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A REVIEW OF GLASSLIKE CARBONS

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A REVIEW OF GLASSLIKE CARBONS

by

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April 1968

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FOREWORD

This report was prepared by Dr. Shigehiko Yamada to fulfill the need for a review of the status of glasslike carbon materials.

Dr. Yamada is Chief of the Research Section of Tokai Electrode Manufacturing Company, Ltd., Nagoya, Japan, and concurrently is associated with the Department of Applied Chemistry, Aichi Institute of Technology, Nagoya, Japan.

Dr. Yamada, a pioneer in the development of glasslike carbons, gave this report to the Defense Ceramic Information Center for publication and dissemination in the interests of scientific and technological progress. DCIC is operated for the Department of Defense under Air Force Contract F 33615-67-C-1472 administered by the Materials Information Branch, Materials Support Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio.

For support of his work on glasslike carbons, Dr. Yamada wishes to thank the Tokai Electrode Manufacturing Company, Ltd., and the United States Air Force Materials Laboratory. In addition, he expresses his appreciation to the Alexander von Humboldt Foundation, Prof. Dr. E. Fitzer, Prof. Dr. T. Noda, Dr. K. H. Lüdde, and J. J. Krochmal for their help, as well as to the many other scientists and engineers engaged in work relating to glasslike carbon who have provided valuable discussions.

The report was edited for the Defense Ceramic Information Center by M. C. Brockway and J. J. Breslin of the Battelle staff.

ABSTRACT

A relatively new group of carbons having several characteristics resembling glass is of sufficient interest in connection with technological demands for improved materials to prompt this report. The generic term "glasslike" is appropriate for these carbons because they exhibit a glassy surface appearance, conchoidal fracture, internal-friction characteristics resembling glass more closely than normal graphite, and gas impermeability comparable to glass. The structure of glasslike carbons in not well understood; it resists change by graphitization at temperatures up to about 3000 C.

This report reviews the preparation, formation mechanisms, structure, properties, and applications of glasslike carbons.

The unique combination of properties and resulting potential applications has stimulated manufacture of glasslike carbons by several companies. Available property data on the various products are included in the report.

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A REVIEW OF GLASSLIKE CARBONS

by

Dr. Shigehiko Yamada

INTRODUCTION

About 10 years ago, in connection with the development of a high-temperature gas-cooled reactor, an impermeable carbon, thermally stable from 1000 to 2000 C, was required as a sheath material for the fuel elements. As a consequence, various methods for the preparation of impermeable carbon were proposed and developed. Two kinds of glasslike carbon pipe were developed at about the same time and both had interesting impermeability properties(1, 2). Industrial development of impregnation as a means to obtain impermeable carbon seems to have lagged, perhaps because of the difficulty in obtaining homogeneous impermeability. Although the glasslike carbon pipes were found to have adequate impermeability, their behavior under irradiation was observed to be unsatisfactory for the purpose.(3)

However, glasslike carbon has been finding other application possibilities(4) as various sizes and shapes are developed and fundamental research on the structure(5, 6, 7), properties(8), and formation mechanisms(9, 10) progresses. For example, filaments made of glasslike carbon have been used in composite structures because of the materials' high strength and isotropy.(11)

So much literature on glasslike carbon has now been published that a review of this material has become desirable.

PREPARATION OF GLASSLIKE CARBONS

Preparation of Cellulose Carbon by General Electric in the United Kingdom

Cellulose powder, prepared by digesting the pulp, is dispersed in water, centrifuged to obtain a desired shape, and then dried, machined, and baked under a pressure of 140 kg/cm^2 up to 500 C. Then it is heat treated at a selected final temperature of 1300 to 3000 C under ambient pressure.(12, 13)

Editorial Note: Several companies manufacture glasslike carbon under different names, as follows:

(1) Glassy Carbon - Tokai Electrode Manufacturing Company, Ltd., Minato-kw, Tokyo, Japan

(2) Vitreous Carbon - Vitreous Carbons, Ltd. represented in U. S. by Atomergie Chemetals Company, Carle Place, Long Island, New York.

(3) LMSC Glassy Carbon - Lockheed Palo Alto Research Laboratory, 3251 Hanover Street, Palo, Alto, California

(4) Carbone Vitrenx - Product of Le Carbone Lorraine, 45 Rue Acacias, Paris

(5) Vitro Carbon - Resources Research Institute, Agency of Industrial Science and Technology, Ministry of International Trade and Industry, 188, Kotobuki-cho, Kawaguchi-shi, Saitma, Japan

(6) Cellulose Carbon - Produced by General Electric Co., Ltd., 1 Stanhope Gate, London W1, England.

Preparation of Glassy Carbon by Tokai Electrode in Japan

As basic preparation methods, three patents were registered:

(1) Multiple Painting Method. An initial resin condensate of furfuryl alcohol is painted repeatedly on a die of the desired size and shape. This method is particularly useful for preparing pipe and crucible shapes.(14) Other raw materials, such as phenol-aldehyde resins, can be used.(15)

(2) Molding and Extruding Method(16). A cured powder of phenolic, furanic, and several other thermosetting resins is used as a filler of an initial condensate of the corresponding resin. Properties such as strength and impermeability are not so good as those obtained by the other methods. The size and shape of the product are also limited.

(3) Aging Method(17). Several kinds of the above-mentioned initial condensates are aged with a small amount of hardener at about room temperature for several weeks prior to machining, followed by carbonization.

The size and shape of the desired product generally determine which of the above three basic preparation methods is employed. Additionally, special methods have been developed to make particular products:

(1) Method to Prepare Small Globes(18). The same condensates are immersed in or blown against a cloth, followed by hardening and carbonizing. The diameters of the globes thus obtained are 0.05 to 1.0 mm. They are almost perfectly spherical because of the effect of surface tension during gelation.

(2) Method to Prepare the Monofilament*. The general description is given in the basic patent(19) and more detailed explanations have been just published(20, 21). A mixture of resol, novolak, and furan resin at a ratio of 7:2:1 by weight is used to make the initial condensate. This is extruded through a die and simultaneously wound and quenched in 20 percent HCl solution at 2 to 5 C. Then it is aged in the solution at room temperature prior to the normal carbonization. Details will be described later.

Preparation of Vitreous Carbon by Vitreous Carbons in the United Kingdom

The principle is said to be a molding of phenol-formaldehyde resin followed by a careful carbonization.(22) One can see the same procedure described in one of the Japanese patents for the preparation of glasslike carbon.(16) Another method is a centrifugal formation of pipes.(23)

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*Supported by the U. S. Air Force through Metals and Ceramic Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio.

Preparation of Vitro Carbon by Resources Research Institute in Japan

A mixture of 2 moles of acetone and 1 mole of furfural is resinified and hardened by aging for a few months prior to carbonization.(24) More detailed information has been presented by Nippon Carbon Company and by the Japan Atomic Energy Research Institute.(25, 26)

Preparation of LMSC Glassy Carbon by Lockheed in the U. S. A.

Recently a paper was presented in which carbonization under pressures such as 2000 or 10,000 psi was recommended.(27) Naphthalenediol is used as one of the raw materials.

Other Information on Preparation of Glasslike Carbons

Rivington proposed baking under a pressure of about 140 kg/cm^2 at temperatures up to 400 C for 3 days before carbonization in vacuo or in an inert ambient gas, starting from furan resin or cumarone, indene, cyclopentadiene, or their mixtures.(28)

Fitzer, Schäfer, and Yamada(10) have presented a paper describing the changes in various properties of phenol and furan resins during carbonization under conditions giving the glasslike carbons.

No method to prepare Carbone Vitreux has been published, but a method for preparing porous vitreous carbon was patented by Le Carbone Lorraine.(29) Ishihara et al.(30) of the Japan Atomic Energy Research Institute have also proposed a method to prepare the porous material.

Ohtani(31) presented a novel method to prepare a nearly glasslike carbon filament from different kinds of pitch. Details will be described in a later section.

FORMATION MECHANISM OF GLASSLIKE CARBONS

Formation of Cellulose Carbon Pipe

The pyrolysis of cellulose to form carbon fiber has been largely explained(32-35), but knowledge of the formation mechanism of Cellulose Carbon pipe is relatively slight.

Using electron microscopy, Phillip and Losty(36) tried to resolve an apparent dilemma which is present in all kinds of glasslike carbons: although a remarkable amount of gas evolves during carbonization, the product is gas-impermeable. The presence of porosity during the thermal decomposition of the starting material was demonstrated by a comparison between the helium and bulk densities. The electron microscopic examinations revealed the existence of extensive tubular pores of diameters on the order of 500 A during the critical stages of decomposition. It was found that this tubular porosity progressively breaks down as the heat-treatment temperature is increased and is completely absent in material heat treated to 1500 C. In the finished product a uniform and very fine structure with the pores in the size range of 20 to 100 A was revealed by the transmission examination.

Formation of Glassy Carbon

Changes in the light microscopy of specimens made of Glassy Carbon were observed at every stage of heat treatment, as shown in Figure 1, indicating the development of pores with diameters as large as 2 to 20 μ. No pore structure was evident in the specimen heat treated at 500 C. The maximum surface area, determined by the normal dynamic BET method, was observed with the specimen heat treated at 800 C, where the maximum moisture adsorption was also recognized.(9) In other specimens heat treated at higher temperatures, such as 1600 to 2000 C, no pore structure could be seen.

In the region 800 to 1000 C, it can be observed, as shown in Figure 2, that moisture adsorption and "A + P" (the percentage of disorganized carbon atoms) decrease, the percentage of relatively large aromatic carbon rings, such as 20 to 30 A, increases, and the percentage of medium-size rings, such as 5.8 to 15 A, shows almost no change. A remarkable decrease of electrical resistivity in this stage further indicates the aromatization, where the change in weight cannot be seen differing from that in volume.

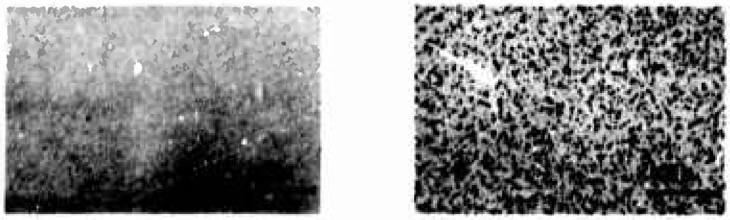
Formation of Vitro Carbon

The statistical analysis made by Van Krevelen et al.(37-40) was applied by Honda et al.(24) to the study of the formation of Vitro Carbon. In this case, no change in the degree of ring condensation was observed up to 500 C, and a rapid increase during heat treatment above 600 C was seen.

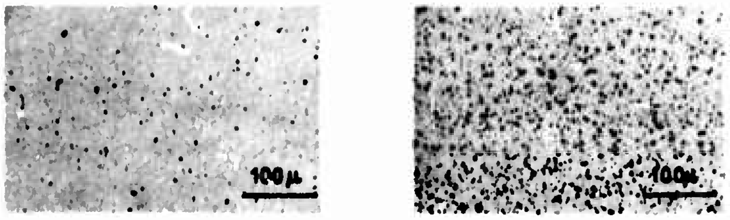
Formation of Glasslike Carbons by the Pyrolysis of Nonmelting Resins

Fitzer et al.(10) have carried out a systematic research on this problem by employing furanic and phenolic resins. The results were remarkably different from those obtained in the case of Glassy Carbon as mentioned above. First of all, no structure such as that seen in Figure 1 was recognized at any stage of carbonization. The BET area was determined by the static volumetric method, which is said to detect only pores smaller than 800 A. The results are given in Figure 3. One can see that the change in water adsorption is the only phenomenon the two forms have in common.

