FOREWORD

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This report covers work conducted from January, 1960 to January, 1961.

ABSTRACT

In this investigation silicon carbide whiskers were grown under various experimental conditions. The strength and modulus of elasticity of several whiskers were determined at room temperature. Methods of heating the whiskers for high temperature measurements were investigated. The specific gravity of the whiskers has been inferred from measurement of the unit cell dimensions by X-ray diffraction patterns.

Silicon carbide whiskers were grown by pyrolysis of methyltrichlorosilane in hydrogen. In some cases dense growths of whiskers from 1.2 to 1.5 centimeters in length and from 2 to 5 microns in diameter were observed. The longest whisker obtained, thus far, was 5 centimeters in length.

The tensile strength of these whiskers ranges from 100,400 to 1,650,000 psi. The elastic strain at failure varied from 0.41 to 1.10 per cent and the observed values of elastic modulus varied from 12,700,000 to 123,300,000 psi. These results indicate that silicon carbide whiskers can be strong, high modulus of elasticity materials. Much research remains to be done to improve the methods of measurement, and to define the conditions of measurement and the types of whiskers that will give the best performance as structural materials.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

H. S. Schwartz

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INTRODUCTION

In spite of considerable research effort, we are still not able to exploit the potential strength of materials. The strengths predicted from cohesive forces between atoms are roughly one to two orders of magnitude greater than the strengths observed in ordinary commercial materials. Some progress has been made toward explaining these differences in strength. A partial understanding of the role of dislocations has been helpful. It is now possible to conceive ways in which the potential strength of materials can be used in practical applications. One of the most promising approaches is through the use of materials in whisker form.

Whiskers have been studied intensively in recent years. Herring and Galt (1)* found that the strength of tin whiskers was close to the calculated strength. They measured elastic strains of approximately 3% which corresponds to a stress equivalent of approximately 100 Kg/mm^2 (140,000 psi) and greatly exceeds the tensile strength of 2.8 Kg/mm^2 (4000 psi) for polycrystalline bulk tin. Subsequent studies on the mechanical properties of both metallic and non-metallic whiskers by Brenner (2,3), Eisner (4), and Riebling and Webb (5), as well as others, have yielded encouraging results.

The study of whiskers has also provided valuable information about crystal growth mechanisms. Frank (6), treating crystals growing from vapors and liquids, describes the growth mechanism as one generated and propagated by screw dislocations. The screw dislocation theory was used by Brenner and Sears (7) and Sears (8) to describe the growth of whiskers. Webb and Forgeng (9) attributed the high strength of whiskers to the absence of edge dislocations. They concluded that introduction of a few dislocations into ductile metal whiskers decreased the strengths manyfold but in the light of the somewhat contradictory observations by Pearson, Read and Feldmann (10) on silicon, make a distinction between the effects of dislocations in ductile and brittle crystals. The proceedings of a recent conference on growth and perfection of crystals (11) are a convenient source of information on the state of whisker research.

As a result of requirements for good, high temperature semi-conductors, much effort has been devoted to growth of silicon carbide crystals in recent years. The results of this research have been reviewed (12) and cannot be considered to be completely satisfactory. The quality of the crystals must be substantially improved before widespread semi-conductor applications are possible. During the search for ways to grow good silicon carbide crystals, long thin crystals were grown by Merz (13), Hamilton (14), and the group at

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*See references, page 25

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Armour Research Foundation (15). The crystals grown by Merz had large length-to-diameter ratios and were characterized as whiskers. The possibilities for practical application of these filamentary crystals do not seem to have been considered.

The purposes of this program were to investigate techniques for obtaining optimum silicon carbide whiskers and to measure the mechanical properties of the whiskers in order to provide the information necessary to evaluate these materials as possible reinforcements for structural composites. The properties of silicon carbide that may make these whiskers useful as reinforcing material for composites are high strength, high modulus of elasticity, high index of refraction, low specific gravity, stability of decomposition and oxidation products, hardness, and corrosion resistance. The high index of refraction of silicon carbide may be important in scattering thermal radiation in solid composites or residual materials during ablation.

Silicon carbide whiskers that are longer than those previously known were grown by pyrolysis of methyltrichlorosilane in hydrogen. The tensile strength and modulus of elasticity were measured. This experimental work is described and the results are discussed in the following sections.

PROCEDURE

Preparation of Silicon Carbide Whiskers

There are several possible methods for growing silicon carbide crystals. The techniques used in this investigation are based upon those reported by Merz (13). These techniques involve pyrolysis in hydrogen of gaseous compounds containing Si and C. The hot zone temperature, reactants, and proportions of reactants and hydrogen carrier gas were varied in an effort to determine optimum growth conditions.

