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Motive force for a R & D work in carbon field —— Pursuing blind-points

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According to vicissitudes of industrial need during these over 40 years' technological history, the author has been obliged to find out the blind point, to solve the problem responsing to every industrial need,in 7 cases of carbon field.They played their own role for atomic energy,electronic,space and aeronautical,metal and ceramic industries.At the presnet time-point,the whole picture seems a tiny lineage of carbons.

1.INTRODUCTION

Carbon is regarded as one of the typical inorganic materials, observed from the view-point of inorganic chemistry in former days. Accidentally the author was forced to take part in carbon works inspite of his keen interest in organic compounds, since an advanced carbon product at that time —— in around 1950, was a structural material for chemical equipments,made of graphite impregnated by thermosetting resins.

This product was the source of several rivers of advanced carbons such as glassy carbon and high-performance carbon fibers,as well as C/C composite,developed 10 or more years later. This stream has been continuing so far that carbon can be regarded now, as a derivative of organic polymers. *Most* recently,poly(phenylcarbyne) has been found to be a polymer precursor to diamond-like carbon(1),for example;whereas C60 was investigated starting from crystallographic view-point.

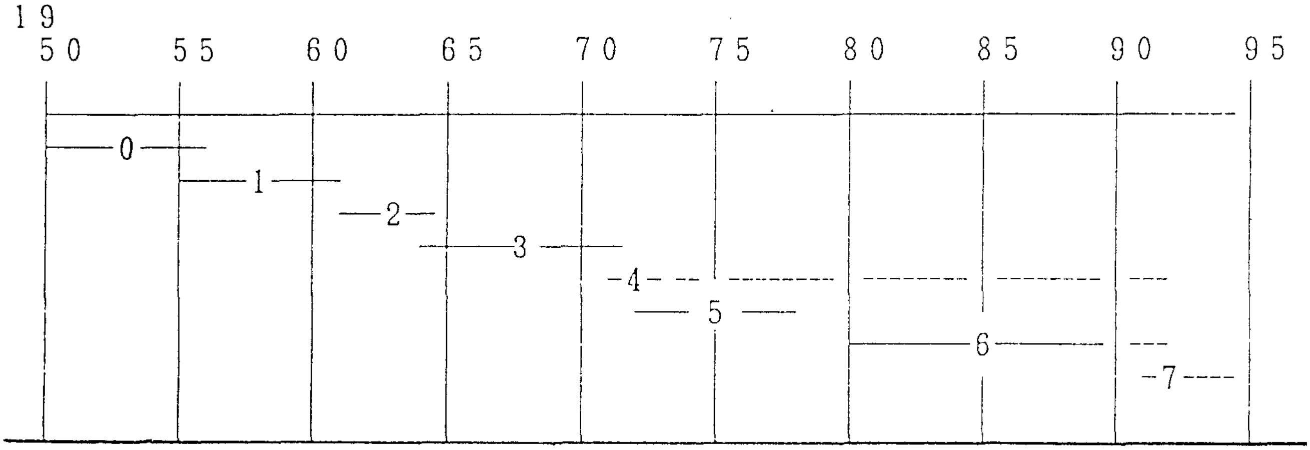
After over 40 years' R & D work in this field, the author has become to be aware of the fact that the common element to have driven this series of work must have been the technological blind-point,being obligingly derived from every social need at every *time-point*.It can be summarized,parallelled with time lapse, as shown in Table 1.

