A LINEAGE OF CARBONS

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ABSTRACT

A lineage of carbons is described, relating with over 40 years history on relevant R & D work of the author, through which a resonance of social needs with corresponding technological blind points has been observed as the common term. Seven sorts of carbons and their relatives are selected and their points are briefly elucidated from this view-point.

1. High Density Graphite

In the middle of 1950's, the high density graphite was reqiured for the main moderator material of nuclear reactor. Actually, the procedure to densify the graphite body was a repeated impregnation of pitch followed by carbonization and final graphitization.

From the standpoint of view that the densification can be derived from the polycondensation of binder-pitch by dehyrogenation, a variety of oxidizing agents was investigated, where several organic nitro-compounds were found to be very effective for the purpose. Figure 1, 2 and 3 are typical results of such an organo-chemical approach[1] which can be regarded as a blind point of investigation on carbons as an typical inorganic material.

The bulk density was finally improved as high as over 1.9, comparing with 1.5 - 1.6 in the case of no addition of dinitronaphthalene, a representatiev nitro-compound, prepared by parallelled procedures upto graphitization. The flexural strength was, for example, also ramarkably improved as high as over 2.5 times. The porosity was reduced to 8% as the minimum from 30 - 35% of regular graphite. The element of contribution

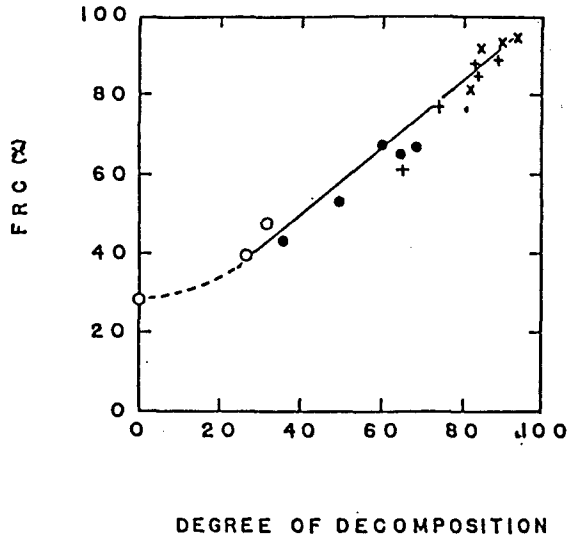

Fig.1. A linear relationship between the free-carbon content and the degree of decomposition of the nitro-radical.

(Fig.1 shows the fact that the increase in free carbon content in pitch was closely related with the decomposition of nitro-compound added to the pitch.)

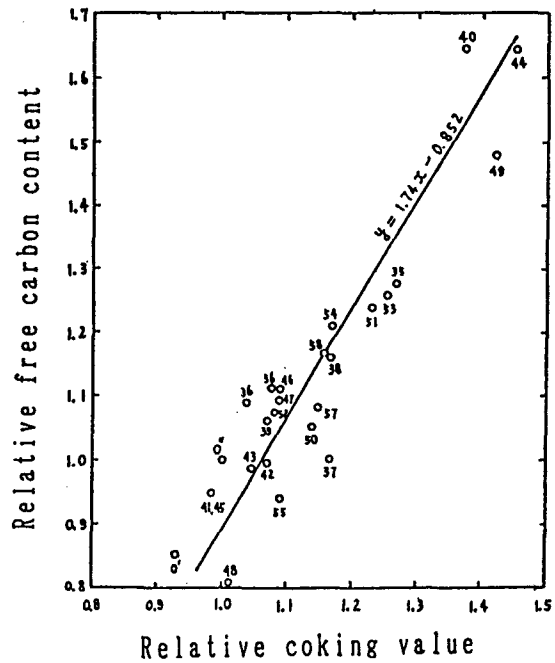

Fig.2 Relative free carbon content as a function of relative coking value of pitch

(Fig. 2 illustrates a linear relationship between the relative free carbon in pitch and the relative coking value, based upon the pitch itself without additives. Number· means the sort of additives, a variety of oxidizing reagents.)