Judging from the variety of solid products observed in the reaction tube, the reactions which occur depend very much on the local conditions. Therefore, it is not possible to specify a single reaction which adequately describes the processes. In addition, the details of the processes, which occur at each location, are not understood. In the case of experiments in which silicon tetrachloride and toluene are used as reactants, the silicon tetrachloride presumably is partly decomposed and then reacts with carbon from the toluene to form silicon carbide and hydrochloric acid. In the case of experiments in which methyltrichlorosilane is used as the reactant, the gaseous molecules decompose leaving silicon carbide. A simple reaction that can be helpful in understanding the overall process is presented below.

$$CH_3SiCl_3 \longrightarrow SiC + 3HCl$$

The equipment for crystal growth by gaseous reaction consists essentially of a 10.5 kw SiC resistance heated muffle kiln modified to accommodate a 1 1/4" I.D. x 42" long impervious, vacuum grade, mullite tube. Within the mullite tube an 18" long graphite tube, 1" I.D., is positioned so as to extend over the length of a reaction and crystal growth zones. The ends of the mullite tube are sealed with neoprene stoppers each with stainless steel tubing inserts which permit introduction and discharge of the gaseous products. In addition, the inlet stainless steel tubing is constructed with a sealed window which facilitates temperature measurements by optical pyrometry and permits observation of the crystal growing process. Commercial grade hydrogen, supplied to a flowmeter manifold, is allowed to bubble at predetermined rates through the liquid reactants. The liquid reactants are evaporated into the hydrogen carrier, combined in a feed manifold, and introduced into the reaction zone. The process of crystal growth by gaseous reaction and the features employed in this study are illustrated schematically in Figure 1. A photograph of the apparatus is presented in Figure 2.

Diameter Measurement

In determining the mechanical properties of the SiC filamentary crystals having diameters of the order of 2 to 4 microns, it is essential that pertinent measurements be made by sensitive methods. A magnification method is required. A circular whisker cross section was assumed since no evidence to the contrary was found in the many microscopic examinations made in the course of the investigation.

The whisker measurement technique developed in this study involves comparison measurements wherein the magnified diameter of the whisker is compared with a calibrated grid enlarged to the same magnification. Each whisker to be mechanically tested is photographed in a Leitz petrographic microscope at a magnification of 750X and compared with a lined 0.01-mm metallographic grid photographed under the same conditions. To check the accuracy of this method, a number of whiskers of various diameters were mounted on an electron microscope grid, identified, and then photographed at 750X in the petrographic microscope. These crystals were compared with the magnified 0.01-mm metallographic grid and the size determined. The same whiskers were then re-identified and photographed in an electron microscope at 30,000X and compared with a 28,800 lines per inch diffraction grating photographed at the same magnification. The maximum variation in diameter observed, for individual whiskers of a group of 9 specimens so measured, was 0.2 microns and this amount only for whiskers larger than 3 microns in diameter. The slight observed variation, however, may or may not be error depending upon whether delicate focusing of the whiskers or small diameter variations along the length of the whiskers are involved. In any event, the measurement technique appears to offer an acceptable degree of accuracy for whisker size determination.

Mechanical Property Measurement

In the measurement of the mechanical properties of whiskers, the ability to apply and measure small loads and the ability to measure the resulting strain are important. A review of the literature on whisker testing techniques reveals that a number of different procedures have been employed. Brenner (3), testing whiskers in the 5 to 25 micron diameter range, has developed a technique by which a calibrated solenoid applies the load. Strain in this apparatus may be measured optically or by microformers. This equipment is assigned an accuracy of $\pm$ 10% in both stress and strain. Schlicta (16), testing Cu whiskers 1 to 5 microns in diameter, used a modified version of an analytical balance for applying load and a microformer technique for strain measurement. The microformer is sensitive to several tenths of a micron but no accuracy limits are placed on the apparatus. Webb and Forgeng (9) and Pearson, Read and Feldmann (10) employ bend testing techniques in which micromanipulators apply a bending load and optics are used to measure the resulting deflection. The results of the bend tests are

converted into tensile properties through related formulae in which certain assumptions are made. Admittedly, the conversion of bend test characteristics into tensile properties may invite some uncertainty but results so obtained appear to be in general agreement with direct tensile observation for identical materials. This agreement is demonstrated by the work of Eisner (4) and Pearson, Read and Feldmann (10), each testing silicon whiskers. Eisner, employing the tension test, obtained 2.03% elastic strain prior to rupture while Pearson et al., performing bend tests, observed elastic strains up to 2.6%.