2.DENSIFICATION OF GRAPHITE BODY

To make up a fundamental improvement of the new carbon product for structural uses mentioned above, was to densify the graphite body to be impregnated by the resins. This procedure used to be normally the pitch-impregnation,followed by carbonization. It took actually too much time and trouble to make the author consider about a new economical approach. The most effective agent to raise the coking value of binder-pitch for densification, several nitro-compounds were found out after investigating not a few sorts of organic and inorganic oxidizing compounds.The mechanism of effect of nitro-compounds was elucidated in detail(2). The behavior of dinitronaphthalene,a typical industrial nitro-compound, was found to be a *simple dehydrogenation* to result in condensation of pitch,which consists of as many as over several thousands of hydrocarbons,having brought about a remarkable increase of coking value. The degree of decomposition of nitro-radical,as illustrated in Figure 1 and 2,was closely related with water formation through dehydrogenation between pitch molecules,resulting in increase of benzene-insoluble content (FRC=so-called,free carbon,%). This increase was directly connected with that of coking value. The electric resistivity of FRC thus obtained, can be an index of poly-*condensation* degree which must be closely related with carbonization degree. The result is illustrated in Figure 3 with regard to Figure 2. This way of approaching to make clear the reaction of such a compound with a big mixture like pitch, must have been a blind-point of carbon science. As a result,the bulk density was

Table 1
Main items of R & D work on C & SiC as the advanced materials

No. Item of Research (time)	Industrial Need as a Stimulus for the Research	Blind-Point as a Starter of the Research	Reason why to next item
1. High density graphite over 1.9 (1957-8)	Economizing nuclear energy	Few information of organo-chem. way of thinking in carbon field	Development of HTGCR
2. Glassy carbon, GC (1960-1)	" "	1) " " 2) A fixed idea on resin-chars	Curiosity at filament formation
3. Carbon fibers, CF			
A. GC fiber (funct.)	A. Strengthening of regular PAN-CF	A. No information on spinning of thermoset. resins	Dream on toughened carbon
B. PAN-der'd (1963-7)	B. Lightening of struct. mater. for aeronaut. uses	B. High temp. proc. under stress	
4. C/C compo., GC & high mod. CF (1970-1)	Basic improvement of GC-brittleness	Unexpected interact'n betw. both components at very high temp.	Revolut'l use of electrode
5. Big graphite electrode for UHP uses (1972-5)	Economizing elect. steel-making	Free from the common sense on trad. old product	Desire for whisker-reinforced aluminum
6. SiC whiskers (1981-90)	Limitation of applicability of CF to Al	Lack of keen obs. of prep'd SiC pulver	Limit of K_{IC} in whisker-reinforced ceramics
7. Siliconizing of CF surface (1991-)	Need to raise heat-proof temp. to 400°C	High temp. react'n in vacuo	



ca.20% improved, whereas the strength was doubled, which is summarized as shown in Table 2.

The condensation at the organo-chemical stage before carbonization, influenced graphitizability, detailed analysis of which might have contributed to the investigation of graphitization mechanism.

On the other hand, the oxidizing reaction of the nitro-compound resulted in hardening of binder-pitch, which made the binding force poorer, particularly in the case of extruding process for an economical production. To improve this deffect, a basic concept of high polymer solution was utilized, where a dilute solution of polyvinyl chloride or the other thermoplastic high polymers in binder-pitch was employed so that the visco-elastic properties could be favorably changed for extruding of the coke-aggregates (3).

In addition, this oxidizing process also played a role to the need of high density graphite for nuclear uses.

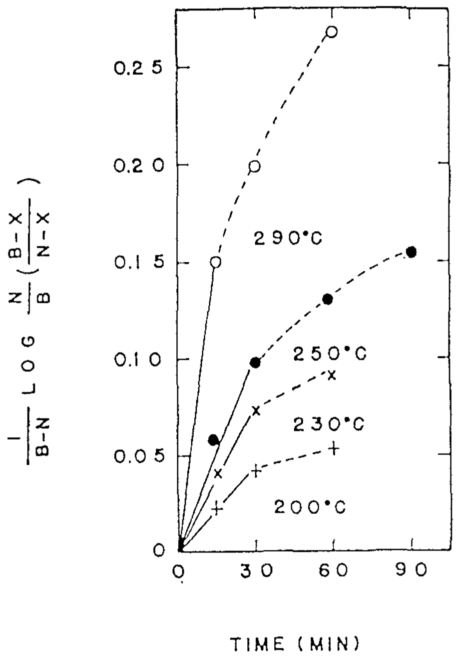


FIG. 1. Decomposition rate of the nitro-radical.

