounds are said by Noda [46] to form unstable complexes with carbon, leading to formation of the G-component. In studies of the manufacture of nuclear-grade graphites by Parker *et al.* [47] the catalytic graphitization of a needle-coke by Fe, FeO, Fe₂O₃, Fe₃O₄ and FeSiO₃ was attempted. The Fe₂O₃ was the most effective catalyst, yielding a graphite of high density and large crystallite size, suitable for use with neutron radiation [48, 49]. Yokokawa *et al.* [50] found that additions of Cu, CuF₂, CuSiF₆, CuO and CuCl₂ behaved similarly because they all formed Cu initially in the graphitization treatment. However, because of the remarkable catalytic activity of Si in carbons at temperatures above 2500 K, the use of FeSiO₃ and CuSiF₆, distinct from other Fe- or Cu-compounds, has to be considered carefully.

Boron is a catalyst because it forms B₄C [51].

B₂O₃ is less efficient as a graphitization catalyst. There are two possible reasons for this: one is that when a high heating-rate is used B₂O₃ is readily volatilized above 2150 K before conversion into B₄C; the other is that B₄C formed from B₂O₃ may be covered with an exterior layer of glassy B₂O₃ [52].

CeO₂ exhibits catalytic activity but is not effective with cokes containing sulphur. Ce₂S₃ is thermally stable and is easily formed from CeO₂ and S [38]. Addition of Ca to the system removes the sulphur as CaS and permits the CeO₂ to act as a graphitization catalyst.

The complex clay minerals are effective graphitization catalysts. In particular, celicite was studied by Ishikawa and Yoshizawa [53], who suggested, on the basis of the structural similarity between celicite and graphite, a pseudo-epitaxial growth of graphite on the surface of celicite. Ōya *et al.* [54] consider that the clay minerals exert an activity at higher temperatures of decomposition of the clay (1470 to 1770 K) as well as at higher temperatures (2470 K) when the decomposition products of the clay exert their individual catalytic activities. The catalytic activity of the clay is initially attributable to its high reactivity, resulting from its decomposition.

3.4. Particle size of catalyst

In an initial study Baraniecki *et al.* [40] observed for ferro-silicon alloys that an optimum particle size was 50 to 70 μm. The area of contact between catalyst and carbon depends upon the size distribution in both systems [55, 56]. On the other hand, the catalytic activity of SiO₂, of particle sizes 0.07 to 0.12 mm and 1 to 2 mm, towards an anthracite was not influenced by particle size [51].

Whereas, conventionally, catalytic activity has produced essentially G-component graphite, the use of more finely-dispersed catalysts has created a new phenomena, that is, the formation of T_S-component graphite [57-59]. Suitable organo-metallic compounds are mixed with resin homogeneously to form a solution with monomeric materials subsequently polymerized to resins, etc., which can easily be carbonized (e.g. phenolic and furfuryl alcohol resin). Also, a suitable solution can be added to a powder of the carbon [11, 60-62]. The formation of this T_S-component graphite may be influenced by the presence of the organo-metallic compound, or may be formed from it,