In this investigation it appeared most desirable to measure the tensile properties directly. The technique involves application of an analytical balance adapted for whisker testing. The balance, a chainomatic type with a load calibrated accuracy of 0.1 mg, is enclosed in a glass case to reduce draft disturbances and the leveled case is insulated against external vibrations by mounting on isomode pads. In modifying the balance for tensile testing, an adjustable whisker mount assembly, consisting of a fixed platen and a movable beam pivoted on a knife edge, replace the balance weighing pan. The whisker mount is adjustable in both the horizontal and vertical directions to allow whiskers of varying length to be tested and at the same time to provide alignment latitude for mounted whiskers. By this arrangement the load introduced into the weighing system is transmitted to the whisker directly with very little frictional effect. The load applying chain normally supplied with the balance was replaced with a heavier chain. This heavier chain increased the range of loads that could be applied with the chain to five grams. While this modification decreases the readable weighing accuracy from 0.1 mg to 5.0 mg, it has the advantage of permitting tests to be performed without weight manipulation interruption. The schematic representation in Figure 3 illustrates the modifications which were made in adapting the analytical balance for whisker testing. The procedure for preparing whiskers to be tested consists of the following sequence of events: (a) cement one end of the whisker to the movable loading lever of the whisker mount assembly with DuPont Duco household cement, (b) photograph the whisker at 750X to determine its diameter, (c) replace the loading lever in its properly aligned position in the whisker mount assembly, (d) balance the weighing system and (e) cement the remaining loose whisker end to the fixed platen of the whisker mount assembly.

The known inaccuracy associated with the tensile strength measurement is that occurring because of uncertainty in the measurement of diameter. This is a maximum of 0.2 microns for a 3-micron diameter whisker, which introduces an error of $\pm$ 13% in the determination of tensile strength. An unknown error may have occurred because of inability to align the specimen perfectly with the direction of the load, although provision was made for

such aligning. Were it imperfect, a bending load would have been introduced and, presumably, this would have decreased the rupture load. Actual tensile strengths are, therefore, considered to be at least as high as the values so determined.

A calibrated filar microscope was used to measure deformation. The microscope, a Gaertner type with a fixed magnification of 50X, has a calibrated accuracy of 0.00001 inch. Deformation readings were made directly on the whisker either by sighting on natural surface imperfections or on reference marks produced by spot spraying when necessary. The material used for spot spraying was "Steelcase" gray lacquer. This deformation measuring technique has the disadvantage that it is exceedingly delicate and the slightest movement, even that produced by hand pressure in manipulating the micrometer, may yield erroneous readings. In addition, the whisker test section is limited to the magnified field of the microscope and generally represents a deformation gauge length between 0.04 and 0.05 inch. Figure 4 illustrates this strain measuring microscope and its relationship to the analytical balance loading apparatus.

Difficulty occurred in aligning the crosshair of the filar microscope exactly on the reference marks used to denote the gauge length. The extent of the difficulty varied with the different whisker specimens. It is judged that this difficulty introduced a maximum uncertainty of approximately 0.00002 inch in the determination of deformation. With a minimum total deformation of 0.0002 inch in the determination of modulus, this may have introduced an error as large as $\pm$ 20%. Combining this with the maximum error in the measurement of diameter, which was 0.2 microns for 3-micron diameter whiskers, one judges the modulus determinations to be accurate to within approximately $\pm$ 33%.

Attempts were made to incorporate a high temperature capability into the test apparatus. Two methods of whisker heating were investigated. One of these involved the passage of current through the whisker while the other involved enveloping the whisker by a heating coil. In the direct resistance heating method, the whisker was mounted on electrical terminals with low resistance silver micropaint and the whisker terminal joints were reinforced with Duco cement (SC13, Micro-Circuits Co.). When current was passed through the whisker an irregular heating pattern, indicated by color discontinuity along the whisker length, resulted. At low values of current flow, microscopic blue-white spots were observed. These spots may have been caused by electroluminescence. Broader bands caused by uneven heating were also observed.

In the indirect heating method the whiskers were threaded through a small electrical heating coil made from 0.005-inch diameter chromel wire and then cemented to the whisker mounts. When current was passed through the coil, color variations in the coil disclosed the presence of a very large temperature gradient which is probably indicative of the temperature profile of the radiantly heated whisker. While both of these heating techniques may have merit for high temperature testing of whiskers, neither was sufficiently refined with regard to temperature control and temperature measurement. Therefore, the tensile properties of SiC whiskers were not measured at high temperatures.