3. GLASSY CARBON (4)

The R & D on HTGCR (High Temp. Gas Cooled Reactor), a national project at that time, needed an impermeable carbon for the work at 1000°C. The fact that carbonization of resins accompanied with inevitable crack formation, was a fixed idea, sometimes bringing forth a blind-point. Moreover, the cracks and voids were regarded as residues of volatile matter during carbonization.

The volatile matter of the precursor of glassy carbon was so high as about a half of the initial weight that glasslike 'body' - no partilcles - without cracks and voids, as the carbonized product, seemed contradictory, from the view-point of how the matter volatilized. This conflict has not yet been elucidated still now.

Figure 4-A shows an optical microscopy of the initial probe comparing with B (normal graphite) and with C (high density graphite), where B and C correspond with graphitized specimens shown in Table 2, * and A, B respectively. The voids observed in Figure 4-A were remarkably disappeared by repeated improvements of preparation process.

Owing to the unique properies such as gas-impermeability, higher strength, modulus, hardness

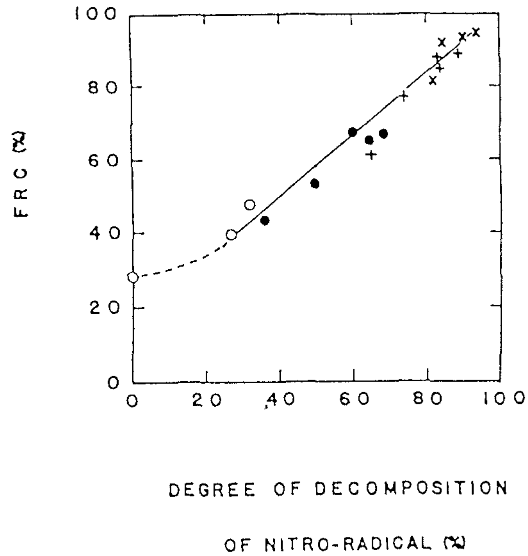


FIG. 2. A linear relationship between the free-carbon content and the degree of decomposition of the nitro-radical.

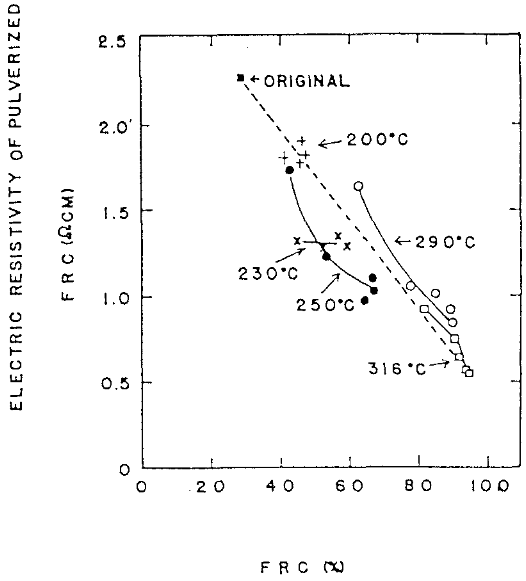


FIG. 3.. Relation between the electric resistivity of the free-carbon produced and the corresponding content of the free-carbon content.

.frictional and chemical stabilities, as well as higher electrical resistivity,have been made use to a variety of industrial fields. Recently it is utilized for electronics in particular.

This uniqueness of properties is due to the solid-state carbonization differing from gas- and liquid-state ones as observed in formation of carbon black and coke respectively. The expression of "hard carbon" is originated in this material, which provides the difference in graphitizability because of its obstructive behavior in crystal-growth of graphite.