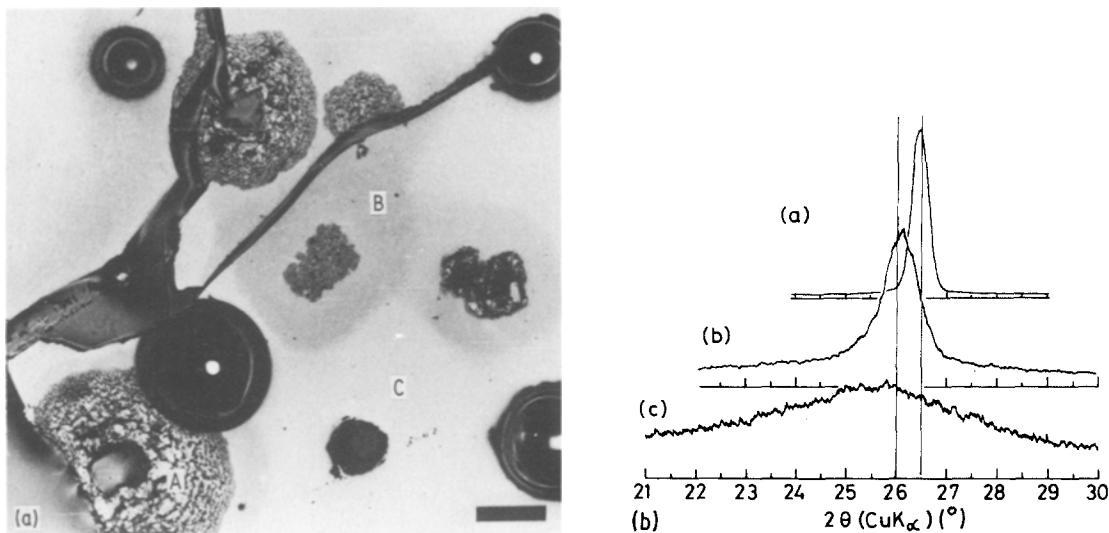


Figure 4 (a) Optical micrograph of a phenolic resin carbon to which are added nickel particles (150 μm diameter) prior to heating to 2900 K [16]. A shows G-component, B shows T_S -component and C shows A-component. (b) X-ray diffraction (002) profiles of carbon taken at A, B and C [66].

but these suggestions are not thought to be accurate.

Yajima and Ōmori [63, 64] detected free atoms of iron, Fe^+ clusters, iron clusters, supermagnetic and ferromagnetic iron in carbon from acetylferrocene-furfuryl alcohol resin (at HTT: 673 K). Ōya *et al.* [16] carbonized phenolic resin doped with Ni-acetylacetonate to various HTT and observed catalytic activity and they were able to correlate particle size of Ni with activity. The T_S -component was found in carbons containing nickel particles of size about 20 nm. When the nickel particle was 80 nm only the G-component graphite was formed.

The addition of larger particles of Al (74 to 250 μm) [59, 65], Be ($\sim 74 \mu\text{m}$) [65] and Ni (150 μm) [66] to a non-graphitizing carbon produced, on heating, both G- and T_S -components. Possibly small sizes of metal particles were created during the graphitization process. Using a micro-focus X-ray diffractometer Ōya *et al.* [66] observed the G-component graphite existing around a void created by the vaporization of a larger nickel particle (Fig. 4). The G-component graphite was surrounded by a shell of the T_S -component graphite. The crystallite size of the G-component graphite decreased from the inner to the outer regions. A similar phenomenon was observed using ferro-silicon [40] as well as nickel which was electro-plated onto the surface of carbon fibres [67]. During the graphitization process nickel

metal diffuses into the carbon matrix. With increasing distance from the central nickel particle the size of diffusing clusters of atoms diminishes as nickel is left within precipitated G-component graphite. Thus, a stage is reached in this process when a change in mechanism occurs because of the reduced size of the nickel particles and formation of the T_S -component results [59, 66].

The phenomenon of formation of the T_S -component graphite suggests further experimentation into the effects of even smaller sizes of catalyst particles, for example, the use of a substitution element in the carbon. In early studies, Noda and co-workers [68–70] heated petroleum coke and a thermal black under an oxidizing atmosphere (O_2 or CO_2). This atmosphere was effective in the homogeneous graphitization of both carbons, that is, the A-effect without formation of either G- or T_S -components. In studies of catalytic graphitization by metal vapours, Ōya and co-workers [23, 71, 72] heated the metal and powdered graphitizing carbon (from 3,5-dimethyl phenol formaldehyde resin) and non-graphitizing carbon (from phenol formaldehyde resin) in a close graphite reaction cell. The metals Ca and Mg exhibited the A-effect. Further, using a charcoal at a temperature above 1900 K, calcium vapour also catalyzed the formation of T_N -component carbon.

Boron will exchange with carbon in the lattice

(substitution) and is also located interstitially. The presence of substitutional boron results in homogeneous graphitization, that is, the A-effect [73–77]. Additions of amounts of boron to a carbon in excess of the solubility of boron in carbon results in the formation of B_4C particles which, on heat treatment, lead to the formation of G-component graphite [73, 78, 79].