RESULTS AND DISCUSSION

Whisker Growth

Eighteen experiments were performed in which the reactants, reaction temperature, flow rates and reaction times were varied. In the first nine experiments, the reactants used were silicon tetrachloride and toluene. The conditions prevailing in these experiments are summarized in Table I. In the early runs (Runs 1 and 2) in this series the only solid product observed was an unidentified white powder found on the exit side. Accumulation of this powder resulted in clogging of the exit tube. Clogging of the exit tube halted runs 1,2,3,4, and 6. Addition of a stainless steel cooling tube allowed more space for these products. In these early runs, we were unable to duplicate Merz' (13) results in forming silicon carbide whiskers. The lack of solid products was attributed to failure to achieve a reaction with the silicon tetrachloride.

In order to make available more products of reaction with silicon tetrachloride, the proportion of silicon tetrachloride was increased (Runs 3-9). The immediate result of this change was deposition of silicon metal on the mullite tube. Still no silicon carbide was formed. In a further attempt to reduce the silicon tetrachloride, zinc was added as a reactant (Run 9). There was no significant improvement.

Due to lack of success using the silicon tetrachloride and toluene as reactants, a change was made to the use of methyltrichlorosilane when this material became available. Methyltrichlorosilane was selected because, upon decomposition, the products may contain Si-C bonds. In all except one of the subsequent experiments, silicon carbide whiskers were produced. Table II summarizes these nine runs.

In the first of these runs (Run 10 and 11) the principal objective was to determine the correct ratio of hydrogen required to evaporate the methyltrichlorosilane to the excess hydrogen. In Run 10, silicon was formed and too much methyltrichlorosilane was evaporated. Therefore, in Run 11 the volume of hydrogen used to evaporate methyltrichlorosilane was reduced substantially. In this run silicon carbide whiskers were produced in the extreme exit end of the graphite tube.

The following experiments (Runs 12-18) were directed toward determining the optimum conditions for growing silicon carbide whiskers using methyltrichlorosilane as the principal reactant. Since low temperatures are believed to favor whisker formation, one objective of these experiments was to grow

whiskers at the lowest possible temperature. In the next run (Run 12) the furnace controller temperature was reduced to 1425°C. Also, since the whiskers in Run 11 were formed at the extreme exit end of the tube, an additional graphite insert tube was added to provide more sites for whisker growth at this end of the tube. In this experiment whiskers were grown at both ends of the reaction tube. In Run 13, the furnace controller temperature was reduced another 25 degrees to 1400°C. In this run an attempt was made to determine the temperature at the entrance to the hot zone where whiskers were grown in the previous run. This temperature was found to be about 1330°C and due to the change in furnace controller temperature was probably 25°C less than the temperature at that location in the previous run. A profuse growth of SiC whiskers 1.2 to 1.5 cm in length was found at the exit end of the tube. In this case no whiskers were found at the entrance end. Run 13 was the most successful crystal growth experiment of the entire series.

In Run 14 an attempt was made to grow whiskers with higher furnace controller temperature and higher flow rate of excess hydrogen and at the same time an attempt was made to measure the temperature at which the whiskers grow at the exit end. In addition the reaction time was increased in an attempt to grow longer whiskers. Whiskers were formed at the graphite sighting block at the exit end. The temperature of this block was about 1260°C. The conditions for this temperature measurement were far from ideal because the sighting block was exposed to radiation from the hot zone of the furnace. On the other hand, the stubby whiskers growing from the front face of the block probably produce a fair black body.

In the following runs (Runs 15-18) several other variations were attempted. In these runs the furnace controller temperatures were kept in the range 1375 to 1400°C and the reaction time was, in general, as long as practical for a regular working day. In Run 15 the excess hydrogen flow rate was reduced to 500 cm^3/min. The result was an unusual growth of silicon metal on the entrance end. Silicon carbide whiskers and needles were grown on the exit end. In Run 16, the flow rate of the hydrogen carrier gas was increased to 30 cm^3/min, thus increasing the flow rate and concentration of the methyltrichlorosilane. The result was a growth of silicon metal on the entrance end. Silicon carbide whiskers and needles were grown at the exit end. Run 17 was an attempt to duplicate Run 13. However, due to lack of control of the rate of evaporation of the methyltrichlorosilane, the concentration of this reactant was less than expected. The use of a constant temperature bath to control the temperature at which the hydrogen picks up the reactant should improve the control of the rate of evaporation. Silicon carbide whiskers and needles were grown at the exit end but the whiskers were not as long or pro-

fuse as in Run 13. In Run 18 toluene was added in an attempt to provide excess carbon and the concentration of the methyltrichlorosilane was increased. Whereas in Runs 15 and 16 the increased concentration of methyltrichlorosilane resulted in formation of silicon metal at the entrance end, this was not observed in Run 18 and its absence can be attributed to the presence of carbon from the toluene. Again silicon carbide whiskers were formed at the exit end.