4.GLASSY CARBON FIBER (5)

There has been, so far, no literature on spinning of thermosetting resin that can provide glassy carbon,since the resin is insoluble and infusible,being basically different from thermoplastic resins. The blind-point in this case was to employ only one thermoplastic form of phenolic resin, novolak, as an intermediate for

Table 2. An Example of Physical Properties of Densified Carbon and Graphite with the aid of Dinitro-naphthalene

SPECIMENS (*REGULAR)	CARBONIZED A	B	*	GRAPHITIZED A	B	*
ELECTR. RESIST. ($\times 10^{-4}$ ohm-cm)	28.0	28.2	54-55	11.5	12.7	10.8-11.8
FLEXURAL STRENGTH (MPa)	61	64	24-28	41	42	21-25
COMPRESS. STRENGTH (MPa)	—	—	—	82	83	43-51
BULK DENSITY(g/cc)	1.73.	1.71	1.47-1.54	1.91	1.91	1.57-1.62
APPARENT DENSITY(g/cc)	1.817	1.828	—	2.025	2.007	2.171-2.182
POROSITY (%)	4.7	6.4	—	5.6	4.8	26-28
WATER ADSORPTION (%)	3.7	3.7	20-22	4.2	3.8	21-23
CTE($\times 10^{-6}$/°C)	—	—	—	2.2	—	2.5

spinning. Immediately after spinning, it should be turned to an essentially thermosetting resin by a chemical procedure, ie.hardening with acid. Actually the molecular weight of novolak is as low as less than 1000 being unsuitable to the normal spinning. However, its spinnability was found to be similar to that of cellulose acetate by the same apparatus to determine the spinnability, as illustrated in Figure 5.

This approach was initiated by a need to improve the strength of regular grade of PAN-carbon fiber (CF), followed by being supported by US Air Forces for the structural use.

It is of interest to note that this isotropic sort of CF now plays an important role as a functional,not a structural material, because of its unique structure providing an excellent surface activity for an electronic use and so forth.

5.HIGH MODULUS CF DERIVED FROM PAN (6)

The contract research with USAF mentioned above, made us improve the low modulus of glassy CF,although of its strength was found to be high enough. Then the precursor was changed to the others to obtain a high anisotropy for the improvement from another extreme,the perfect isotropic properties of glassy CF,because the

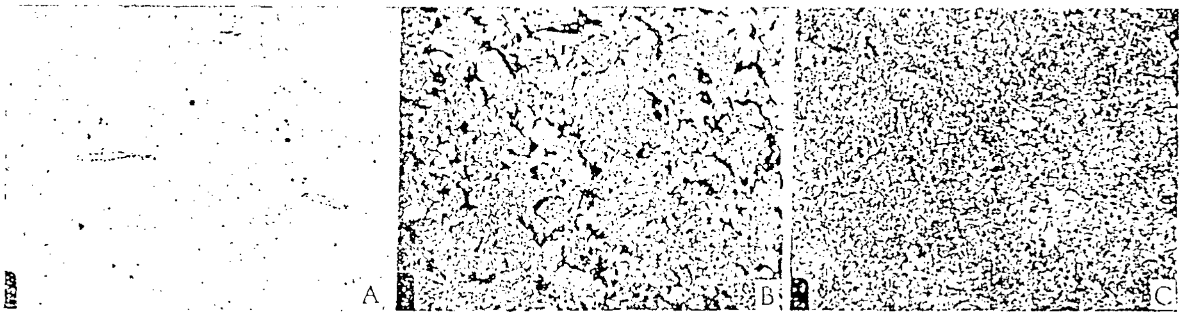


Fig. 4 *A*, glassy carbon; *B*, normal graphite; *C*, high-density graphite. (All × 50)

high orientation of graphite crystalline must provide the high modulus. After all, PAN precursor was found out to satisfy the target value of modulus. It was revealed later that RAE-group conducted by Watt in England carried out similar research work, preceding us about 2 years. The initial stage of those researches was kept secret. However, better properties of precursor PAN itself prepared here in Japan than that in Europe and USA for this purpose, accelerated the industrialization of high performance CF. The need of high petrformance CF in aeronautical field, actually did not exist in Japan, and therefore the marketing work was not so easy here. At any rate, it should be noted, not only that the fundamental research could be carried out here only due to the financial support of USAF, but also that the support was originated in finding of glassy carbon material. Moreover, the basic idea to obtain the high modulus and strength from viscose rayon by heat-treatment under tensile stress, was preceded and realized by an amercian research group, although PAN-derived CF was invented by a japanese researcher, as is well known. In such a way, the competition of initial stage of R & D of CF was so violent.