The technique of co-chemical vapour deposition (Co-CVD) can be used to prepare carbons containing homogeneous and finely dispersed particles of other elements [80–82]. Such a carbon containing 0.18 wt% Si exhibited very significant catalytic graphitization [81]. This content corresponds to the maximum solubility of silicon in carbon. The carbon produced is probably A-component. A similar effect is observed using sulphur instead of silicon [83]. However, the use of substitutional phosphorous suppresses the graphitization process [84].

4. Properties of the carbon used

4.1. General considerations

Fitzer and Kegel [85] and Gillot *et al.* [86] postulate that the formation of the G-component, isothermally, results from the negative free energy of transformation of carbon to graphite. This is well-established and frequently demonstrated, for example by Presland and co-workers [87–89] who observed that, during the heat treatment of an isotropic carbon, on one side of a metal plate (Ni or Co) the carbon dissolves into the metal and reappears on the other surface of the plate as G-component carbon. The catalytic activity of Al, Be [65], Zr, Ti [90], Ca [91], Cu [50] and Ni [11] are explained in these terms. The less ordered is the carbon the larger will be the value of $-\Delta G$ for the transformation into graphite. Gillot and Lux [92] used chromium to graphitize a non-graphitizing furfuryl alcohol coke ($d_{002} = 343$ pm, $L_c = 9$ nm) but were unsuccessful with a graphitizing carbon. Wewerka and Imprescia [61] co-heated a less crystalline filler carbon with a more crystalline binder carbon with organometallic compounds (Ti-oxyacetylacetonate, V-acetylacetonate, Zr-acetylacetonate, etc.). Only the filler carbon was graphitized. Oberlin and Rouchy [93] describe a non-graphitizing carbon as consisting of a turbostratic domain with less-ordered boundary carbon. This concept that the less-ordered carbon is preferably catalytically graphitized must be carefully examined when

boron is used because a larger amount of boron is dissolved into a less-ordered carbon [94].

On the other hand, the preferential graphitization of anisotropic graphitizable carbon is reported using titanium, Murty *et al.* [95], and by chromium, Mochida *et al.* [96]. It is thought that with crystallites orientated approximately parallel to each other but being prevented from growing into larger crystallites by carbon atoms at the periphery of the crystallite, the chromium may react with, and remove, these peripheral carbon atoms. Consequently, crystal growth can occur.

4.2. HTT of carbon

Carbons of increasing HTT become more ordered; this tendency is more pronounced with graphitizable carbons. Accordingly, carbons of increasing HTT should be less influenced by graphitization catalysts. This concept was examined by Oya *et al.* [97] using carbon from a phenolic resin and finely-divided nickel particles, of particle size 20 nm [16]. Larger amounts of the T_S -component were found in carbons of lower HTT. In another study, Torikai *et al.* [98] heated mixtures of Ca or CaO with petroleum cokes of increasing HTT. The cokes with HTT of 1300 to 1700 K behaved similarly but the modification to cokes with $HTT > 2100$ K diminished significantly. Oberlin and Rouchy [99] report that increased amounts of G-component graphite are formed when an iron catalyst is heated with a non-graphitizing carbon of increasing HTT.

5. Experimental conditions of graphitization

5.1. Method of catalyst addition

Graphitization phenomena are sensitive to methods of addition of the catalyst to the carbon. T_S -component graphite is formed on reaction of a homogeneous mixing of urethane foam or naphthalene diol with FeF_3 ; without mixing, the G-component is formed [60]. This effect is no doubt due to differences in the reactivity of iron particles of different sizes. Similarly, the catalytic ability of Si is very sensitive to the mode of addition of the Si to the carbon [58]. Additions of $Si(OC_2H_5)_4$ to a phenolic resin carbon, regardless of the methods of addition, always yield finely divided particles which produce the T_S -component. Silicon particles of larger-size (44 to 57 μm) [58] produce the G-component when

buried in a phenolic resin carbon and the T_S-component when added into the phenolic resin carbon particle. In the former specimen, the matrix (parent) carbon diffuses into the larger-sized particles of silicon to form larger-sized particles of SiC when they yield the G-component on evaporation of the silicon at 2473 K [100]. In the latter system, the larger-sized particles of silicon evaporate and reprecipitate on the surfaces of carbon particles to produce finely divided SiC particles which yield the T_S-component.