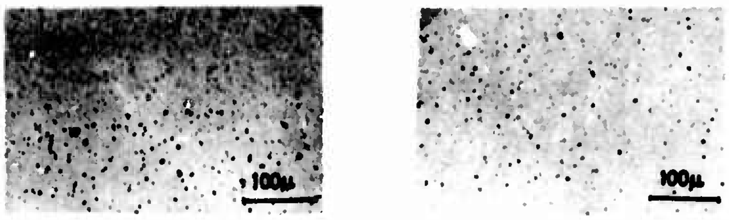
Moreover, the intensity of small-angle scattering independent of the scattering angle was determined on specimens heat treated at 700, 1000, 1200, and 3000 C. Pore diameters of 25 to 30 A for all specimens heat treated up to 1200 C and pore diameters



At 500 C At 800 C



At 600 C At 1000 C



At 700 C At 1300 C

FIGURE 1. CHANGE IN THE OPTICAL MICROSCOPY OF GLASSY CARBON DURING THE CARBONIZATION

A relative BET surface-area determination (dynamic method) corresponding to the above by Fitzer, Schäfer, and Yamada(10), is as follows:

Material	Heat Treatment Temperature, C	Relative Surface Area, m^2/g (±0.05)
Glassy	500	2.4_2
Carbon	600	7.8_9
	700	17.0
	800	37.8
	900	19.1
	1000	15.3
	1100	1.0_4
	1200	0.9_9
	1300	1.2_1
Furan resin		1.0_4
Quartz glass		0.4_7

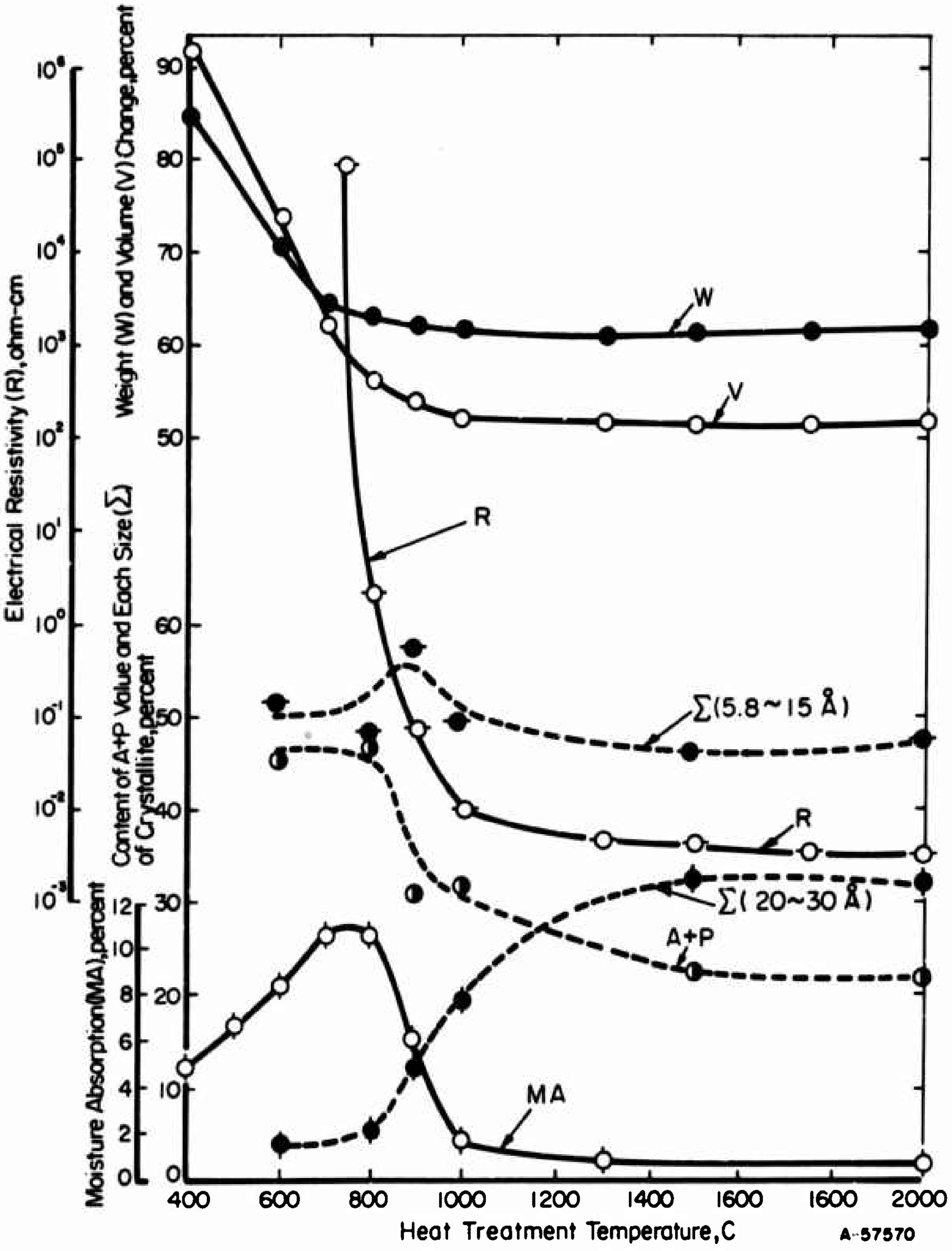


FIGURE 2. PROPERTY CHANGES IN GLASSY CARBON WITH HEAT-TREATMENT TEMPERATURE

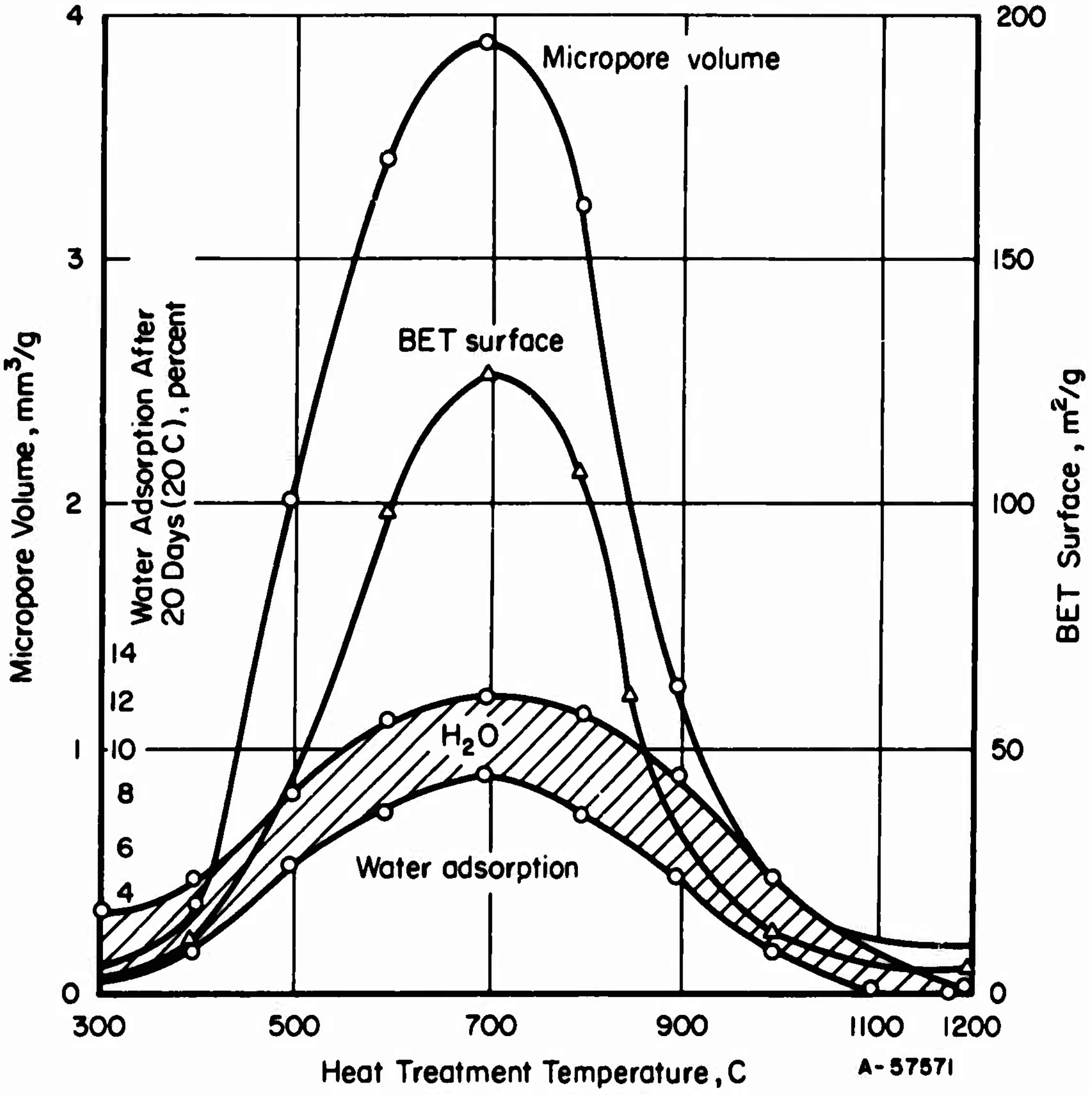


FIGURE 3. CHANGES IN BET SURFACE AREA, WATER ADSORPTION, AND MICROPORE VOLUME AS A FUNCTION OF HEAT-TREATMENT TEMPERATURE IN GLASSLIKE CARBONS FORMED BY THE PYROLYSIS OF NONMELTING RESINS

up to 40 A for the specimens heat treated at 3000 C were indicated. Gas analyses for the volatiles during the carbonization were also obtained, and the vapor pressure of formed water was compared with the capillary pressure. The results indicated that the total pore volume in the glasslike carbon thus obtained was sufficiently large to hold the whole volume of the formed water as a liquid. Pertinent results are shown in Figures 4, 5, and 6.

PROPERTIES OF GLASSLIKE CARBONS

General Characteristics of Glasslike Carbons

Table 1 shows the general characteristics of various glasslike carbons and should be helpful in developing a conception of what these materials are like. It should be obvious from Table 1 that each kind of glasslike carbon is fundamentally similar to every other. The difference in some properties is considered to be due to the different raw materials and carbonization processes.

Chemical Properties

Oxidation Resistance

As far as wet oxidation is concerned, glasslike carbon differs remarkably from graphite in the stability exhibited in a mixed solution of concentrated H_2SO_4 and HNO_3 (1:1). Normal graphite plate was destroyed to powder in 40 hr at room temperature in this solution, while Glassy Carbon showed no change in weight or volume after 150 days. A similar result is reported in the case of Carbone Vitreux. For another example, it was reported that the weight decrease of Vitreous Carbon in the mixed solution of concentrated HNO_3 and H_2SO_4 (4:1 by volume) at 120 C after 6 hr was only 0.5 percent.(43)

On the oxidation rate in a dry atmosphere such as oxygen or carbon dioxide, most of the available information concerns Vitreous Carbon.(41, 42, 44) The kinetics of oxidation were studied in detail. It was noted that the rate of oxidation in dry air was much lower than that of pyrolytic graphite, which has been believed to be the most resistive form of carbon.

Compatibility with Various Metals

Shimada made a qualitative investigation of the compatibility of glasslike carbon with alkali metals and other elements, a total of 35 elements (chiefly metallic), and with 7 kinds of chloride fused salts.(45) The results showed that, from the compatibility standpoint, there was generally no difference between glasslike carbon and graphite in suitability for nuclear-reactor use. A kinetics study based on diffusion, giving the temperature dependence of free energy, was not made.