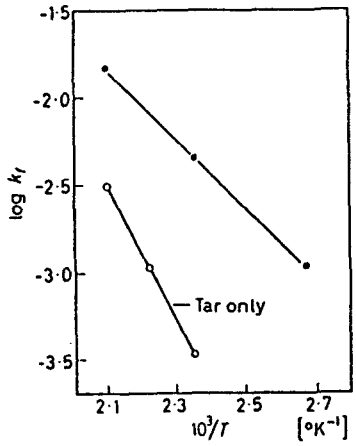

Fig. 3

. Relation between log k_f *and* $1/T$, *for calculation of each activation energy*

Note: ΔE (tar only) ≈ 18 kcal/mol (150° to 200°C)

ΔE_T (tar with DN) ≈ 9 kcal/mol (100° to 200°C)

Thus, the activation energy is halved by the addition of the nitro-compound.

(in Fig 3, k_f means the velocity of reaction between DN, dinitronaphthalene, and a coal-tar.)

to the densification was found as, not only the increase of carbonized residue owing to the dehydrogenating behavior of the nitro-compound, but also the big increase of shrinkage during graphitization due to the oxidizing effect of the nitro-compound, giving criss-cross linkage prior to cabonization, followed by graphitization.

This result suggested that there remained so high potential of such an organo-chemical approach to the carbon field. As a matter of fact, this R & D work became the original point of following researches on new artifacts of carbon, such as glassy and fibrous carbons as well as their composite, a sort of C/C.

2. Glass-like Carbon[2)]

It was well known that the carbonized residue of thermosetting resins, such as phenolic and furan, so-called resin-char, is grain- or particulate-shape due to the catastrophic crack formation during the carbonization.

In correspondence with the severe need of higher operating temperature of HTGCR(High Temperature Gas Cooled Reactor) to economize the nuclear energy, the resin char having glass-like appearance was noted, since any fission product had to be protected at high temperature such as 1000°C. Then, a consideration about the possibility that any crack could have

not appeared by controling the preraring condition, was born. This might have been a blind point on the common sense of resin-char at that time, although it turned to one of the common sense in the present carbon field. At any rate, this research was an extended one of the previous work above mentioned, derived from the similar need in the nuclear field. In fact, this was originated as one of the model experiments to clarify the mechanism of the behavior of nitro-compounds to pitch relating with the preparation of high density graphite.

It has taken over 20 years long for such a novel material to find out a stabilized market, because the initial purpose for nuclear use could not be practiced due to its inadequate property against neutron irradiation.

3. Carbon Fibers

There have been found out, not a few sorts of carbon fibers mainly consisting of HP(high performance) and GP(general purpose), as well known. The author refers here to only two kinds with which he has been engaged.

3.1 Glassy Carbon Fiber

The precursor of glass-like carbons is several kinds of thermosetting resin, as above described. It is also known that any thermosetting resin cannot be spun to obtain the filamental form so far. However, an application of thermoplastic form of phenolic resin known as novolac led to the successful spinning, which turned to the regular thermosetting one just after the spinning, so that the next procedure carbonization could be carried out with ease. Such a two-step procedure might have been a blind point of thermosetting resin. Relevant report [3] describes that this procedure is the first successful spinning of thermosetting resin. At the starting point, a fundamental research on spinnability in comparison with that of well-known artificial fibers was carried out, as illustrated in Figure 4 for example.

On the other hand, the reason why such a type of carbon fiber was required, lay in the fact that there was then scarce carbon fiber having higher mechanical properties being enough to response the need in aeronautical field. Accordingly, this research work was commenced with this material as a Contract Research with US Air Forces[4] in 1967. Only after half a year, it was found out that the amorphous structure of this sort of carbon could not provide any high modulus in essence, in contrast to its high strength as had been anticipated.

It is of interest that this fiber has, during these several years, played a big role for a functional purpose, such as an indispensable material, as a high grade active carbon for the condensor having an electrical double layers in batteryless watches due to the amorphous structure, being quite different from engineering ceramic field like composite materials.