5.2. Amounts of catalyst added

With increased percentages of catalyst in a carbon there is an increase in the extent of graphitization of the carbon. However, the formation of the T_S-component can be replaced by the G-component, resulting from the coalescence and growth of finely divided particles of catalyst. Some catalysts, dependent upon the percentages present, can form A-, T_S- and G-components. When less than 1 wt% of boron is substitutionally added to carbon, resultant graphitization produces the A-component [74–76, 79]. When 1 to 5 wt% of boron is present in a non-graphitizing carbon the formation of the T_S-component is observed on heating to 2500 K [79]. When 10 wt% of boron is present in a phenolic resin carbon then the G-component is observed at 2673 K [79]. The formation of the G-component by the catalytic action of boron or boron oxide is also reported for other carbons [74–76, 101, 102].

Marinkovic *et al.* [81] found that heat treatment of a pyrolytic carbon containing 0.15 to 0.2 wt% of silicon produced the A-component. Kaae [103] measured the sizes of silicon carbide particles in a pyrolytic carbon and found for 10 wt% Si that the particles were about 20 nm diameter and for 16 to 34 wt% Si particles were about 100 nm diameter and distributed non-uniformly. Kaae does not report graphitization behaviour but T_S- and G-components can be expected, respectively [16, 58].

5.3. Effects of graphitization temperature

Some graphitization catalysts behave differently at higher graphitization temperatures. Two reasons may be considered. As discussed above, catalyst particles can sinter and agglomerate with increasing temperature, leading to a cessation in production of the T_S-component, being replaced by the G-component [16]. Other catalysts may melt.

Mochida *et al.* [96] observed that chromium oxide exhibits different catalytic effects using a non-graphitizing carbon. At temperatures of 1550 to 1850 K a process of homogeneous graphitization occurs, leading to production of the A-component. Between 2200 and 2300 K the non-graphitizing carbon was converted into the G-component, caused by the presence of molten chromium. Gillot *et al.* [92] earlier reported the formation of two phases of carbon using chromium as a catalyst. At 1300 K the carbon had $d_{002} = 343$ pm and $L_c = 9$ nm. This presumably must be the A-component. The G-component was formed at 1900 to 2100 K and remained unchanged on heating to 3100 K.

Baird [104] found that when propane gas is cracked over nickel foil at 590 to 650 K a columnar carbon is formed, $d_{002} = 340$ pm. At 650 K to 1070 K a laminar carbon is formed $d_{002} = 336$ pm [104]. Bulk diffusion and surface diffusion mechanisms have been proposed to account for the growth of the columnar and laminar products, respectively.

5.4. Effects of ambient atmosphere

The presence of oxygen and carbon dioxide can induce some form of graphitization phenomena [68–70]. Although nitrogen is not a graphitization catalyst its presence appears to enhance the activity of calcium as observed by Ōya *et al.* [23] and Hirano [105] when nitrogen was replaced by argon in graphitization studies. It is thought that intermediates such as CaCN₂ and Ca₃N₄ are more readily formed than CaC₂. Boehm [106] confirmed this behaviour by reporting the formation of graphite, $d_{002} = 336$ pm, during the production of calcium cyanamide from calcium carbide and nitrogen at 1270 to 1420 K.