As one of the fundamental researches by the author's group, an approach to characterize the wettability of CF to its matrix, epoxy resin, was investigated. It is no static determination like contact angle, but a dynamic method to determine the wetting velocity by a simple weight uptake. This method might be one of the blind-points to investigate the high performance CF. A closed relationship between the velocity constant and ILSS (interlaminar shear strength) of correspond-ing CFRP at 4 levels of wetting temperature, should be noticed, which is as illustrated in Figure 6.

8. C/C COMPOSITE

The brittleness of glassy carbon for a mechanical use hindered the application to tribological field. Such a need made us prepare a glassy carbon composite having high fracture toughness. The blind-point was an unexpected interaction (7) between reinforcer (high-modulus CF) and matrix (glassy carbon, GC) occurred at as high as 2600°C. The mechanical strength of the former and that of the latter, reduced to about a half, when CF and GC were heat-treated independently at over 2600°C, being coincident with the common sense in carbon technology. The resulting strength was found to be doubled, which means about 4 times as high as normally anticipated. It is summarized in Table 3, on all 4 sorts of composite specimen having various volume-fractions of CF. In sharp contrast to the present popularity of C/C composite itself, this interaction is still not very widely known yet inspite of over 20 years' lapse after the publication. The stress formed by a large amount of shrinkage of matrix GC during carbonization, is considered to be one of the reasons why such an interaction occurred, in the sense of stress graphitization. Reconsidering the fact (8) that the graphitized body starting from a mixture of artificial graphite powder and GC showed no content of GC, the interaction between the both had been known by the author already about 8 years before this finding, although the shape of

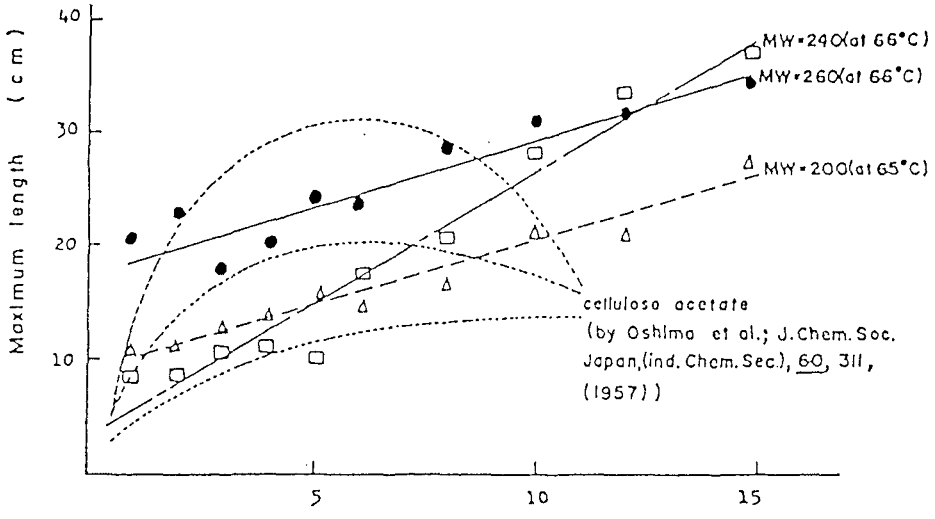


Fig. 5. A representative result of spinnability test.

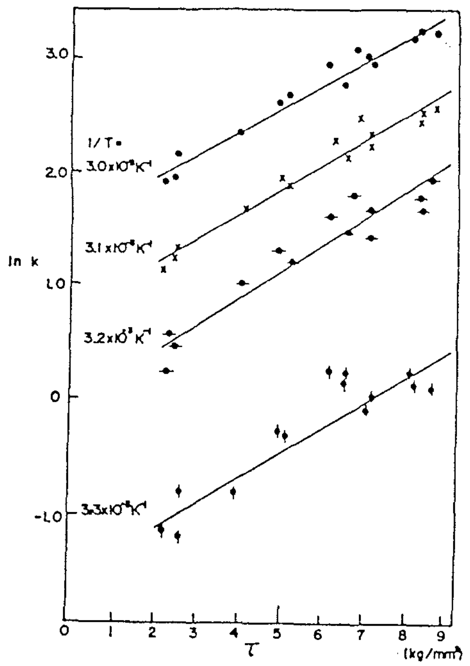


Fig. 6 Relationship between wetting rate and interlaminar shear strength.

graphite was not fibrous but powdery and the effect to increase the strength was not recognized. SEM of graphitized composite comparing with the carbonized upto 1000° C, as well as with the heat-set (upto 180° C) ones suggested that the interacted GC changed to the fibrous structure having a high strength in this case.