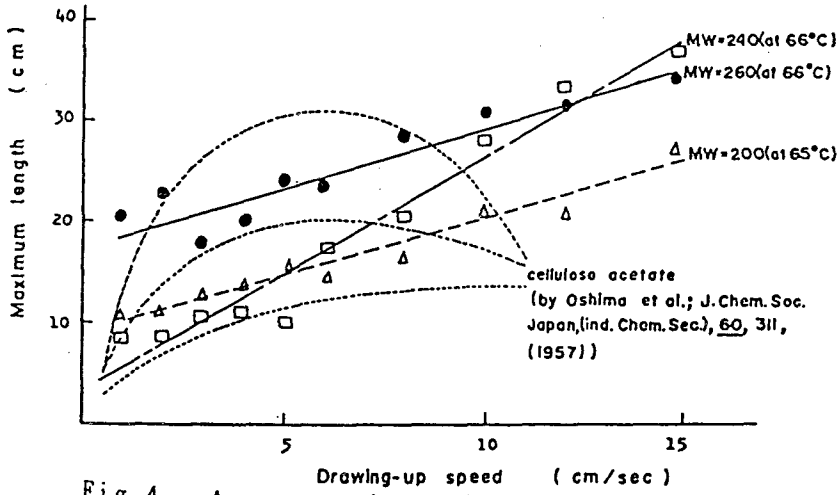

Fig. 4. A representative result of spinnability test.

3.2 High Modulus Carbon Fiber derived from PAN

The Contract Research continued by changing the precursor from thermosetting resins to PAN(polyacrylonitrile), so that another extreme, well-orientated structure, having a capability to provide higher modulus, could be obtained after carbonization.

It was made clear afterwards that a similar research was preceded by a British (RAE) group, which was, however, not known at that time-point, since no concrete information about their activity was brought in. For as long as 6 years before this research work, PAN-precursor provided considerably low mechanical properties in Japan which retarded relating development. The requirement of US Air Forces for the high performance fibers was a fresh stimulus, because there was scarce need like this in japanese industries, not including aeronautical one.

However, immediately after the publication of the result of this research, as well as the fibers themselves, a keen interest was concentrated from various industrial fields in Japan. Such a change in situation of the market made the author's group produce a very long length fiber upto 4000m in only half a year. It was then confirmed that this length was sevral times longer than the foreign ones in 1971[5], which may suggest that the quality of PAN , the domestic precursor, was superior, as well as the technological level to prepare such endless fibers at high temperatures. It is noted with interest that the japanese market of high performance carbon fibers was quite different from those in USA and Europe mainly consisting of space and aeronautical fields.

Figures 5, 6 are relating illustrations for reference.

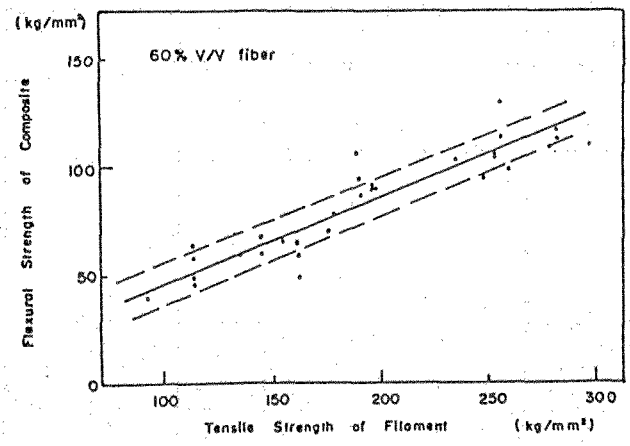

Fig. 5. Relationship between tensile strength of filament and flexural strength of composite.

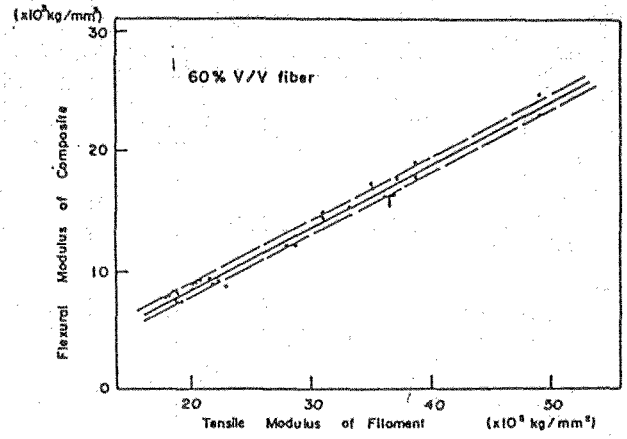

Fig. 6. Relationship between tensile modulus of filament and flexural modulus of composite.