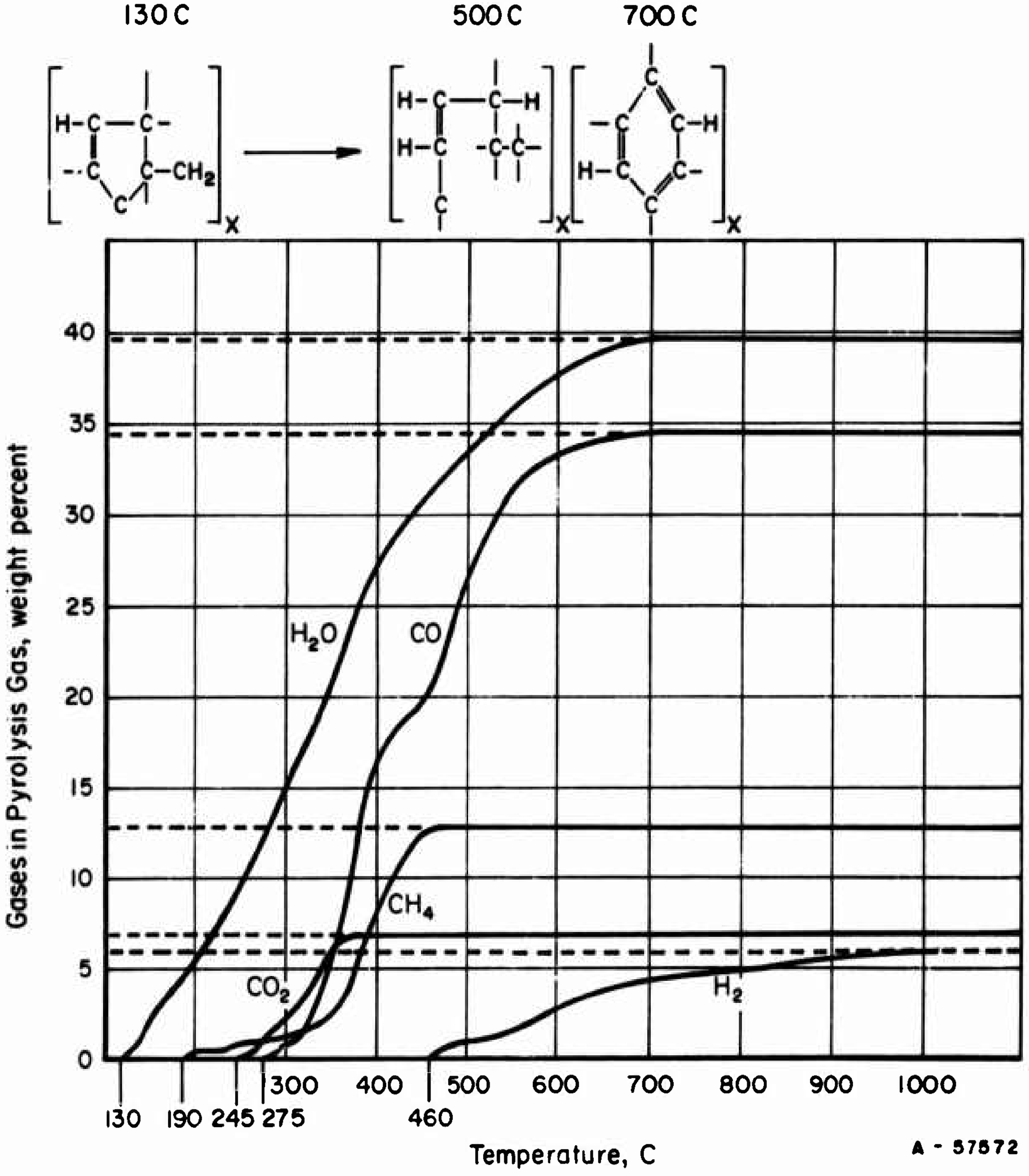


FIGURE 4. GAS FORMATION DURING THE PYROLYSIS OF FURFURYL ALCOHOL RESIN

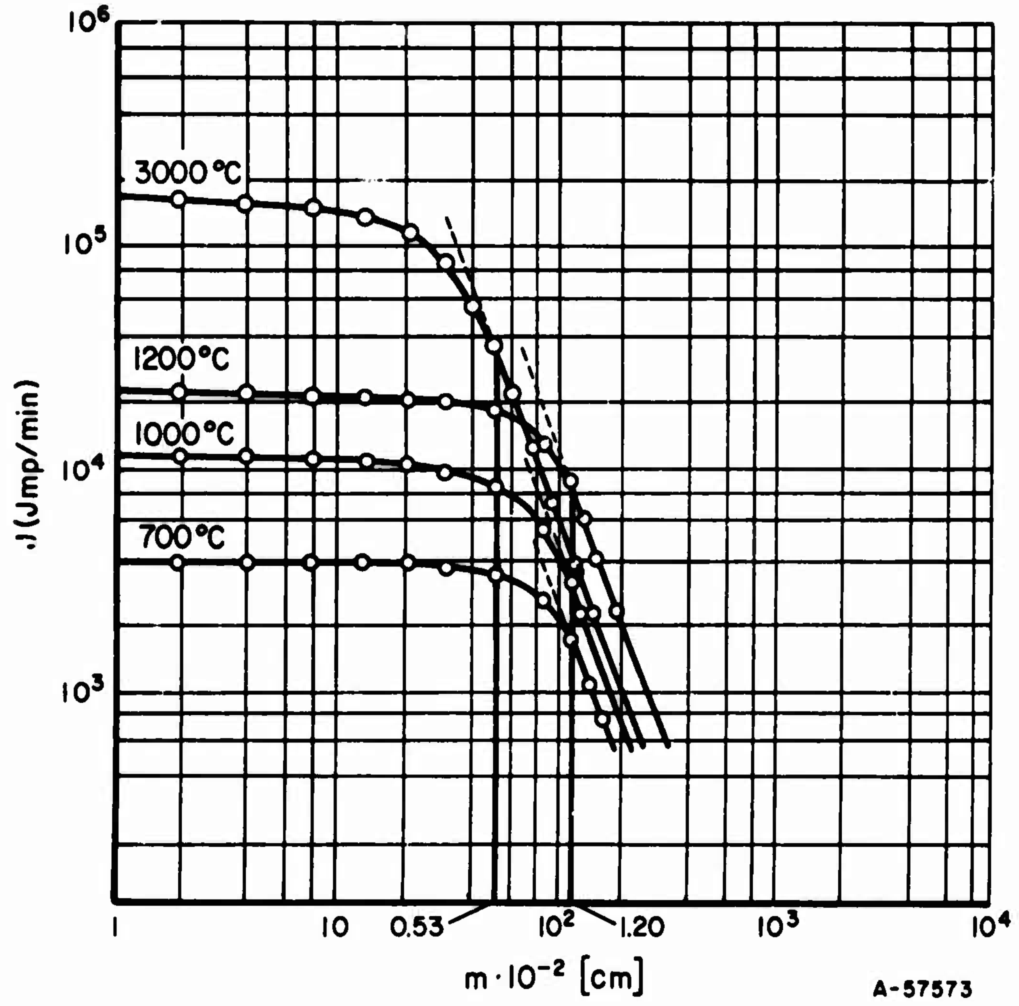


FIGURE 5. BRAGG'S APPROXIMATION OF THE SCATTERING OF PARTICLE DIAMETER

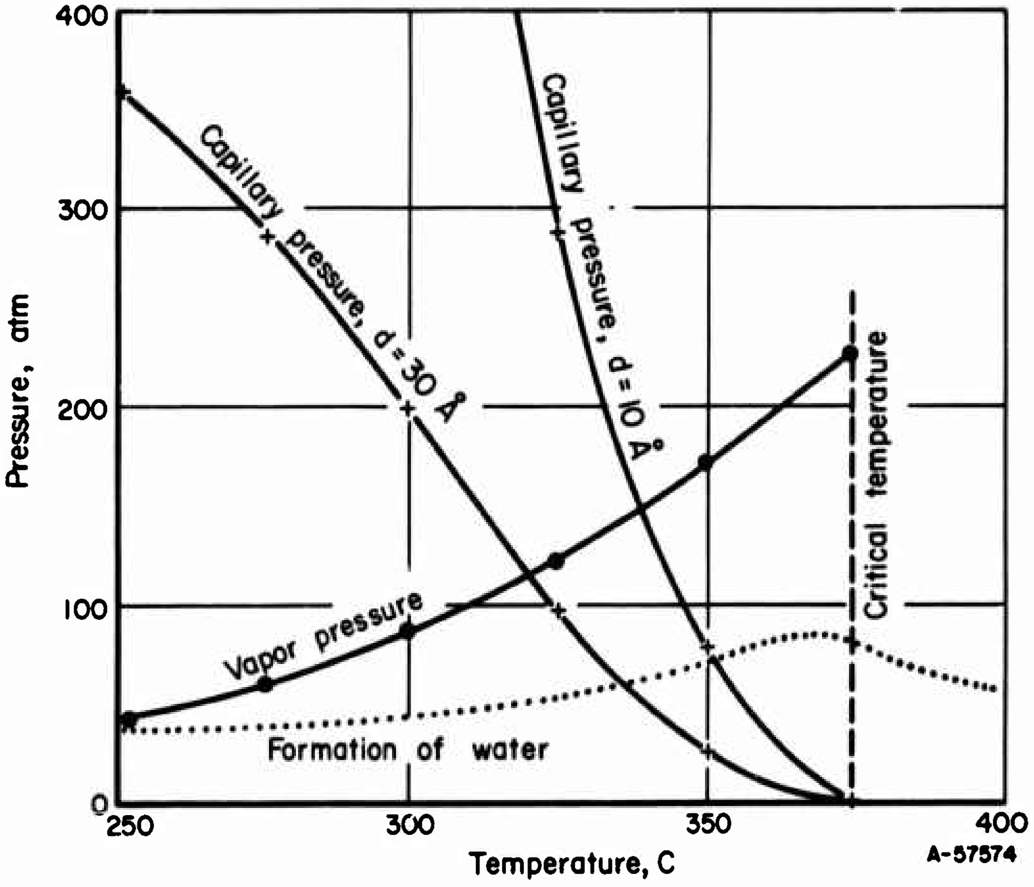


FIGURE 6. COMPARISON OF CAPILLARY PRESSURE WITH VAPOR PRESSURE IN GLASSLIKE CARBON FORMED BY PYROLYSIS OF NONMELTING RESINS

TABLE 1. GENERAL CHARACTERISTICS

	Cellulose-Carbon Pipe(13)	Glassy Carbon		
		GC-10	GC-20	GC-30S
Heatproof Limit, C	1700	1300	2000	3000
Apparent Density, g/cm^3	1.55	1.48 to 1.51	1.47 to 1.50	1.44 to 1.47
Apparent Porosity, percent	--	0.2 to 0.4	1 to 3	3 to 5
Gas Permeability, cm^2/sec	10^{-12}	10^{-11} to 10^{-12}	10^{-10} to 10^{-12}	10^{-7} to 10^{-9}
Ash Content, ppm	--	1000 to 2000(c)	1000 to 2000(c)	70 to 100
Sulfur Content, ppm	--	--	--	--
Boron Content, ppm	--	1 to 2	0.5 to 1.0	0.08
Oxidation Rate	--	--	~ 1/3 of graphite at 800 C in air	--
Compressive Strength, kg/cm^2	--	3695(d)	1960(d)	952(d)
Tensile Strength, kg/cm^2	--	--	450 (25 C)	1040 (2700 C); 420 (25 C)
Flexural Strength, kg/cm^2	1800	900 to 1000(f)	1000 to 1200(f)	500 to 600(f)
Shore Hardness	95	110 to 120	100 to 110	70 to 80
Vickers Microhardness (30-G Load)	--	--	--	--
Young's Modulus, kg/mm^2	2800	3000 to 3300(g)	3000 to 3300(g)	2200 to 2500(g)
Thermal Expansion Coefficient, 10^{-6}/C	3.4 (700 C)	2.0 to 2.2 (100 C)	2.0 to 2.2 (100 C)	2.0 to 2.2 (100 C); 4 to 5 (2000 C)
Thermal Conductivity, cal/(cm)(sec)(C)	0.01 (25 C); 0.04 (1500 C)	0.009 to 0.011	0.020 to 0.022	0.036 to 0.042
Electrical Resistivity, 10^{-4} ohm-cm	40	45 to 50	40 to 45	35 to 40
Charpy Impact Value, kg.cm/cm^2	--	2.1 to 3.0	2.1 to 3.6	2.1 to 2.6

(a) Note surprisingly low value.

(b) Meaning no adsorption of oil and mercury. Glassy Carbon also showed no adsorption of mercury under the pressures up to 950 kg/cm^2.

(c) Can be reduced to 150 to 300 ppm by an appropriate process.

(d) The sample shape was a round bar.(42)

(e) Exceptional values, perhaps because of the pyrolysis under a very high pressure such as 10,000 psi.

(f) Dependent upon the sample shape. These values were determined on plates. In the case of round bars, the strength obtained is shown in Table 3.

(g) Approximately the same as the values obtained by sonic method.(42) It was also found that the relationship between Young's modulus and determining temperature up to 1600 C was negative; the reverse of normal graphite.(42)

OF GLASSLIKE CARBONS

Carbone Vitreux		Vitreous Carbon	Vitro Carbon		Lockheed MSC Glassy Carbon		
V 10	V 25						
1000	2500	2750	1000	2000	1000	2000	3000
1.50 to 1.55	1.50 to 1.55	1.3(a) to 1.5	1.28(a)	1.30(a)	1.48 to 1.55	1.43 to 1.50	1.33 to 1.39(a)
0(b)	0(b)	--	13	12	--	--	--
10^{-10}	10^{-6} to 10^{-8}	2.5×10^{-11}	10^{-9}	10^{-9}	--	--	--
200	50	50	--	--	--	--	--
50	50?	--	--	--	--	--	--
--	2	--	--	--	--	--	--
1 mg/(cm^2)(hr) at 600 C; 25 mg/(cm^2)(hr) at 800 C	0.1 mg/(cm^2)(hr) at 600 C; 2 mg/(cm^2)(hr) at 800 C	See Reference (41)	--	--	--	--	--
300	1500 to 2000	--	--	--	--	9000(e)	6000(e)
--	--	--	--	--	760	920	890
1000	600 to 8000	700 to 2100	--	--	1000	1260	920
120 to 125	120 to 125	--	100 to 120	90 to 110	--	--	--
225	150 to 175	--	--	--	--	HV-120 (1600 C)	HV-165 (2500 C)
2850	2200	--	--	--	--	1400(e)	--
3.2 (100 C); 3.5 (650 C)	3.2	3.0 (700 C)	--	--	3.4	--	--
0.06?	0.06	0.01 to 0.02	--	--	0.005	0.017	--
55	45	10 to 50	200	80	--	--	--
--	--	--	--	--	--	--	--

Compatibility with the Compound Semiconductors

The III-V compound semiconductors, such as GaAs, GaP, are very aggressive, and there has been scarcely any appropriate material in which to prepare the single crystal. Knight(46) had obtained GaAs single crystal by the horizontal zone-melting method with a vessel made of Vitreous Carbon for the first time. Detailed information was described by Lewis et al.(43) On the other hand, Hara and Okasaki(47) reported silicon contamination during the process of crystallization of GaAs in a graphitized Glassy Carbon boat (grade GC-3OS) because of the reaction between the quartz containment vessel and the graphitized surface of the boat. If the results reported by Knight and Lewis et al. prove reproducible, nongraphitized glasslike carbon would bring a better result since a graphitized one was not employed in the former case. It might be concluded that there is a big difference in reactivity as well as in surface area between the graphitized and the nongraphitized vessels.

Resistance to Other Chemicals

It is reported that Vitreous Carbon can be employed to make vessels for preparing tellurium compounds and MgF_2 as well as for vacuum vaporization of aluminum and Nichrome.(43) As described later, this material is quite stable to alkali or alkaline-earth halides such as CaF_2, which is known to be one of the most aggressive compounds at higher temperatures. It is also very stable to ZnS and CdS at high pressure and temperature.

Impurity Content

Semiquantitative spectrochemical impurity analyses of Glassy Carbon are given in Table 2.

TABLE 2. CONTENT OF IMPURITIES IN GLASSY CARBON

Grade	Total Ash, ppm	Impurities(a), ppm											
		Al	B	Ca	Co	Cr	Cu	Fe	Mg	Mn	Ni	Si	V
GC-20	800	24.7	1.0	72	ND	ND	10.0	100	5.5	10.2	ND	27.3	53
GC-S(b)	200	ND	1.6	ND	ND	25	8	31	12	10.8	13.5	16	ND
GC-30S	70	15.2	0.08	ND	ND	ND	0.1	2.1	0.6	ND	ND	1.8	ND

(a) ND = not detected.

(b) Newly developed grade for electronics use, heat treated at 2000 C.