The conditions most favorable to silicon carbide whiskers growth were conditions present in Run 13. In this run the flow rate was 3.43×10^{-4} moles/min of CH_3SiCl_3 in a total hydrogen flow of 1020 cm^3/min. The reaction time was five hours at a furnace controller temperature of 1400°C. The whiskers grew at about 1260°C.

The longest whisker produced during these experiments was five centimeters in length. This whisker was produced in Run 16 and is twinned in several places. The more typical whiskers such as those observed in Run 13 are from one to 1.5 cm in length and from 1.5 to 4 microns in diameter.

It is of interest to note that the pyrolysis of the methyltrichlorosilane and/or reaction with hydrogen and the graphite tube produces a variety of substances, each being deposited or formed in various locations relative to the hot zone. Figure 5 is a photograph of the longitudinal section of a typical graphite reaction tube insert after completion of a whisker growing experiment. Area A, identified as the upstream end of the reaction tube, usually contains a splatter deposit of silicon metal. On several occasions, however, the silicon metal formed in this region grew in very peculiar forms resembling either "moose antlers" or "bushy clumps" as illustrated in Figures 6 and 7. Area B, identified as the region downstream of A and lying between Area A and the hot reaction zone, contains a dense but short and stubby brittle needle-like growth of SiC as shown in Figure 8. The SiC structure appears to be in doubt since X-ray diffraction patterns identify it as the cubic beta form but examinations under polarized light disclose these crystals to be birefringent with parallel extinction. Area C, located on the downstream side of the hot reaction zone contains dense, white to pale green, cotton-like growth of SiC. The SiC crystals from this area were identified by X-ray diffraction as the hexagonal alpha form. The specific gravity of this form ranges from 3.214 to 3.217. Examination of the crystals under polarized light shows them to be birefringent verifying their anisotropic structure. These crystals are comparatively long flexible whiskers and are shown in Figure 9. Closer examination of the individual whiskers as illustrated in Figures 10 and 11 reveals that the growth pattern is not consistent since some whiskers from identical locations in Area C show banded structures while others do not.

The whisker growth is restricted to the parts of the system in which the conditions are appropriate for whisker growth. It seems likely that the temperature is the most important of these conditions since whiskers have been found at both the entrance and exit of the reaction tube and it is unlikely that the concentrations of the reactants and gaseous products are the same at both of these locations. Therefore, in order to increase the number of whiskers produced it would be appropriate to increase the volume in which the desired whisker growth temperature prevails.

Merz (13) in his experiments at temperatures from 1400 to 1550°C observed the presence of both alpha and beta silicon carbide and concluded that generally accepted stability relations between these form are in doubt. The results of the experiments reported here confirm Merz' observations with respect to the coexistance of both forms at these relatively low temperatures.

Mechanical Property Measurement

Prior to determining the stress-strain properties of the SiC whiskers prepared in the whisker growing phase of the program, several loading tests were conducted in the course of apparatus development and refinement. These preliminary tests indicated the approximate strength to be expected in subsequent determinations and the nature of the rupture of SiC whiskers. The whiskers are completely destroyed in the uncemented portion. It is unlikely that this is caused by cracking at many sites on the whisker during tensile loading. Instead it appears that an explanation dealing with elastic strain recovery is more appropriate. During loading, the whisker is placed in a state of high elastic strain energy which when released, due to primary rupture of the whisker at a localized site, produces a recovery strain wave with sufficient force to destroy the whisker. From an analysis of these observations, it is concluded that SiC whiskers exhibit little or no plastic strain and that rupture is sudden and of characteristically brittle or cleavage type.

With this background in SiC whisker testing, a series of experiments was performed in which the stress-strain properties were measured. The whiskers for the stress-strain determinations were selected on the basis of surface regularity (i.e., whiskers showing the least amount of banding were selected). The test whiskers were generally in the 2 to 3.5 micron diameter range although a few with diameters up to 4.5 microns were tested. The results of the series of tests are summarized in Table III and show a rather pronounced scatter in strength, elastic modulus and strain which seems characteristic of mechanical property observations on whiskers of other types as well. These results, nevertheless, show that SiC whiskers can be very

strong as evidenced by the 1.6×10^6 psi tensile strength recorded for one whisker. In the other eleven cases the observed values ranged from 1.0×10^5 to 5.0×10^5 psi.