4. C/C Composites

The first incentive to prepare this sort of composite was to improve the brittleness of glassy carbon for tribological uses in the automobile industry. It was unexpected fact that the strength of the composite was found to be doubled value after graphitization, whereas the strength of carbons decreases, in general, to about a half after graphitization, including the cases of glassy and fibrous carbons. It is certainly known that the co-existing graphite with glassy carbon makes the latter graphitizable, but such a remarkable improvement of strength had never been noticed and expected, which can be, therefore, a blind point by considering about the interaction between them at some higher processing temperature. Such a behavior was observed only in the case of glassy carbon matrix, not in that of graphitizable matrices with high performance carbon fibers.

Figure 7 [6] is a representative picture of the graphitized glassy carbon matrix located in a C/C composite in comparison with the pictures of the composite prior to the graphitization, showing a fibrous shape having a completely different texture from isotropic, glass-like one. It must have played an important role to make up such a marked improvement of strength. The interaction was found to have occurred at 2600°C [7].

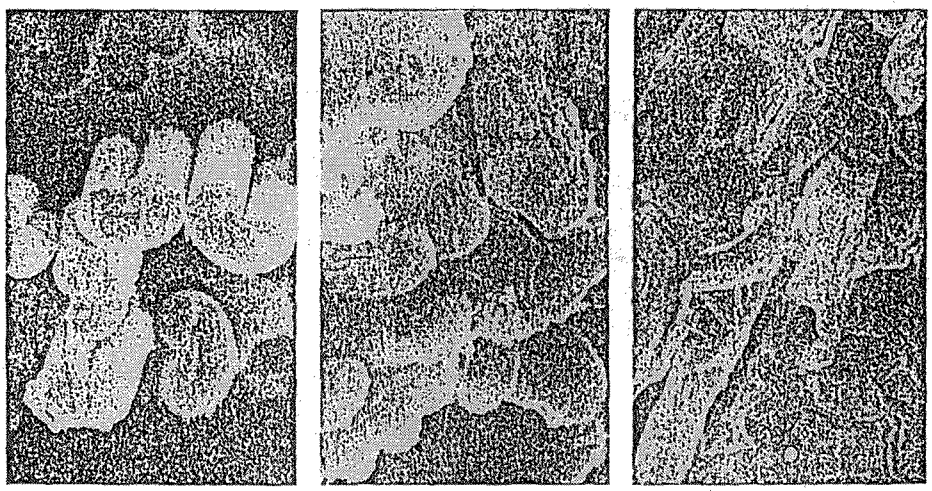

Fig. 7. Scanning electron micrographs of carbon fibre-glassy carbon composites (volume fraction of the carbon fibre is 30% at the forming stage)—from left to right: before carbonization (after hardening); after carbonization; after graphitization.

The improved flexural strength, having attained upto as high as nearly 500 MPa, is comparable with that of metals which had never been expected so far. Accordingly, the C/C composite thus obtained, can be regarded to be situated in the intermediate among three main materials——metals, plastics and ceramics. In fact, this composite is free from any week points of these three materials, except the poor resistivity vs. oxidative atmosphere.

5. Graphite Electrode for UHP(Ultra-High Power)-Use

A revolutional change in the electric steel making process by employing UHP in 1970-75 in order to economize the process, did require a completely new type of big graphite electrode having a superior resistivity against violent thermalshock, as well as a high electric and thermal conductivity. For this purpose, the traditional concept on the properties and textural structure was obliged to be improved.

In consideration about every procedure to prepare such a thermally stabilized electrode, not a few blind points had to be discovered against traditionally settled common sense. Owing to commercial secret, the technological details cannot be disclosed here, but surely a remarkable change in the way of

thinking about the preparation of this sort of graphite electrode took place, resulting in a development of such an old product.