These values do depend upon each lot of purified Glassy Carbon and, therefore, Table 2 reports a representative example. Another example obtained(48) by mass-spectrometric analysis of a sample of GC-3OS Glassy Carbon is as follows:

Analysis, ppm

Al: 20
B: ND
Ca: 3
Co: ND
Cr: 0.2
Cu: 0.1
Fe: 6
Mg: ND
Mn: 0.2
Ni: 0.1
Si: 30
V: 0.2
Te: 0.3
Na: 2
S: 20
K: 2
Ti: 8
As: 0.05
Ga: 0.3
Total ash: 130.

However, it must be noted that the total amount of ash is not so sensitive as is the case with normal graphite because of the extremely small surface area of Glassy Carbon. This is suggested, for example, by the fact that GC-S and sometimes GC-20 are, in practice, quite as useful as GC-3OS in the electronics field, as in the epitaxial growth of high-purity silicon.

Mechanical and Physical Properties

Mechanical Properties

Tsuzuku early investigated the internal friction of glasslike carbon with respect to mechanical damping, comparing it with normal and pyrolytic graphite.(49-51) It was used as a model substance to discuss the structure of graphite.

Concerning the tensile strength of glasslike carbon at higher temperatures, it is now well known that Kotlensky and Martens(52, 53) found an increase in elongation to a value greater than that reported for the other graphite materials at 2500 and 2700 C.

The effect of internal defects in glasslike carbon on its strength is considered to be much greater than in graphite because of the fragility of the glasslike carbon. Sato and Asakura(42) determined the standard deviation as well as fluctuation and homogeneity coefficients of strength of the material, as shown in Table 3.

TABLE 3. COMPRESSIVE AND FLEXURAL STRENGTHS OF GLASSY CARBON ROUND-BAR SPECIMENS

Type of Strength	Grade of Glassy Carbon	Average Value, kg/cm^2	Standard Deviation, kg/cm^2	Coefficients	
				Fluctuation(1), percent	Homogeneity(2), factor
Compressive	GC-10	3694.5	1305.21	35.3	3.06
	GC-20	1955.9	430.38	22.0	5.2
	GC-30	952.2	150.03	15.8	7.38
Flexural	GC-10	1651.3 1884.3	640.6 190.3	38.8 10.1	2.7 11.9
	GC-20	1321.1 1520.6	269.8 192.7	20.4 12.7	5.6 9.3
	GC-30	1208.4 880.6	303.7 265.3	25.1 30.1	4.5 3.6

(1) Fluctuation coefficient, C_v, is defined as

$$C_v = \frac{\text{Standard Deviation}}{\text{Average Value}} \times 100 \quad .$$

(2) Homogeneity factor, m, is the material constant contained in Weibull's function* on the distribution function f(y), a probability density function of the strength, x, of crack propagation in the specimen. The following equation is derived in relation with C_v**:

$$C_v = \left[\frac{2m\,\Gamma(2/m)}{\Gamma^2(2/m)} - 1 \right]^{1/2} \quad .$$

* Weibull, W., Ing. Vetenskops Akad. Hondl No. 151 (1939), ibid, No. 153 (1939).

** Sato, S., Japan Atomic Energy Research Institute, NSJ-Tr-46 Feb. (1966).

With respect to wear, Nishimoto and Tsukata(54) found that GC-10 and GC-20 showed better results than several kinds of carbon and graphite rings made for sealing. However, the graphitized Glassy Carbon, GC-30, was worse under the same conditions of wear testing. Other data from this type of testing are reported in Table 4.

TABLE 4. PV-VALUE OF GLASSY CARBON BEFORE AND AFTER WEAR TESTING[(a)]

	Before Test			After Test		
Material	Average Pressure (P_m), kg/cm^2	Contact Area (A), mm^2	$P_m \cdot V$	Average Pressure (P_m), kg/cm^2	Contact Area (A), mm^2	$P_m \cdot V$
GC-10	905	0.033	820	280	0.18	250
GC-20	1180	0.026	1060	560	0.09	500
GC-30	1200	0.025	1080	280	0.29	250
Carbon[(b)]	680	0.045	610	170	0.30	150
Graphite[(b)]	680	0.045	610	160	0.33	140

(a) Load, W = 0.5 kg; velocity, V = 0.9 m/sec; time = 3 hr; specimen = 40-mm-OD x 20-mm-ID x 3-mm-thick ring; 7/16-in-diameter steel ball for bearing use.

(b) Special grades for mechanical sealing.

As given in Table 1, the Charpy value, an indication of resistance to mechanical shock, is similar to normal graphite and normal glass, but the fact that glasslike carbon has no self-lubricating ability limits its mechanical use considerably.

Thermal Properties

Recently the thermal-shock resistance of LMSC Glassy Carbon was measured by Bradshaw et al.(27) to be over two times higher than that of Tokai Glassy Carbon and also somewhat higher than ATJ graphite. Concerning Tokai Glassy Carbon, several qualitative tests made by repeated thermal shocking of 2000 C specimens with coke powder kept at room temperature showed good results for plate, crucible, and pipe. However, when water replaced the coke powder a difference in the resistance was observed even when 980 C was employed as the higher temperature. Graphitized GC-30 and GC-30S gave the worst results. If one plane surface of the graphitized Glassy Carbon plate is taken off mechanically, one can observe a slight bending to the rectangular direction of the surface, perhaps because of the relaxation of stress owing to the heterogeneous macrostructure, where only the surface material is graphitized. This might also suggest the poor resistance of the graphitized Glassy Carbon to shocks. Although the spalling coefficient (thermal conductivity x flexural strength/Young's modulus x coefficient of thermal expansion) of graphite is approximately two times and three times greater than that of GC-20 and GC-10, respectively, the graphitized Glassy Carbon showed the worst result. Furthermore, by the above test between 980 C Glassy Carbon and water, it was calculated by Akimoto(55) that the λ value of GC-20, in the well-known formula,

$$E_n = E_o e^{-\lambda n} \quad ,$$

where E_n and E_o are Young's modulus after and before the thermal-shock test, and n is test number, was 0.15, which is about two times that of GC-10, the λ value of which is 0.08. This ratio corresponds with that of the spalling coefficient, GC-20 = 9,800 to 12,000 and GC-10 = 4,500 to 6,400 kcal/(m)(hr). Therefore, the poor resistance of the graphitized Glassy Carbon should be explained in some other way, namely, the heterogeneous structure mentioned above. In this case, the spalling coefficient of the graphitized Glassy Carbon can be derived to be 17,000 to 21,000 kcal/(m)(hr), while that of electrode graphite is 80,000 to 100,000 kcal/(m)(hr). The λ value of the graphitized Glassy Carbon could not be obtained because Young's modulus was not calculated after the thermal-shock test.

Electrical Properties

Tsuzuku and Saito(56) estimated the approximate energy gap of Glassy Carbon to be 10^{-2} to 10^{-3} ev by determining the temperature dependence of electrical resistivity, Table 5 shows relevant results.

TABLE 5. TEMPERATURE DEPENDENCE OF THE ELECTRICAL RESISTIVITY OF GLASSY CARBON

Temperature, C	Electrical Resistivity, 10^{-4} ohm-cm GC-10	GC-20	GC-30
25	48.1	45.2	34.8
100	44.1	41.4	33.2
200	42.3	38.7	32.8
300	40.0	37.3	32.0
400	39.1	36.6	27.6
500	38.2	36.1	25.5
600	37.0	35.6	22.6
700	35.7	34.3	21.4
800	34.6	33.2	20.3

Yamaguchi(57) found a marked difference in Hall coefficient R, magnetic resistivity ($\Delta\rho/\rho_o$), and electrical resistivity between soft carbons and Glassy Carbon, at 20, 77, and 300 K. These results show that the electronic behavior of Glassy Carbon specimens heat treated at various temperatures corresponds to that of soft carbons treated at lower temperatures. Even with the Glassy Carbon heat treated at 3200 C, one carrier system can be considered to prevail because the Fermi level is low enough. Tsuzuku and Saito(56) determined the Hall coefficients at various measuring temperatures, from which the electronic parameters given in Table 6 could be derived, by considering the Hall coefficient at 77 K obtained by Yamaguchi.(57) It should be noted that the mean free path was much smaller than the apparent diameter of crystallite obtained by X-ray diffractometry.

TABLE 6. ELECTRONIC PARAMETERS OF GLASSY CARBON

	Heat-Treatment Temperature 2000 C (n-Type)	3000 C (p-Type)
Hall Mobility (H), cm^3/coulomb	-4	+17
Carrier Concentration (N), cm^{-3}	3×10^{20}	0.8×10^{20}
Mean-Free-Path Length (1), Å	3	10

Mizushima and Kishigami(58) made a study of electron spin resonance in glasslike carbon heat treated at temperatures from 700 to 3200 C. It is remarkable that the absorption line appears only in the ranges of heat treatment where most carbonaceous substances do not show any absorption, and is absent in the range where the latter give resonance. The glasslike carbon is just the opposite of ordinary carbons. Considering the poor graphitizibility of glasslike carbon, it seems that the intensity maximum at around 700 C of ordinary carbons is shifted to about 1200 C in this case. Such a tendency coincides with that observed in the Hall coefficient.(57) Honda et al.(59) made a detailed determination on several kinds of phenolic resin carbons, including a systematic study of the correspondence to changes in the chemical structure.

On the other hand, Nakamura et al.(60) estimated the isotropy of Glassy Carbon with the aid of the determination of electrical resistivity. Smitz's method(61) was applied to obtain more accurate values of the short distances involved, such as a wall thickness of 3 mm. As shown in Table 7, the isotropy of the plate was considered to be confirmed from this standpoint.

TABLE 7. ELECTRICAL RESISTIVITY OF GLASSY CARBON PLATE OF EACH DIRECTION

	Batch A(a)		Batch B(a)		Batch C(b)	
	Specimen 1	Specimen 2	Specimen 1	Specimen 2	Specimen 1	Specimen 2
Resistivity with Plane, 10^{-3} ohm-cm	6.0	5.5	5.1	5.0	5.0	5.0
Resistivity across Plane, 10^{-3} ohm-cm	5.5	5.7	5.0	5.0	5.0	5.0

(a) Heat treated at 1300 C.
(b) Heat treated at 3000 C.

In this research it was found that the coexistence of artificial and natural graphite within Glassy Carbon did not disrupt the isotropy. However, a resultant remarkable enhancement of the graphitizibility of Glassy Carbon was clearly observed by X-ray diffraction examination of several model substances.

Yamaguchi(62) determined the thermoelectric power of Glassy Carbon at higher temperatures and compared it to that of normal graphite. Satoh and his coworkers(63) made more detailed research on the same topic for the preparation of thermocouples, the same purpose as Yamaguchi's, and found such an application possible.

Irradiation Behavior

A preliminary study on the change in internal friction after a neutron irradiation of 10^{14} nvt was made by Tsuzuku.(64) Glassy Carbon showed a reverse change to that observed in normal graphite. Shimada and Kikuchi(65) also made a comparison with reactor-grade graphite under an irradiation up to 1.15×10^{20} nvt. Changes in the electrical resistivity of GC-10, GC-20, and GC-30 were very much smaller than that of graphite. For example, GC-30 showed the minimum change, less than +1 percent, while graphite showed as much as approximately +30 percent after the ultimate irradiation. Shimada and Kikuchi studied the mechanism of the damage. They noted that the change in thermoelectric power of Glassy Carbon was hardly observable, a sharp contrast to the large change found in graphite (from -2v/C to +8 v/C). This means that Fermi level or carrier concentration in Glassy Carbon undergoes almost no change during irradiation.

Quite a small change in thermal conductivity as well as in Young's modulus was also observed by the same authors under the same irradiation, while the graphite showed pronounced changes.(3) Unfortunately, the Glassy Carbon underwent a remarkable change in appearance, in spite of both of the above observations and the observation of no change in size or c_0-value after irradiation.

Relationship Between Apparent Density and Thickness After Carbonization

As shown in Figure 7, a linear relationship between the apparent density of Glassy Carbon plate and its thickness after carbonization has recently been found. The maximum thickness of 4.8 mm that was obtained in Tokai's laboratory was achieved in disks 150 mm in diameter. It is of interest that LMSC Glassy Carbon(27) shows a behavior similar to that of Tokai Glassy Carbon except for the case of the material subjected to a 10,000-psi pressure during pyrolysis, as illustrated in Figure 7. The reason for this is uncertain.

Optical Properties

Taft and Philipp(66) found that the reflectance minimum was shifted to lower energies by approximately 1.5 ev less than graphite, and reflectance values were generally lower compared to crystalline samples of graphite. Ishikawa et al. also determined the reflectance of Vitro Carbon as a function of heat-treatment temperature.(25)

STRUCTURE OF GLASSLIKE CARBONS

Structure of Cellulose Carbon

Structural determinations by X-ray diffraction techniques on Cellulose Carbon(1) gave almost the same results as obtained with Glassy Carbon(8) and Vitreous Carbon(43), showing that it is a representative nongraphitizable carbon. A comparison between the observations of electron microscopy and of small-angle scattering was undertaken and a distribution of small pores was recognized which was considered to correspond to the difference between the real and true density, since no other type of pore was observed in practice. Also, it was supposed that the fibrous property of the cellulose macromolecule remained after carbonization.