The reasons for the observed variations are not understood. In some other investigations, the parts remaining after fracture have been retested and found to be stronger than the original whisker. If defects such as surface microcracks are responsible for the reduced strength of the SiC whiskers, the strength of the fractured whisker fragments may approach the highest observed strength. Since the whiskers that were measured were all from Run 13, no information is available to determine the effect of the variables associated with growth conditions on the strength and modules of elasticity. It is likely that a large part of the observed variation is due to experimental difficulties associated with alignment of the applied loads with the axis of the whisker.

In the light of these results, it may be appropriate to compare the mechanical properties of SiC whiskers with the properties of other types of materials. Probably the most complete and significant individual research on the strength of specific types of whiskers is that of Brenner (3) in which he studied iron and copper crystals. He observed a large scatter in results for whiskers with diameters less than 8 microns. For example, the scatter in iron whiskers 4 microns in diameter ranged from 280,000 to 780,000 psi and for 2-micron diameter whiskers from 425,000 to 1,250,000 psi. He concluded that the average strength is inversely proportional to whisker diameter and he attributed the size dependence and scatter to defects or dislocations which react with varying degrees of effectiveness in promoting flow or fracture. Similar size effects, however, have not been observed in zinc or cadmium whiskers in the range of 1 to 10 microns (17) nor have they been observed in silicon whiskers in the range of 16 to 28 microns (10). The number of measurements on SiC whiskers has not been sufficient to determine whether or not there is a size effect.