The improved flexural strength thus obtained, attained upto as high as nearly 500 MPa, being comparable with that of metals. It had never been expected to any sort of carbons. Thereafter, this type of carbon composite can be situated in the intermediate among three main materials —— metals, plastics and ceramics.

Table 3. Flexural strength and modulus of carbon materials before and after graphitization, together with benzene density for each graphitized specimen.

Material	Carbon fibre (vol.%)	Flexural strength ($kg\ mm^{-2}$)[b]		Flexural modulus ($10^3\ kg\ mm^{-2}$)[b]		Benzene density ($g\ cm^{-3}$)
		before	after	before	after	
Composite	30	$21{\cdot}_1$	$40{\cdot}_0$	$8{\cdot}9_5$	$23{\cdot}_6$	$2{\cdot}14_5$
(Carbon fibres	40	$19{\cdot}_4$	$36{\cdot}_5$	$9{\cdot}4_3$	$22{\cdot}_1$	$2{\cdot}12_0$
+ glassy	50	$22{\cdot}_8$	$39{\cdot}_1$	$10{\cdot}_1$	$23{\cdot}_7$	$2{\cdot}10_5$
carbon)	60	$21{\cdot}_6$	$47{\cdot}_5$	$10{\cdot}_8$	$21{\cdot}_4$	$2{\cdot}09_7$
Carbon fibres	-	202^c	103^c	$20{\cdot}_2{}^c$	$35{\cdot}_0{}^c$	$1{\cdot}94_4$
Glassy carbon	-	$11{\cdot}_5$	$5{\cdot}_9$	2·8	1·8	$1{\cdot}55_7$

[a] Calculated just after the forming stage. [b] Size of specimen for the determination was 2 mm x 4 mm x 120 mm, where the span/depth ratio was 25 and the number of specimens in each case was 4. [c] Tensile strength and modulus.

7.GRAPHITE ELECTRODE FOR UHP-STEEL MAKING

In 1970 - 75, a revolutional process on steel-making by employing ultra-high-power (UHP) was materialized and played a big role to reduce the cost of steel to a remarkable extent. For the purpose,every part of the electric furnace such as graphite electrode as well as brick etc. had to be basically improved from the view-point of material.

The author was,then, forced to change the fixed concept of such a traditional graphite electrode. In particular, the thermal shock resistance had to be fundamentally investigated and improved,for which the way of thinking about composite materials was needed. The history of this sort of product was too long to detect the points of importance solving the problem. In this meaning there were not a few blind-points for this particular use. By this opportunity, the amount of its production in Japan became biggest. It took over 5 years for the author to overcome the relevant difficulties.

8.SILICON CARBIDE WHISKERS

At the beginning stage of R & D work on CFRP, in 1967,CFRAl was another target, which was,however,as not so rapidly developed as the former owing to the reaction of CF with Al during the fabricating process. On the other hand, short fiber as a reinforcer for Al was required for easier handling. Silicon carbide whiskers, SiC(w) were reconsidered under such a situation for industrial production.CVD was a typical process to provide SiC(w) at that time which was too expensive. The author found out a blind-point in the most popular and inexpensive route to get SiC powder. The powdery product was found to be a very short needle by a precise observation. The intensive need for SiC(w) made the author reexamine the basic reaction of carbon and silica to obtain SiC powder (9).