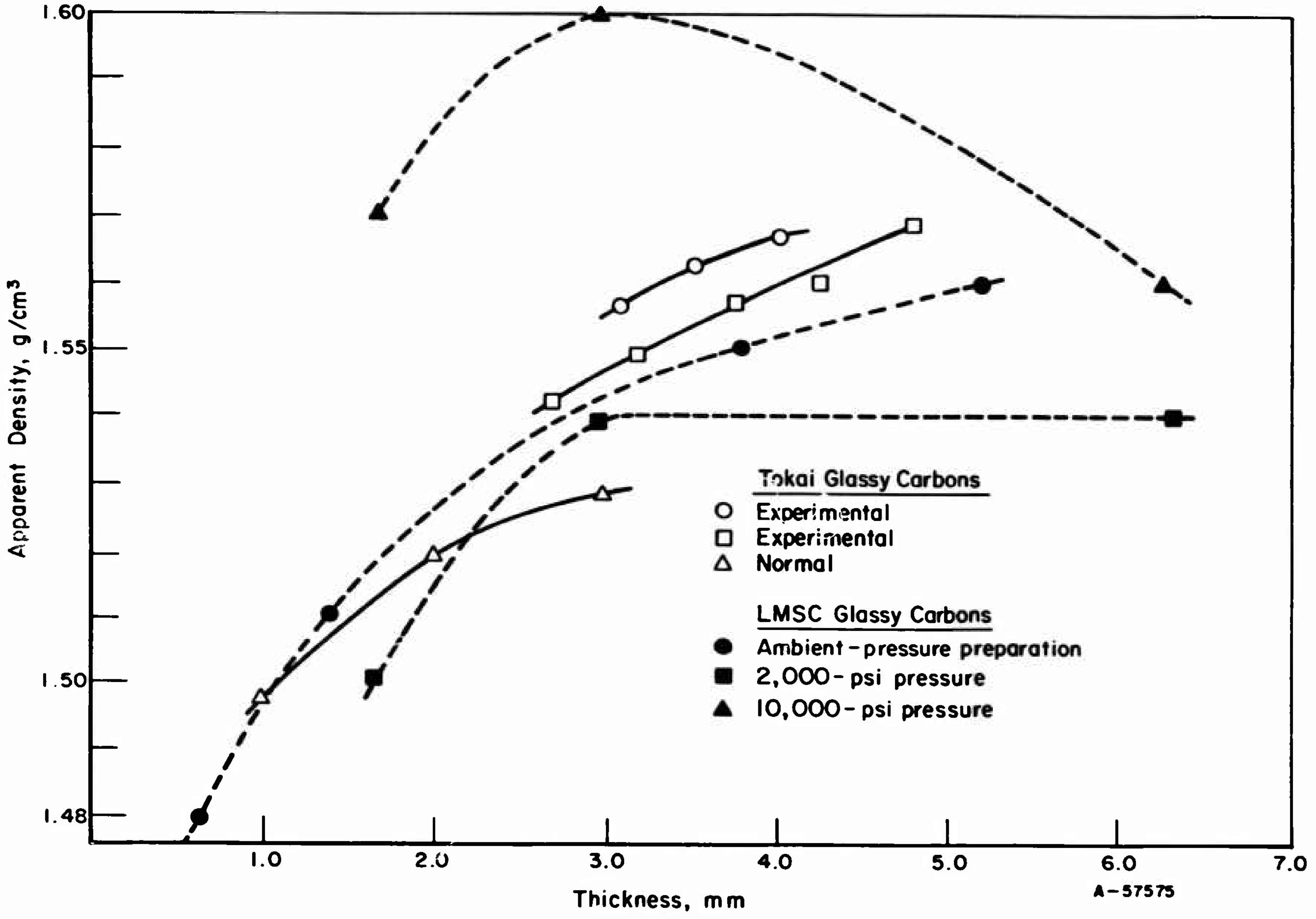


FIGURE 7. RELATIONSHIPS BETWEEN APPARENT DENSITY OF GLASSY CARBONS AND ITS THICKNESS, WHERE
T-n, Tokai's normal Glassy Carbon; T-x and -y, Tokai's made in laboratory;
L-a, LMSC-Glassy Carbon made in the ambient atmosphere; L-2000 and -10000, LMSC's made under pressures of 2000 and 10,000 psi respectively.

Structure of Glassy Carbon

Analysis of Radial Distribution Function

Noda and Inagaki(5) calculated the radial distribution function, $r = 4\pi r^2 \rho$, for Glassy Carbon, and assumed that Glassy Carbon was composed mainly of two types of carbon atom, one having tetrahedral relation to its neighbors, like diamond, and the other having trigonal relation to its neighbors, like graphite. The first peak of the observed radial distribution curve, being located from 1.5 to 1.6 A, was separated into two component curves corresponding to trigonal and tetrahedral carbon atoms. The curve for each was assumed to have the Gaussian form. A good coincidence between the observed curve and the calculated curve on the representative Glassy Carbon samples brought this viewpoint of the structure.

Analysis by a Cubic Model

Furukawa(6) criticized the consideration above mentioned from the standpoint of the remarkable difference between the observed and the calculated density, the calculated being derived from the contribution of the tetrahedral bond. Another model was proposed which was derived from an average coordination number of neighboring atoms, containing three kinds of bonds, tetrahedral, triple, and double. This model is a perfect three-dimensional network, having disordered and also discontinuous interstices, with no contribution of graphitic bond. It is said that there is no contradiction between the physical and chemical properties in this model.

Consideration of Oxygen Bridge

Kakinoki(7) modified the opinion of Noda and Inagaki, adding an oxygen bridge between the trigonal and the tetrahedral part. However, the amount of oxygen in Glassy Carbon which was reported at an informal meeting of the Symposium on Carbon (Tokyo, 1964) by the author should have been corrected to a much smaller figure because of the unexpectedly large moisture adsorption of the Glassy Carbon specimen, heat treated at 1000 C. Kakinoki's model was based on the author's report and, therefore, it might be subject to revision now.

An Analogous Approach to the Chemical Structure of Glassy Carbon

Yamada and coworkers found a marked increase of flexural strength by the addition of very small amounts of platinum salt to the raw material.(8, 67, 68) This approach was grounded upon an analogous phenomenon observed in the case of the modification of mechanical properties of normal glass. The mechanism is also not yet known for glass, but such a result may suggest indirectly that Glassy Carbon might be similar to normal glass in chemical structure.

Melting of Glassy Carbon

Noda and Inagaki(69) treated a round bar of Glassy Carbon under a pressure of over 150 atm of argon at around 4000 K. The central part appeared to be molten, and uner X-ray diffraction examination had exactly the same parameters as those of natural graphite. It was thus made clear that a relaxation of all the strain included in Glassy Carbon leads to a graphitic structure in a short time.

Dependence of c_p Upon T^2

Takahashi and Westrum(70) determined the specific heat, c_p, of Glassy Carbon at 5 to 50 K. From the observed dependence on temperature, one must presume a structure of graphitelike layers in this material, which means that the three models described above based upon analysis of radial distribution function, analysis by a cubic model, and consideration of an oxygen bridge would be denied.

Pending Publication on Structure

A paper entitled, "Comment on the Structure of Glassy Carbon", by T. Noda, M. Inagaki, and S. Yamada, is to be submitted to Carbon concerning the further explanation of the structure by consideration of the several models.

SIZE AND SHAPE OF GLASSLIKE CARBONS

Standard Sizes and Shapes

Glasslike carbons are difficult to machine and to prepare a specific size and shape it is necessary to satisfy various strict requirements. Boats, crucibles, bars, and plates are the main common products. The representative pictures of Glassy Carbon shapes shown in Figure 8 gives a general idea of fabrication possibilities of glasslike carbons.

Glasslike carbon seems to be available in a varied range of sizes and shapes. However, it is often necessary to machine it by ultrasonic techniques as well as by diamond tools or to polish it with green SiC powder in order to obtain the tolerances required in some applications.

Fibrous Form of Glasslike Carbons

Glasslike Carbon Filament(19-21)

With the development of space industry, high-strength and high-modulus carbon fiber has become required. If a fibrous form could be made from glasslike carbons, the industry's requirement should be satisfied to a great extent because of glasslike carbon's higher strength and modulus compared with other carbons. However, there has been no effort to spin the filament from thermosetting resins which give glasslike carbon black because it would be quite difficult to make a filament from any initial condensate of thermosetting resins having low molecular weight, such as only a few hundred. However, thermoplastic resins with molecular weights over 10,000 can give a filament form easily, as in glass-fiber preparation. The optimum condition for preparing glasslike carbon filament, derived from the mixtures of novolak, resol, and an initial condensate

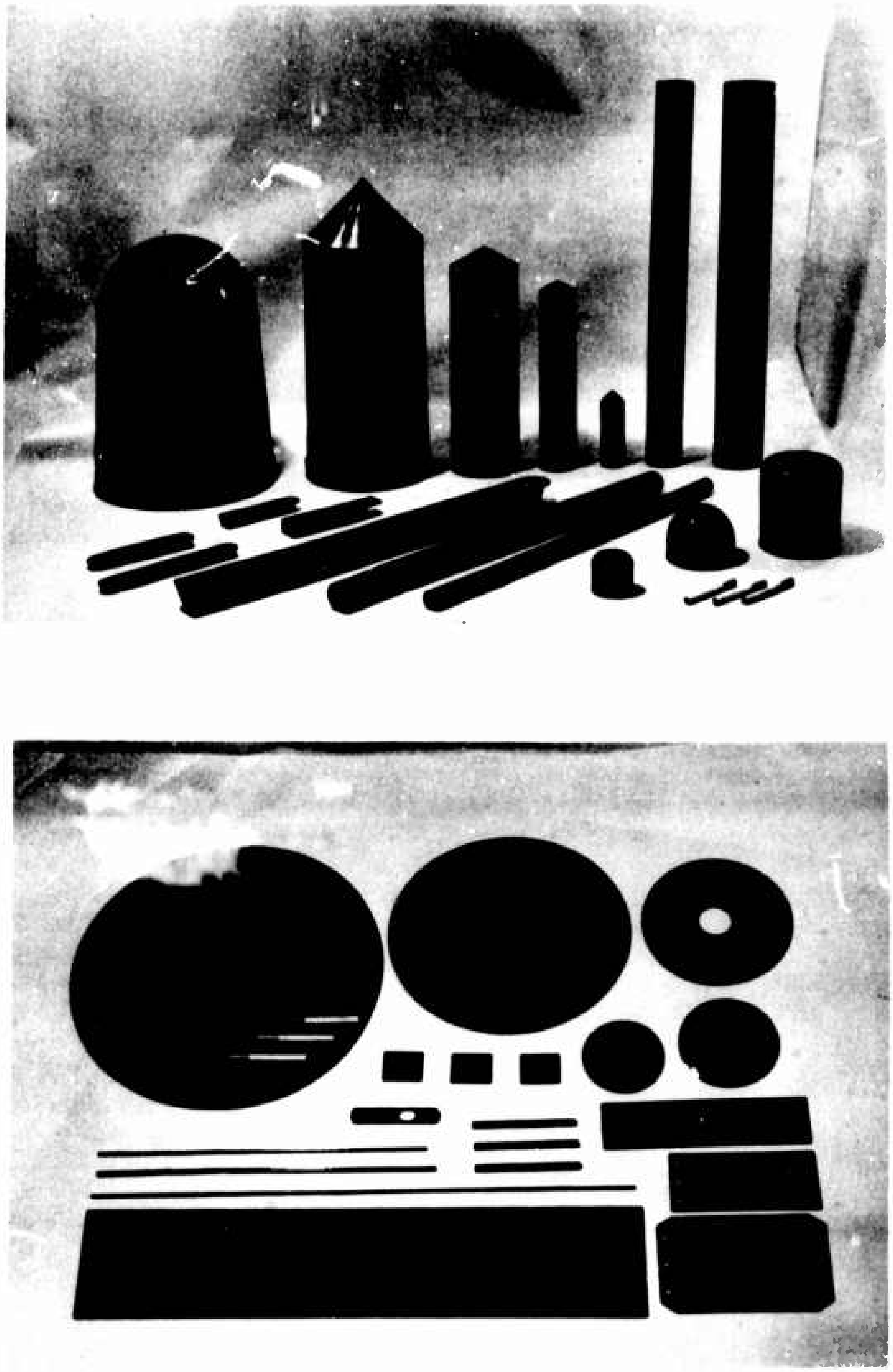


FIGURE 8. GLOSSY CARBON SHAPES TYPICAL OF THOSE AVAILABLE

The cigarettes provide a measure of relative size of the parts.

of furfurol-furfural resin, has been obtained by using a spool-spinning method followed by a rapid gelation and aging in hydrochloric acid prior to carbonizing. A representative result is summarized in the following section.

Resin Preparation and Spinning. The following were carefully mixed into a homogeneous solution:

(1) Seven parts of a resol, derived from phenol and formaldehyde, molar ratio = 1:2, molecular weight = 367, viscosity = 100 centipoises at 70 C, and catalyzed by ammonium hydroxide

(2) One part of a novolak, also derived from phenol and formaldehyde, molar ratio = 1:0.88, molecular weight = 354, and catalyzed by hydrochloric acid

(3) Two parts of initial condensate of furfuryl alcohol and furfural, weight ratio = 8:2, having a viscosity of about 80 centipoise at 30 C, with a molecular weight = 185.

The optimum spinning field in the diagram of this ternary system - resol, novolak, and furan - is as shown in Figure 9.