6. Mechanisms of catalytic graphitization

6.1. The G-effect

This effect occurs with all carbons, regardless of the extent of graphitization, when large particles of catalyst are used of size greater than about 100 nm. Two mechanisms are currently proposed; one is the solution of carbon into the catalyst particle followed by precipitation as a graphite material (G-component), as outlined in Fig. 5. This reaction can proceed isothermally because of the negative free energy change in going from disordered carbon to graphite, see Fig. 6, [85, 86]. It would appear that the metal catalyst need not

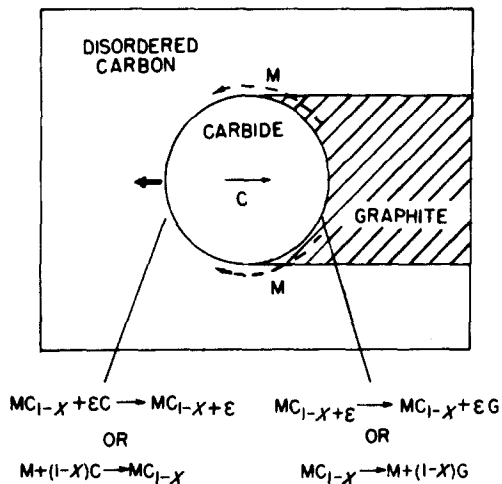


Figure 5 Diagram showing how, during the migration of a metal carbide particle through a carbon matrix, the particle dissolves relatively disordered carbon and precipitates graphite [86].

be molten at the temperatures involved, nor need a stoichiometric compound with carbon be formed. The temperature for catalytic graphitization by a metal is not changed by its particle size. Yokokawa *et al.* [50], in a study of catalytic graphitization by copper, observed unidentifiable X-ray diffraction peaks, thought to be from a copper-carbon compound.

The second mechanism involves the formation and decomposition of carbide intermediates. This mechanism is clearly observed using large particles

of silicon within a carbon from a phenolic resin [58]. It is known that the ionic carbides of aluminium and beryllium leave behind the G-component on evaporation of the metal at their decomposition temperatures [107–109]. However, when aluminium particles are used as graphitization catalysts, G-component material is formed via the solution-precipitation mechanism.

6.2. The T_S -effect

T_S -component material is formed on heating non-graphitizing carbon with finely-divided catalyst by a process not yet clearly understood. Oberlin and Rouchy [14, 93] studied the catalytic action of iron powder, in small concentrations, upon powdered saccharose carbons with HTT of 1873 and 2073 K. Using TEM, SEM, electron diffraction and optical microscopy they observed that iron appears to react preferentially at the boundaries of the turbostratic elementary domains which constitute these non-graphitizing saccharose carbons. In this process, droplets of iron carbide are formed, on the surfaces of which float detached elementary domains. On decomposition of the carbide, a shell of carbon is formed which is graphitizable because the carbon lamellae are parallel to the external surface of the spherical hollow shell. In this model it is assumed that iron reacts preferentially with carbon atoms in the boundaries of domains thus enabling the domains to float on the surface of the droplet.

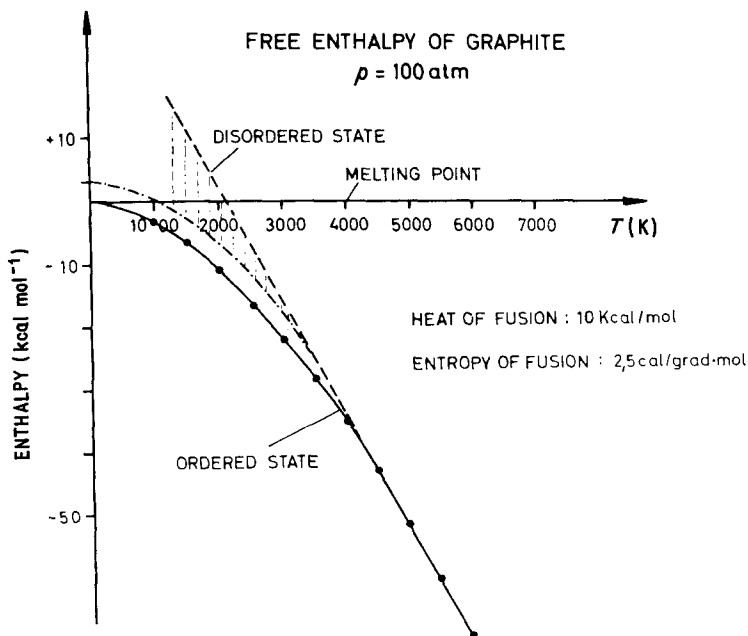


Figure 6 The variation of free energy of graphite with temperature. The free energy of “disordered” carbon is also shown [85].