In order to solve the environmental problem, efforts to prepare thicker whiskers were made,by controling the reaction pressure as well as by improving the catalysor for VLS process. In-situ formation of SiC(w) in Si_3N_4 (10) has been being investigated so that the handling procedures of this mixture can be saved and a more homogeneous mixture can be obtained to improve the properties of the composite.

9.SLICON CARBIDE COATING ON CF

To raise the heat-proof temperature of CF in air, many approaches of SiC coating have been carried out. The reaction of SiO with the surface part of CF is one of those, where the processing under a reduced pressure such as -76cm at a high reaction temperature (1400°C), may be a blind-point. Figure 7 shows the difference in the reaction velocity from the case under normal pressure.

Figure 8 illustrates a typical TG result,where the point of 2%-weight decrease shows a shift of about 100°C to the higher temperature. It may suggest an improvement of the resistivity vs.air oxidation. All the other TG data showed a similar effect of improvement.

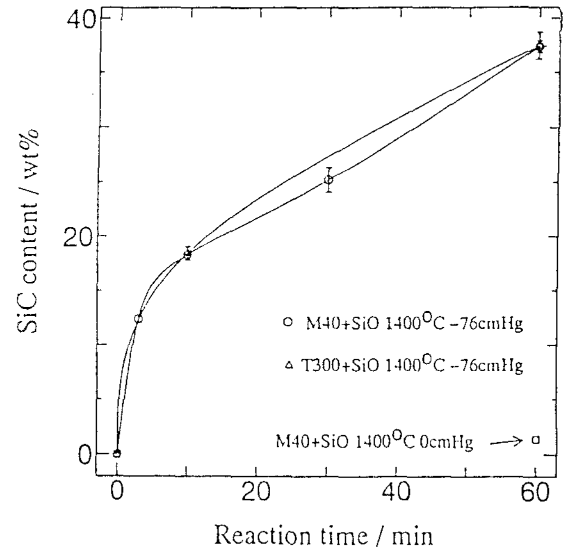


Fig.7. Formation of SiC on the surface of CF

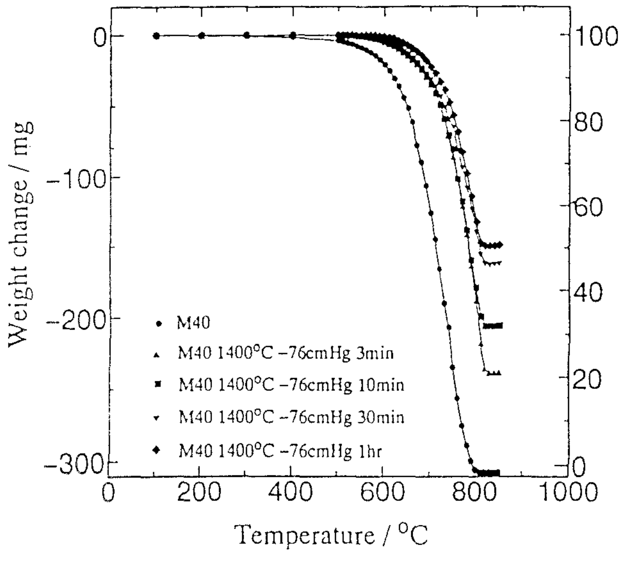


Fig.8. TG curves of SiC-coated CF,comparing with the uncoated

MOTIVE FORCE OF R & D WORK

- RESONATION OF TECHNOLOGICAL BLINDPOINT 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

Fig.9. Motive force of R & D work

10.CONCLUSION

A fact that an interest in organic chemistry and high polymers in carbon field was a motive force to develop several advanced carbons,is expounded, according to the lapse related with the industrial needs. It began with a very practical work to improve a routine carbon product, being apart from fundamental researches.

It is of interest to see that every success in finding and putting into practice in factory was linked together with more general use.High density graphite as an improved carbon product was applied to nuclear uses,glassy carbon to eletronics,and glassy carbon fiber to high performance carbon fibers and their composites, as well as to C/C composites.Troubles at fabricating CFRAl needed inexpensive SiC whiskers by utilizing carbon technology.

Figure 9 summarizes the motive force of R & D work thus performed, based upon the author's consideration during and after the works.

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