This solution was then heated and kept at 70 to 75 C, followed by spinning under pressures of 1.05 to 1.1 kg/cm^2 of nitrogen through a nozzle having diameters of 0.3 to 1.0 mm and then cooled at the spool with 20 percent HCl at 2 to 5 C. The specimens thus spun were kept immersed in this acid solution and aged at room temperature for a few weeks, followed by washing, drying, and finally carbonization. It has been found that the size and shape of the nozzle play a big role in obtaining homogeneous and thin filaments. A quantitative investigation of the relationship between the filament diameter and the nozzle diameter and draft ratio, as well as of the spinnability, is being carried on.

Tensile Strength and Modulus in Relation to the Processing Conditions. Typical results are as illustrated in Figures 10 and 11. The shape of cross-section is, in general, oval, as seen in Figure 12, which is a photomicrograph taken by Pinoli et al.(71) The area was calculated by $\pi \cdot a \cdot b$ where a and b are the minimum and maximum diameters. Pinoli has also taken several pictures of the cured filaments, that is, filaments prior to carbonization, as shown in Figure 13 which should be compared with Figure 12. All of these specimens shown in Figure 10 through 13 were prepared by using a die giving an onionlike mass just after extruding. Owing to an improved die giving no onion shape, the distribution of diameter of carbonized filaments has been considerably improved and the possibility of preparing thinner ones is being achieved. Thin filaments such as 5 to 20 μ in diameter can presently be obtained only by thermal stretching of thermoplastic materials after spinning. Diameter at the spinning process is said to be about 30 to 50 μ in the case of normal thermoplastic fibers. However, Glassy Carbon filament cannot be stretched because of thermosetting in the green state and, therefore, much thinner filaments than the just-spun normal fibers must be directly formed in the spinning. Spinning difficulty itself increases the difficulty in obtaining thinner filaments, which leaves only the one possibility - improving the die - for improving the strength.

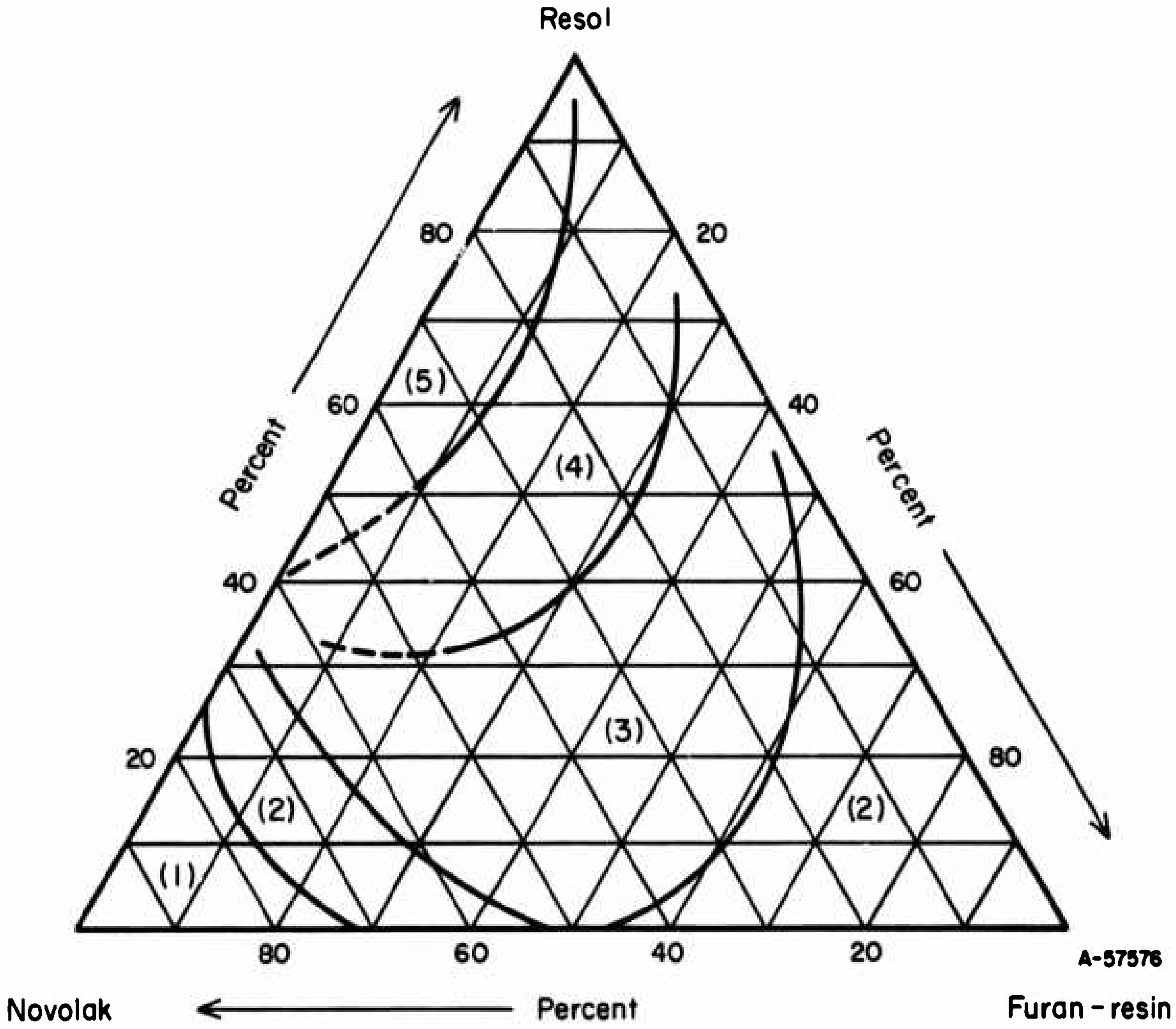


FIGURE 9. DIAGRAM OF THE RESOL-NOVOLAK-(FURAN-RESIN) TERNARY SYSTEM

(1) Thermoplastic field
(2) Low spinnability field
(3) Spinnable field
(4) Optimum spinning field
(5) Unspinnable field.