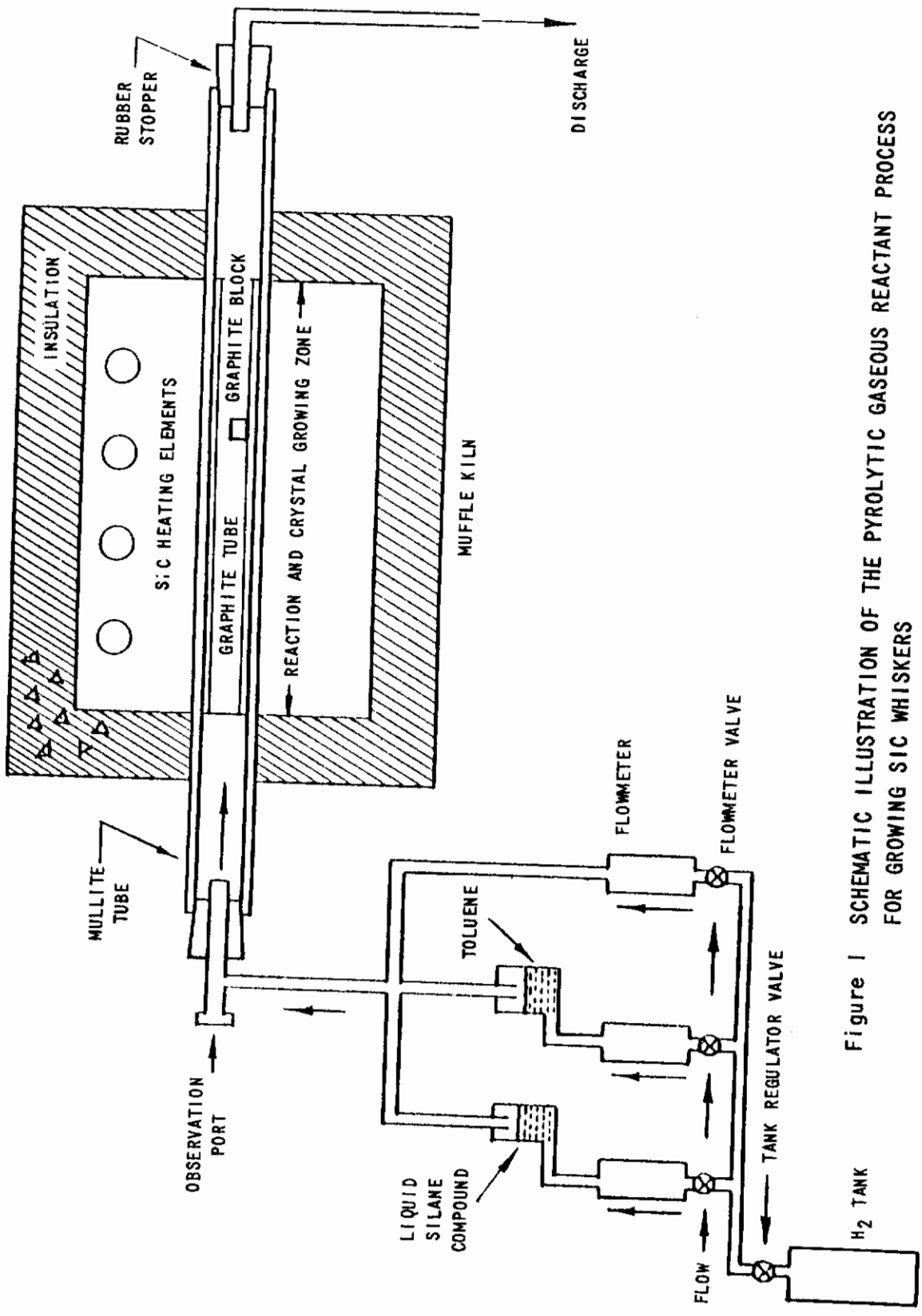


Figure 1 SCHEMATIC ILLUSTRATION OF THE PYROLYTIC GASEOUS REACTANT PROCESS FOR GROWING SIC WHISKERS

Figure 2 APPARATUS EMPLOYED IN THE SYNTHESIS OF SiC WHISKERS BY PYROLYTIC GASEOUS REACTION

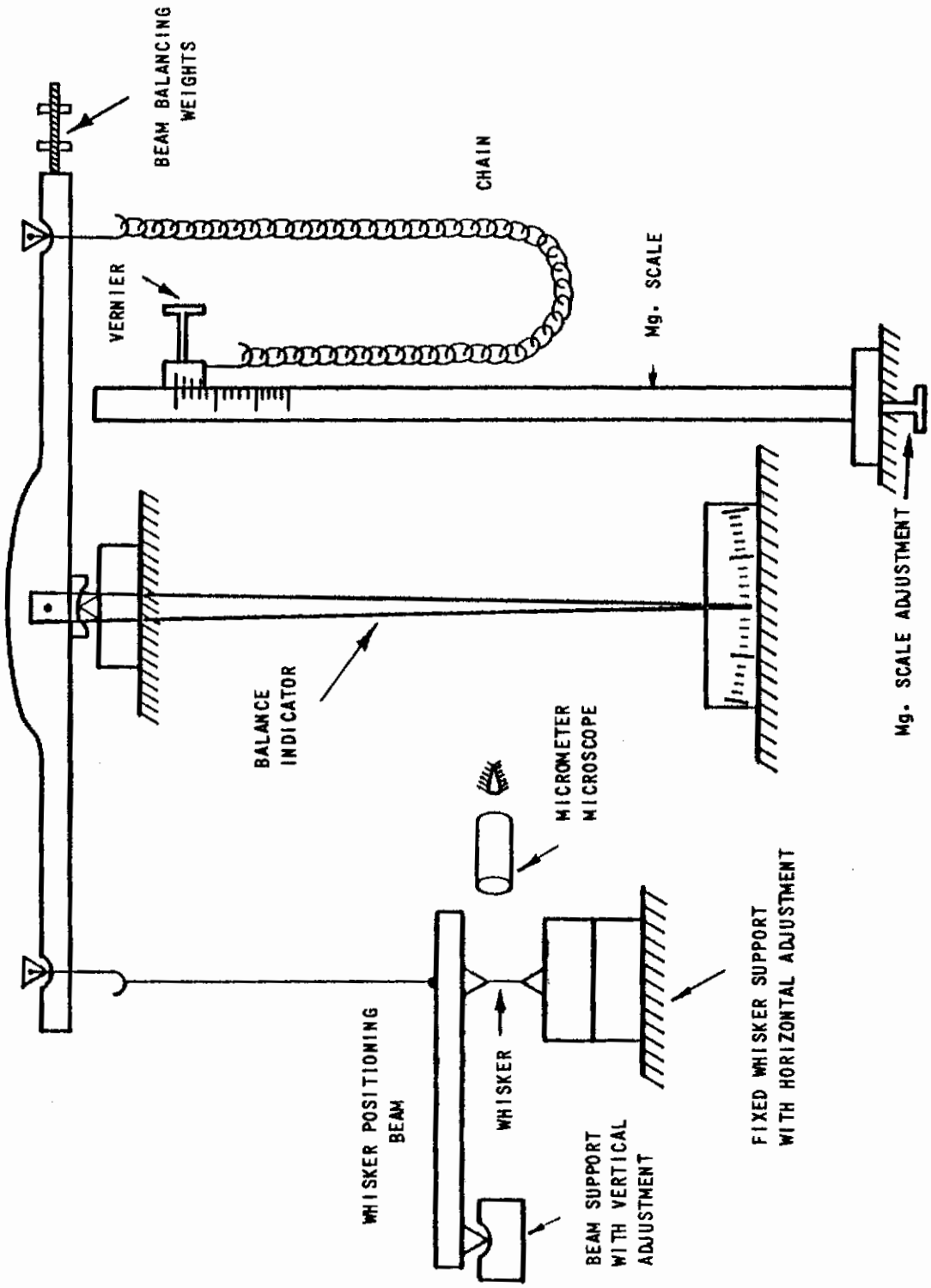


Figure 3 SCHEMATIC REPRESENTATION ILLUSTRATING MODIFICATIONS OF AN ANALYTICAL BALANCE FOR TENSILE TESTING WHISKERS