6. Silicon Carbide Whiskers(SiC_w)

The carbide formation in applying high performance carbon fibers to Al, required a variety of research on the coating procedure of the fibers, which continued as long as over 20 years. In an industrial sense, it can be concluded that this kind of approach brought no satsfactory result yet.

From this view-point, SiC_w was reconsidered, not only because of its innertness to Al during processing but also because of easier handling of Al due to its very short length than the case of long length carbon fibers.

According to the intensive need of Al-matrix composite, the procedure to prepare SiC itself was reexamined with much care to get a general concept to propare SiC_w coming back to the original point. Already in the beginning stage, short and thin needle-like SiC was detected from one of the resulting product of very traditional reaction between silica and carbon. This finding was originated in precise observation of the behavior of SiC product, particularly that of sticky state of the very small amountof residual SiC powder to the internal wall of graphite crucible employed, which was carried out in 1980. It can be regarded also as a blind point, since the reaction condition was well-known, being described in the old text books as a process to prepare SiC powder. Naturally, the efforts were further made to lengthen and thicken the needle to obtain the SiC_w, having the length of several 10 μm and thickness of 0.3 - 2 μm[8].

Since then, the application to a variety of engineering ceramic matrices[9], as well as to Al-matrix composite by employing the industrially produced SiC_w by using this principle, has been carried out.

Concerning the hazardeous problem of whisker size and shape, thickening procedure was considered to be its answer, for which two kinds of approach were made[10]. One of the two, the SiC_w formation under pressure might have been a blind point, because application of pressure to such a high temperature(around at 1600°C)reaction was considered to be in danger. It should be also noted that the thicker SiC_w sometimes give a higher fracture toughness in cases of ceramic matrices.

7. Siliconization of Carbon Fibers

A success in obtaining thicker SiC_w under pressure was found to be owing to much slower formation of SiC. This fact also suggested that the formation under reduced pressure must be accelerated quite contrastly.

Figures 8 and 9 may illustrate that the reaction only under about minus 76cmHg(in gauge) resulted in soft fibers having a gradient structure, SiC to C, across the fiber direction

apparently, differing from the other cases under other higher pressures less than normal pressure[10].

Detailed investigation is being carried on furthermore.