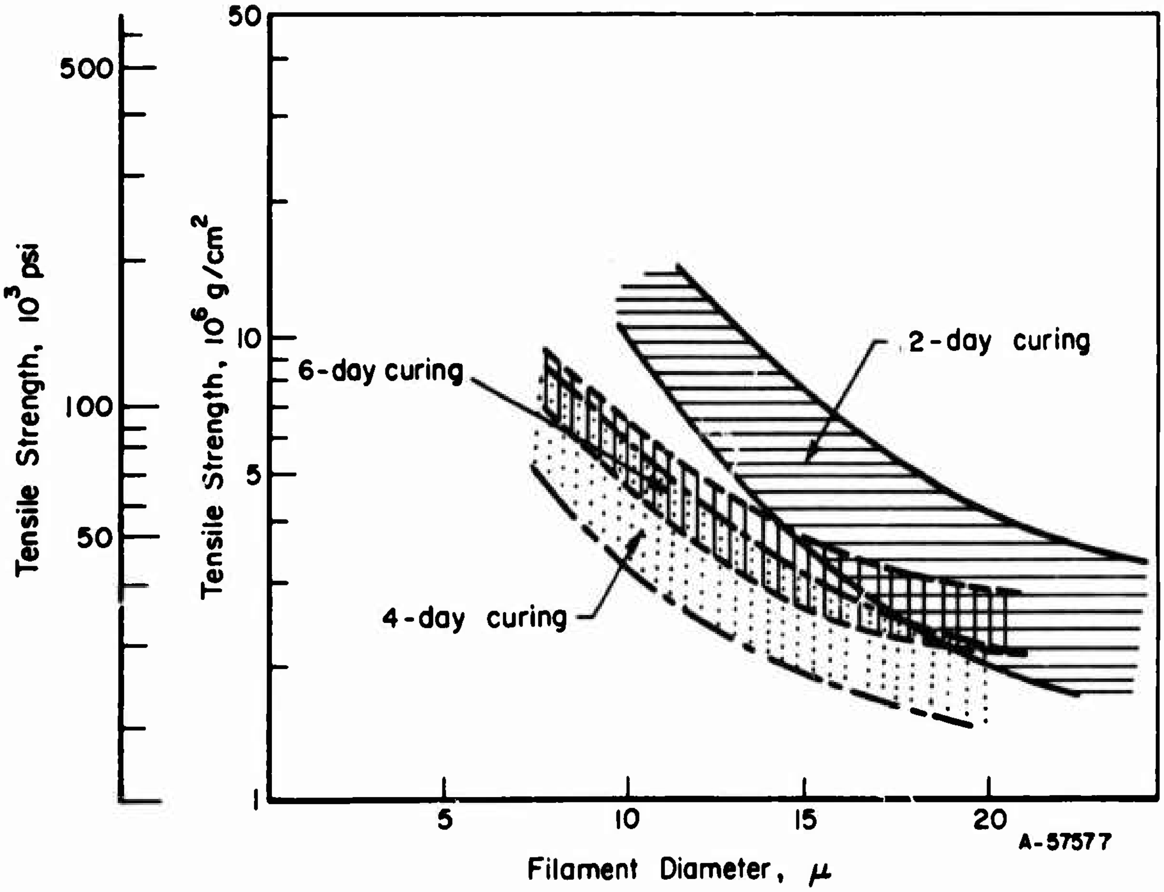


FIGURE 10. THE EFFECT OF THE CURING TIME ON THE TENSILE STRENGTH OF GLASSLIKE CARBON FILAMENTS

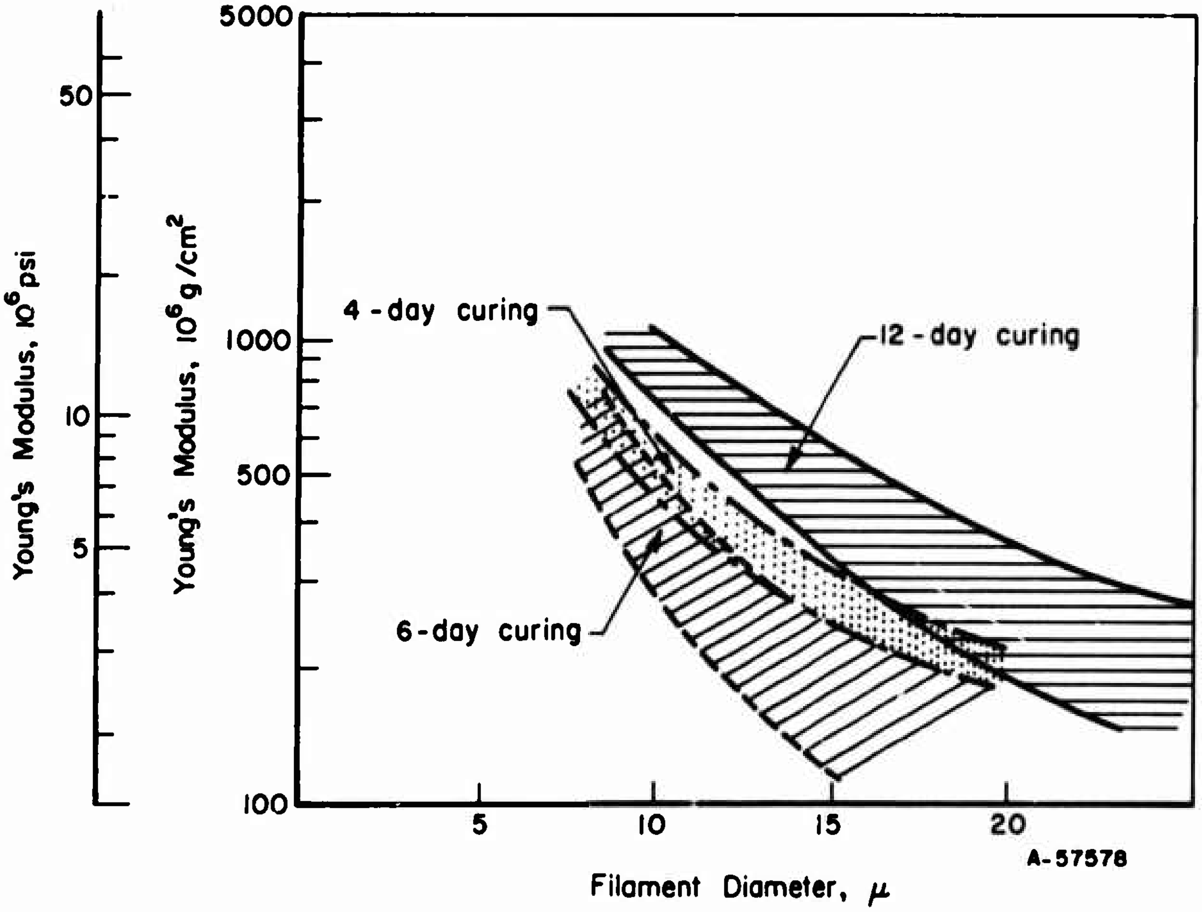


FIGURE 11. THE EFFECT OF THE CURING TIME ON THE ELASTIC MODULUS OF GLASSLIKE CARBON FILAMENTS

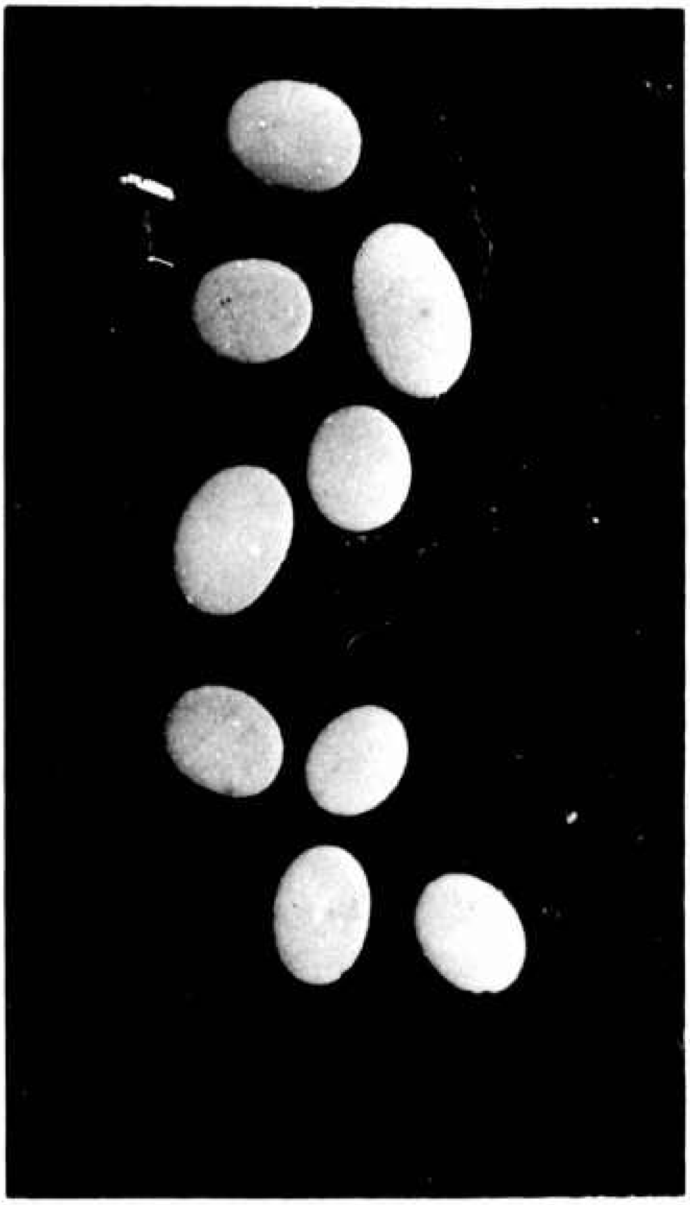


FIGURE 12. TYPICAL OVAL CROSS SECTION OF GLASSLIKE CARBON FIBERS

FIGURE 13. STRUCTURE OF GLASSLIKE CARBON FILAMENTS PRIOR TO CARBONIZATION

The presence of sulfur and ozone during carbonization lead to a considerable increase of strength, approximately 1.5 to 2.5 times as high as that obtained without them, as has been confirmed recently. The carbonization of the filaments between two fixed edges seems to have a similar effect as above. However, no increase of modulus has been observed, unfortunately. The mechanism of these effects should be studied in the near future.

Isotropy of the Filament. Isotropy of glasslike carbon filament material is considered to be quite probable because of the data given in Table 7. This would be one of the advantages in using the material in the preparation of composites. There has been no proof of isotropy until now. Examination of X-ray diffraction patterns is assumed to be almost the only method of ascertaining isotropy in the filament form of glasslike carbon. X-ray results are shown in Figures 14 and 15.(11) According to these results, this kind of filament can be considered to have isotropy up to 2000 C.

With the glasslike carbon specimen heat treated at 2500 C one can observe a slight anisotropy owing to graphitization. However, more distinct orientation has been observed on the raw material of regular carbon fiber, i.e., polyacrylonitrile filament, as well as on the specimen of it heat treated at 1000 C. Figure 16, a representative electron micrograph, clearly shows the glasslike and isotropic appearance of the filaments.

It can be expected that such an isotropy would play a considerable role in the properties of composites employing this material. The tensile strength and Young's modulus of the stretched carbon fiber derived from cellulose(72) are higher than those of this filament, but the fiber is also highly orientated owing to the stretching during pyrolysis. It is not yet sure that this advantage of isotropy could outweigh the lower strength and modulus. X-ray diffraction parameters of the filaments, heat treated at various temperatures up to 2800 C, are quite similar to those of regular Glassy Carbon block, as illustrated in Figure 17.

As described above, this glasslike carbon filament seems to have the same structure, in essence, as that of regular Glassy Carbon, which is known to have a strength similar to normal glass but a poorer modulus than glass. Accordingly, the modulus of glasslike carbon filament would not be expected to become greater, although the higher modulus is one of the most important factors considered in selecting materials for use in composites.

The formation mechanism of the filament is under investigation, particularly regarding the behavior of novolak, which plays the biggest role in spinning.

MP (Molten Pyrolysis) Fiber

Ohtani(31, 73) conducted a systematic investigation concerning the preparation and formation mechanism of carbon fiber derived from molten pitch. It was made clear that this type of fiber can be regarded as being one of the glasslike carbons from the standpoint of X-ray diffraction, electrical resistivity, density, etc. It must be remarked that oxidation of such carbon fibers by ozone and the air at lower temperatures gave properties like those observed in glasslike carbon. In the experience of the author(74-76), the addition of a considerable amount of organic nitro-compound to a tar did not give a low density so long as no chlorine was present.(77) Such a nitro-compound

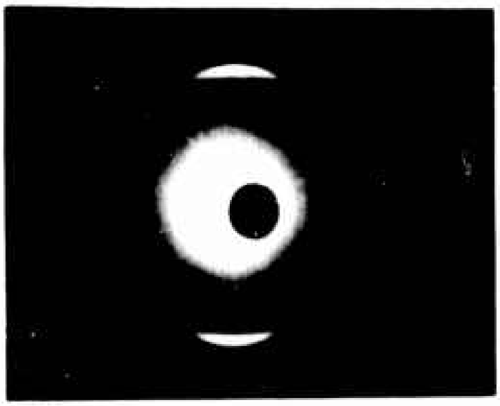
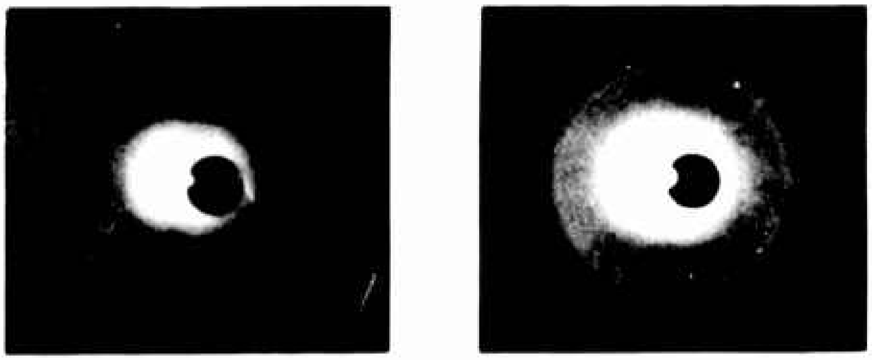


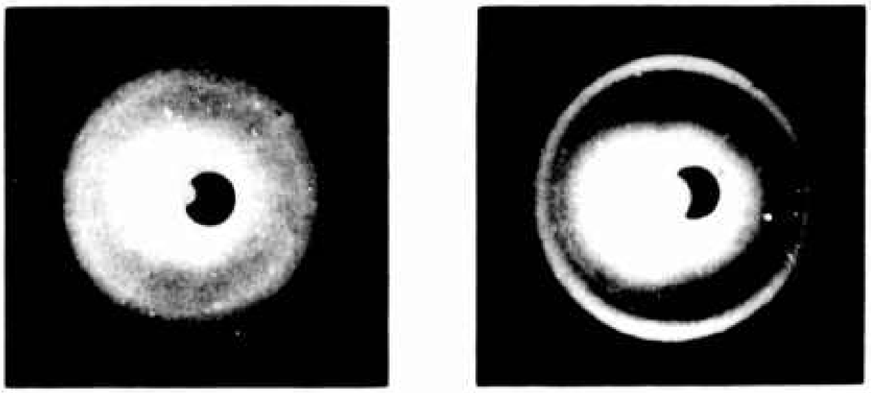
FIGURE 14. X-RAY DIFFRACTION PATTERN OF CARBONIZED REGULAR CARBON FILAMENT DERIVED FROM POLYACRYLONITRILE

This material was heat treated at 1000 C. The raw filament also showed an oriented structure and the graphitized filaments exhibited almost the same patterns as shown here.



a. Cured Filament Prior to Carbonization

b. Filament Heat Treated at 1000 C



c. Filament Heat Treated at 2000 C

d. Filament Heat Treated at 2500 C

FIGURE 15. X-RAY DIFFRACTION PATTERNS OF THE GLASSLIKE CARBON FILAMENTS

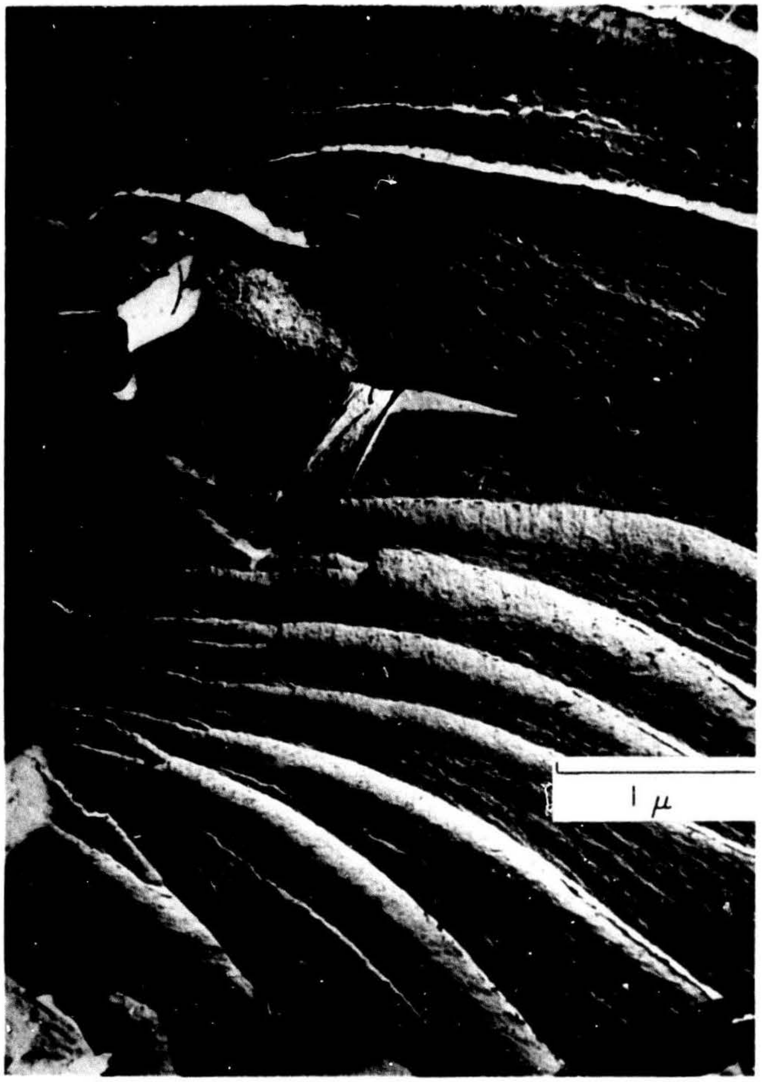


FIGURE 16. TYPICAL ELECTRON MICROGRAPH OF GLASSLIKE CARBON FILAMENT

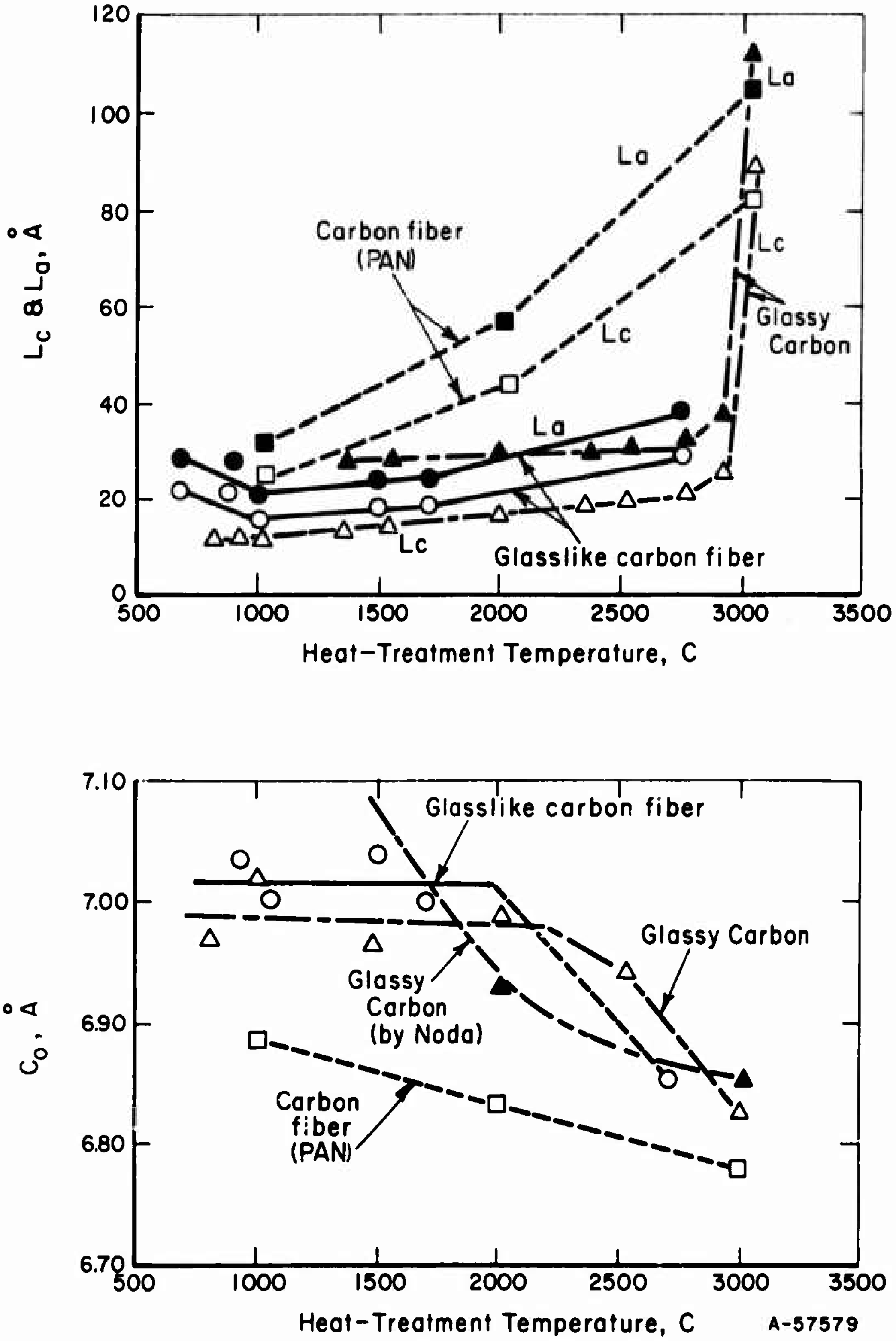


FIGURE 17. X-RAY DIFFRACTION ANALYSES OF GLASSLIKE CARBON MATERIALS

addition is, therefore, to be considered since the filament from the oxidation process has much greater surface area and because the action of air on the tar pitch is unexpectedly effective. The tensile strength and modulus can be estimated to be approximately the same as regular carbon fiber from polyacrylonitrile.