Another mechanism is the solution of carbon into the finely-divided catalyst particle followed by precipitation, as suggested for the formation mechanism of the G-component [66]. As with a nickel catalyst [16] when nickel particles, 20 nm in size, are used it is not possible to form the G-component, of size 80 nm; instead T_S-component of size 11 nm is formed.

Tomita *et al.* [110] decomposed benzene vapour on nickel at a temperature of 1073 K. The resultant carbon, $d_{002} = 339$ pm and $L_c = 12$ to 16 nm, contained finely-divided nickel particles (of size 20 to 30 nm) thought to act as active sites for carbon formation. The X-ray parameters of this carbon and the particle size of nickel are very near to those observed by Ōya *et al.* [16] in a T_S-component ($d_{002} = 342$ pm and $L_c = 11$ nm) formed from phenolic resin carbon by the catalytic action of finely-divided nickel particles (of size 20 nm). The mechanism of formation of carbon from benzene on a nickel surface suggests the mechanism of formation of the T_S-component.

6.3. The A-effect

A-component material is formed on heating carbons in the presence of O₂ and CO₂ [68–70], the vapour of Ca and Mg [23, 71, 72] and elements substitutionally bonded into the carbon lattice [73–77, 81, 83]. Noda and co-workers [68–70] explained the formation of such carbon by an oxidizing gas. Defects within the crystallites develop during the graphitization process. Such defects prevent the growth of lattices. It is probable that such defects can react preferentially with an oxidizing gas and are removed. Thus, the hinderance to further crystal growth is removed and extended graphitization results. The preferential reactivity may also extend to reaction with Ca and Mg vapour [23, 71, 72].

Two mechanisms are proposed to explain the A-effect of boron substitutionally bonded into the carbon lattice. Rouchy and Mering [73], in studies of catalytic graphitization of a non-graphitizable carbon from saccharose, suggest a new mechanism involving a modification to the electronic properties of such cokes when the amounts of boron added are less than 1 wt%. No B₄C is detected. The diffusion of boron through the lattice of the carbon is rejected. Boron substitution is thought to create electronic defects and hence to modify significantly the electronic properties of the carbon. The cross-linkages

between the small elementary domains of structure in the saccharose carbon will become less rigid on heat treatment so facilitating re-arrangement into small but better orientated domains.

Henning [111] and Kotlensky *et al.* [112] suggest the mechanism of diffusion of boron through the carbon lattice, not supported by Rouchy and Mering [73]. Marinkovic *et al.* [81], in studies of siliconated pyrolytic carbon (Si-PC) also used the mechanism of migration of Si through the carbon lattice to explain graphitization.

6.4. The T_n-effect

Heat treatment of a non-graphitizing carbon, without catalyst, occurs because of localized internal stresses set up by anisotropic thermal expansion within the carbon crystallite [18, 113, 114]. This stress is released by breakage of cross-linkages, resulting in the T_n-component and then the G-component (multi-phase graphitization). It is speculated that if gaseous calcium species are present in this system, they can react favourably with cross-linked carbons to remove them. The T_n-component is formed in larger amounts at lower temperatures when gaseous calcium species are present. This mechanism is essentially the same as that for the A-effect by an oxidizing gas or calcium and magnesium vapours. In this review, however, the T_n-effect is distinguished from the A-effect because such large amounts of the T_n-component form only in the charcoal heated with calcium vapour.

7. Changes in properties of carbon by graphitization

It is possible to graphitize carbon fibres by heating nickel-plated fibres [67, 115]. The crystallinity of the fibre was improved but the fibre was too brittle for commercial application.