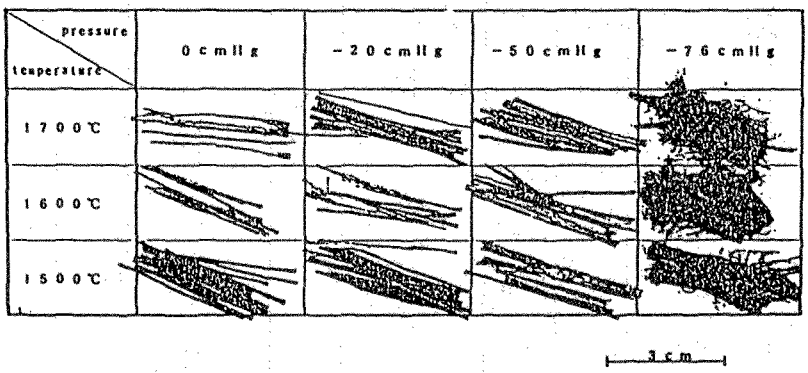

Fig. 8. An overview of carbon fibres(M40) reacted with SiO at various conditions

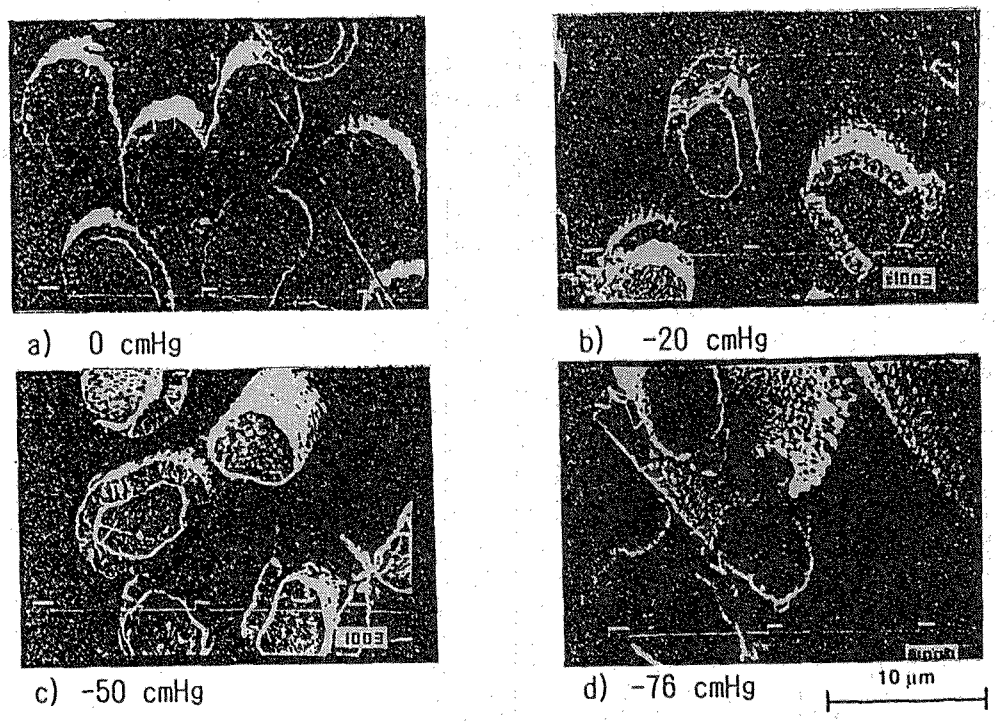

Fig. 9 SEM observations of siliconized samples, heat-treated at 1600°C for 1 hour.

carbon origin : carbon fiber (M40)
silicon origin : SiO

SUMMARY

Table 1 summarizes the essence of the short history. Reconsidering about the history, the author abstracted the motive force making these works in practice, as shown in Figure 10.

Fig. 10. MOTIVE FORCE OF R & D WORK

- RESONATION OF TECHNOLOGICAL BLIND-POINT WITH CORRESPONDING SOCIAL NEED
- A WAY OF THINKING BEING NOT FAITHFUL TO TEXT-BOOKS —NOT BE AN HONOR STUDENT
- A SENSITIVITY AS AN OUTSIDER
- A DOUBT TO READY-MADE POLICY —— A KEEN CRITICISM, RE-CONSIDERATION OF ROUTINE WORKS
- A WILL TO PLAY ANYTHING OF INTEREST FREELY (WITHOUT ANY FIXED CONCEPTION)
- CONSENT BY BASIC RESEARCH TO OBTAIN UNIVERSALITY
- NEGATIVE ELEMENTS DISTURBING R & D WORK——PROVIDING POTENTIAL ENERGY IN OBSCURITY, SUCH AS A LONG SICKNESS, OPPRESSIVE ROUTINE WORK ETC.

Table 1 Summary of this short history

No.	Item of Research (time)	Industrial Need as a Stimulus for the Research	Blind-Point as a Starter of the Research
I	High density graphite over 1.9 (1957-8)	Economizing the nuclear energy	Almost no information of organo-chemical way of thinking in carbon field
II	Glassy carbon (1960-1)	" "	1) " " 2) A fixed idea on the resin-chars
III	High performance carbon fibers A. Glassy carbon fiber (functional) B. PAN-derived high modulus ones (structural) (1963-7)	A. Strengthening of the regular PAN-CF B. Lightening the structual material for aeronautical uses	A. No information on spinning of thermo-setting resins B. High temp. process under stress
IV	C/C composite, glassy carbon & high modulus CF (1970-1)	Basic improvement of the brittleness of glassy carbon	Unexpected interaction between both of the components at graphitizing temp.
V	Big graphite electrode for UHP (ultra-high-power) uses (1972-5)	Economizing the electric steel-making	Deviation from the common sense on the old product
VI	SIC whiskers (1981-90)	Limitation of applicability of CF to Al, i.e., realization of FRM	Lack of keen observation of SIC powder product
VII	SIC long fiber (polycrystalline) (1991-)	Limitation of applicability of SIC whiskers to ceramic matrices	Deviation from the common sense on high temp. process

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