The proposed structural formula for this material was derived from a systematic study of the reactivity of radicals belonging to various organic raw materials. From this knowledge a pilot plant was designed and built to prepare another type of fiber, originated from lignin and polyvinyl alcohol.(78) In this method no oxidation process is necessary, owing to the existence in the materials of a large number of functional groups such as $-OCH_3$, $-OH$, and $-CHO$, some of which are supposedly formed in the tar pitch when an oxidation process is used. Glasslike carbon block derived from modified pitch in this way has been shown at the informal meeting of the Eighth Conference on Carbon.

APPLICATIONS OF GLASSLIKE CARBONS

Originally glasslike carbon materials were developed for use in nuclear reactors. However, many other potential applications are of interest now. This section will review some of the current and potential applications for these materials.

Present State of Application(4, 79)

This review is concerned almost exclusively with uses in Japan(3) since information regarding the work needed to establish glasslike carbons for particular applications could be best obtained through discussions with people active in the development of these materials. The efforts of the author and coworkers concerning glasslike carbon have unavoidably been concentrated upon application and not upon general research work.

Susceptor for Epitaxial Growth of High-Purity Silicon(80-82)

The rapid development of integrated circuits needing the epitaxial-grown silicon accelerated this application. Three or four years ago, at the initial stage of this application, the susceptor of glasslike carbon was regarded as an article of consumption, having a life of a few days. But it turned out to be a permanent part of the apparatus, lasting up to a year and a half. Fundamental improvement in the forming process is considered to have played a big role in this progress, which might mean that the initial state governs the properties of the final product. The GC-S Glassy Carbon is convenient for this purpose because of its low impurity content and low surface area. Larger disks, having diameters of 300 to 400 mm, have recently been requested and made available. The advantages of this material are stability against thermal shock and aggressive gases, the absence of outgassing, lack of contamination, suitable electrical resistivity, etc. The disadvantages of glasslike carbon, such as poor resistance against mechanical shock, poor machinability and tolerance, maximum thickness of only 3 mm in industrial use, and a price higher than that of graphite, have not come into question as in other uses described later.

Glow Electrode for Metallurgical Uses

One example of a glasslike carbon electrode is a 5 x 5 x 100-mm bar which connects a pellet to the top of a golden pen. It has lasted over 200 times longer than normal graphite. Automation of the apparatus has been possible only because of this fact. Unlike the case with the graphite electrode the surfaces of the bar can be machined after a period of use, for further processing. This application is not only of importance in this industry but it also holds promise for other metallurgical uses.

Precise Jigs for Processing Ceramics, Semiconductors, and Metals

Representative of this application is the jig for preparation of diamond needles for long-playing records. This use suggests the extreme exactness that can be obtained in components prepared from this material. Minute and precise jigs do, in general, require special forming techniques to obtain the minimum tolerances economically.

Heaters for Electronic Devices

Various sizes and shapes of heaters are used, particularly in the electronics field. Usually plates are convenient, but a considerable number of minute heaters, for example, approximately 1 x 1 x 7 mm, are sometimes required and have been successfully prepared with glasslike carbon material.

High-Voltage Linear Accelerator Component

A glasslike carbon plate can be employed as a slit for the electron beam of a linear accelerator. This is quite a unique and interesting use. Voltage as high as 6×10^6 v may be charged, and three other important advantages are achieved: low accompanying gamma and X-rays, absence of melting at the center of the energy concentration, and capability of maintaining a vacuum of 10^{-6} torr during the operation due to the absence of outgassing. It is said that the life of the slit might be as long as that of the apparatus. This may give a lead to an application concerning an apparatus using radioactive substances.

Crucibles for the Preparation of CaF_2, CdS, and ZnS

To prepare large single crystals of CaF_2, cone-type crucibles are employed having a maximum volume of about 10 liters. The operation is carried out at a temperature of 1400 C at 10^{-5} torr, and a rate of sinking of 1 mm per hr is used. The advantage lies not only in stability of the glasslike carbon but also in the fact that the discharging process can be greatly simplified owing to the ease of separation. After-treatments such as remelting the surface of crystal are eliminated.

Another shape of crucible, having a dimension of 30 x 26 x 500 mm, has been introduced as a reaction vessel for the crystallization of CdS and ZnS. As is well known, the process is, in general, carried out at about 1500 C under a pressure such as 50 atm. The main advantages are said to be the lack of contamination and the long life of the vessel.

Protective Tubes for Thermometers

Because of the present cost of glasslike carbon, such a use is limited, but it is justified under certain violent conditions.

Future Possibilities for Application

Application to Analytical Chemistry

In Germany, a possibility of applying glasslike carbon as an electrode for spectrochemical analysis, by Peter(83) of Jena-Glass, using an arc method, and also by Dümecke and Wiegmann(84) using a spark method, was reported for the first time in both cases. Morita and Sunahara(85) developed a systematic and quantitative study of this application. Owing to self-purifying effect the prespark and also the ability of repeated use for a few hundred operations, a unique apparatus for a continuous spectrochemical analysis has been made and investigated. Reproducibility, exactness, and sensitivity are maintained by stabilizing the spark between the flat electrode and rotating disk, employing the Compact Atomcounter made by Jarrell-Ash Company. The arc is also quite stable because of the compact and homogeneous surface, the low thermal conductivity, and the simultaneous vaporizing out of the formed oxide gases from the surface. However, the impurities in this material, being irremovable, set a limitation to the arc analysis.

A well-defined reduction wave obtained by Zittel and Miller(86) using a glasslike carbon electrode in voltametry is now well known. Yoshimori et al.(87) obtained excellent results in coulometry by anodic stripping of gold using a glasslike carbon electrode. Sunahara and Ishizuka(88) reported the reduction behavior of dissolved oxygen on glasslike carbon electrode, for which a membranous glasslike carbon was constructed.

Brezina(89) suggested glasslike carbon as a solid electrode for polarography and described the features and defects of this electrode. Schwabe also clarified the behavior of a glasslike carbon electrode in a bromine-bromide redox system in comparison with platinum electrode, again for the anodic oxidation of rhenium and technetium oxides.(90, 91)

It was found that this type of electrode could give good quantitative determination for substances having a potential of over +0.2 v, such as manganese, silver, etc., which cannot be determined by mercury electrode.(92) Recently, Sunahara et al.(93) found that a glasslike carbon electrode for anodic stripping voltammetry gave an excellent sensitivity such as 1 ppb of lead within the error of ±0.5 percent for an electrode having a 0.07-cm^2 surface area. The surface area determines precision and can be enlarged up to 0.33 cm^2 to increase precision. In addition, there have been quite a few similar examples concerning the electrodes for various chemical analyses, such as for electrolytic separation in ultramicroanalysis of silver in high-purity lead and of copper in high-purity zinc(94), for electrolytic chromatography(95, 96), for multistage electrolysis(97), and for chronopotentiometry(98). Morita(99) has found a possibility for using glasslike carbon to make the auxiliary electrode for laser-microprobe analysis. The reasons why a glasslike carbon electrode can be used in such a way are not yet known except for advantages such as surface stability, homogeneity, impermeability, etc. The catalog made by Le Carbone Lorraine also reported the possibility of applying Carbone Vitreux to determining lead content quantitatively and also to spectrochemical analysis.

Sunahara et al.(100) found an unexpected ability to support gas chromatography without any coating material, where glasslike carbon powder showed possibilities in the separation of various kinds of homologs such as water-ethyl alcohol, alcohols, acetone-methyl ethyl ketone and lower hydrocarbons, etc. Quite accidentally Fujinaga et al.(101) also found similar results with the aid of coating materials such as DOP or PEG-600.

Applications in the Electrical and Electronics Industries

It is reported in the manufacturer's catalog that Vitreous Carbon can be applied as the brush for carbon track potentiometers. Its main characteristics are reported to be low electrical resistance, minimum noise, smooth surface, and resistance to erosion. It is also suggested for use as lightning protectors for telephone circuits, for microphone electrodes and relay contacts, and as an electrode to produce metal films by electroplating. With regard to Glassy Carbon, there are quite similar possibilities in addition to those mentioned above. Recently, Kodama and Shigi(102) have found the following relationship between the electrical resistivity of Glassy Carbon, R, and determining temperature, T, within the range of 0.3 to 10 K, having the error of less than 6/1000 K:

$$\log R + K(\log R)^2 = A + \frac{B}{T} \quad .$$

This fact suggests the possibility of application as a thermometer for very low temperatures. The main advantages are said to be the possibility of obtaining a considerable range of resistivity by selecting the final carbonizing temperature and the ability to make thinner plates, owing to the greater strength than normal carbon. It is of much interest that the addition of powder made of a glasslike carbon to electric brushes gave a remarkable improvement for their practical use.(103)

Application to Metallurgy

Glasslike carbon is not wetted by molten aluminum so it is said to be ideal material for dip pipes for the dehydrogenation of molten ingots with chlorine gas. Similar uses can be considered in other metal-processing operations. In one application involving a big crucible and a pipe prepared from glasslike carbon which functioned as the two electrodes for a molten-salt electrolysis, it was found that glasslike carbon material gave less than 20 ppm of carbon contamination. Graphite gave over 4000 ppm of carbon content in the product, tantalum. Concerning the preparation of boron, Akashi and Egami(104) also referred to advantages of glasslike carbon electrodes for the processing. Owing to its possession of a coefficient of thermal expansion that is almost the same as that of graphite, but its poorer resistance to mechanical shock and current availability in only a limited range of wall thicknesses, glasslike carbon is sometimes used as a liner of graphite vessels.

Applications in the Mechanical Field

A waterproof seal made of Carbone Vitreux has been introduced. As to Vitreous Carbon, it is said that many mechanical applications take advantage of its resistance to erosion. Mandrels and other equipment for glass working, process jigs for glass-metal seals, and roller and hydrodynamic gas bearings are under test. Similar prospects for other glasslike carbons can be seen, particularly for electronic use. The poor resistance to mechanical shock limits dynamic uses. However, this disadvantage can be diminished by suitable design, and the successful application of glasslike carbon in a shaft for agitating etching solutions is one good example. This use is spreading in Japan.

CONCLUSIONS

Since the first glasslike carbons were issued as an industrial product, about 4 years have passed. In this report an attempt has been made to review the information on the preparation, properties, formation mechanism and structure, and applications which has appeared during this early stage of development. Developments should accelerate because this material has recently come to the attention of various specialists and also because the knowledge as described here has been so quickly obtained. It is thought that one of the most interesting and important problems will be the further pursuit of the formation mechanism of such an impermeable phase of carbon. Various demands from the application spheres would, of course, accelerate the advance of this branch of carbons.

Concerning the form of filament, any improvement of modulus is probably not to be expected, but the isotropy could be evaluated as a unique property for the composite use. This research is continuing and a considerable improvement of strength can be expected. Progress of research on the formation mechanism may be expected also.

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13. ABSTRACT

A relatively new group of carbons having several characteristics resembling glass is of sufficient interest in connection with technological demands for improved materials to prompt this report. The generic term "glasslike" is appropriate for these carbons because they exhibit a glassy surface appearance, conchoidal fracture, internal-friction characteristics resembling glass more closely than normal graphite, and gas impermeability comparable to glass. The structure of glasslike carbons is not well understood; it resists change by graphitization at temperatures up to about 3000 C.

This report reviews the preparation, formation mechanisms, structure, properties, and applications of glasslike carbons.

The unique combination of properties and resulting potential applications has stimulated manufacture of glasslike carbons by several companies. Available property data on the various products are included in the report.

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