A similar degradation in mechanical properties of glassy carbon, heated with iron particles is reported by Kammereck *et al.* [62]. A bi-phase system is probably produced, so creating considerable internal stresses within the material resulting in a higher electrical resistivity, despite an enhanced crystallinity. Parker *et al.* [47] prepared artificial graphites, from a filler coke and binder pitch containing several catalysts. Every catalyst produced a material with increased electrical resistivity and decreased thermal coefficients of

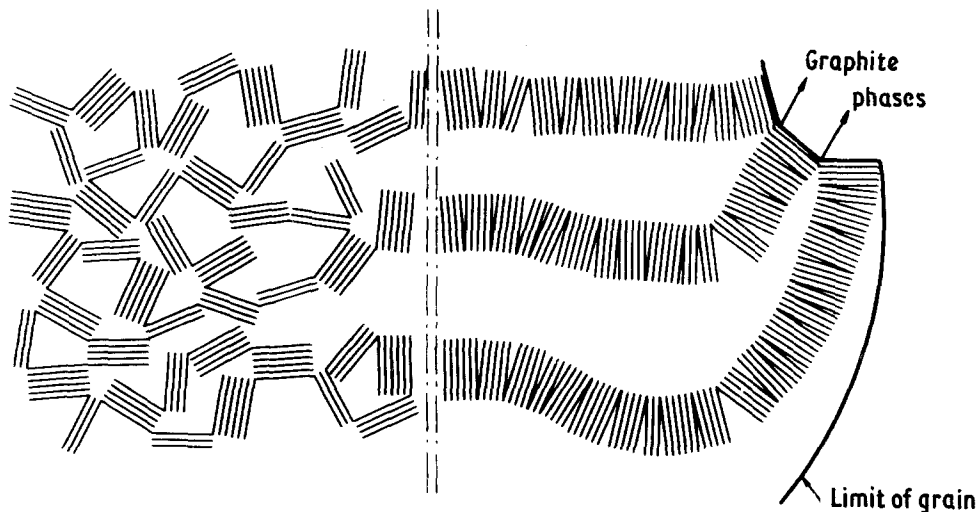


Figure 7 Model for conversion of non-graphitizing carbon into graphitizable carbon, that is the T_S -component [93].

expansion. Flexural strength increased following addition of Fe_2O_3 but decreased following addition of Al_4C_3 .

According to Trask [52] the addition of at least 3 wt% of boron into synthetic graphite from petroleum coke and coal-tar pitch binder enhanced the crystallinity of graphite, improved its oxidation resistance and decreased the coefficient of thermal expansion without causing any deterioration in the flexural strength. Addition of 1 wt% of boron to pyrolytic graphite formed at 1803 K also considerably improved the oxidation resistance. This doped pyrolytic graphite had a high density, $\rho = 2.19 \text{ g cm}^{-3}$, a value of L_c of 15.8 nm and a highly preferred orientation of crystallites [75]. Kotlensky and Martens [116] state that the pyrolytic carbon doped with boron exhibits a larger fracture elongation than the non-doped pyrolytic carbon. Marinkovic *et al.* [117] substituted small amounts ($< 4 \text{ wt}\%$) of phosphorus into a pyrolytic carbon. The resultant carbon increased its apparent density, microhardness and lattice strain in the c -direction with no change in its oxidation resistance.

Although Fig. 4 indicates that the G-component is a well-orientated graphite the isolation of the crystallites does not permit strong bonding to give a coherent material. Hence, catalytically-graphitized material tends to have unsatisfactory mechanical, thermal and electrical properties, in particular with small sizes of carbon and carbon fibres. The formation, likewise, of T_S -component carbon produces a deterioration in properties of

the graphitized material [62]. However, the formation of the A-component by using a substitutional element for catalytic graphitization tends to be free from the above deterioration in quality [52]. This is because the mechanism is one of improvement of an already existing structure rather than the creation of a new material, for example by solution and precipitation for the G-component.

Further to catalytic graphitization, additions of boron are used to sinter carbon particles under hot-pressing 20 MPa. Kobayashi and co-workers [102, 118] fabricated carbon artefacts of density 2.02 g cm^{-3} and compressive strength 60 MPa from 10 wt% of powdered boron oxide in a calcined coke powder. Molybdenum carbide Mo_2C and zinc carbide ZnC may also be used for the same purpose [119, 120].

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