Figure 4 MODIFIED ANALYTICAL BALANCE AND ASSOCIATED FILAR MICROSCOPE FOR THE TENSILE TESTING OF WHISKERS

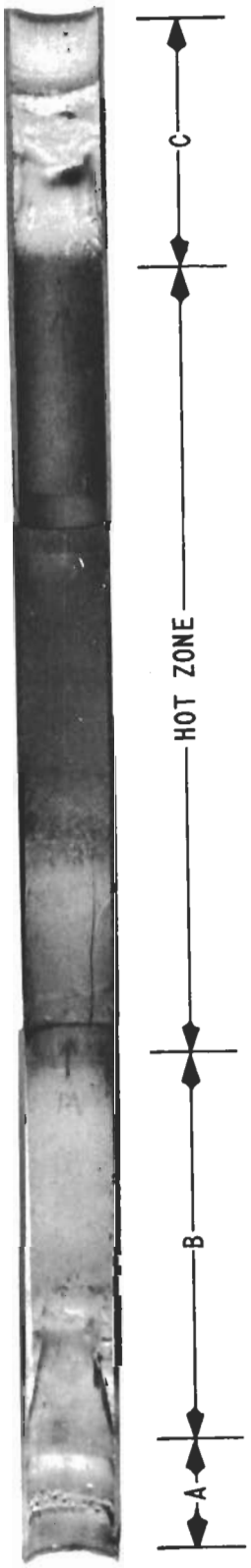


Figure 5 GRAPHITE REACTION TUBE ILLUSTRATING TYPICAL AREAS OF FORMATION AND GROWTH OF REACTION PRODUCTS.

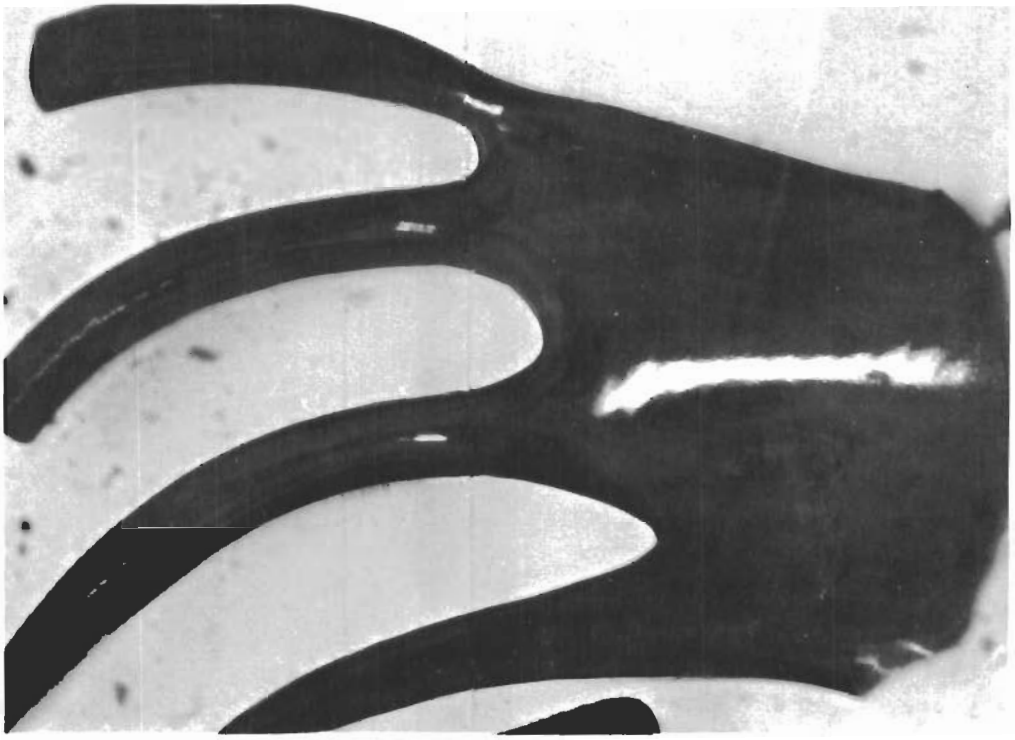


Figure 6 "ANTLER" FORM OF SILICON METAL FOUND TO DEPOSIT IN AREA A OF REACTION TUBE - 55 X MAG.

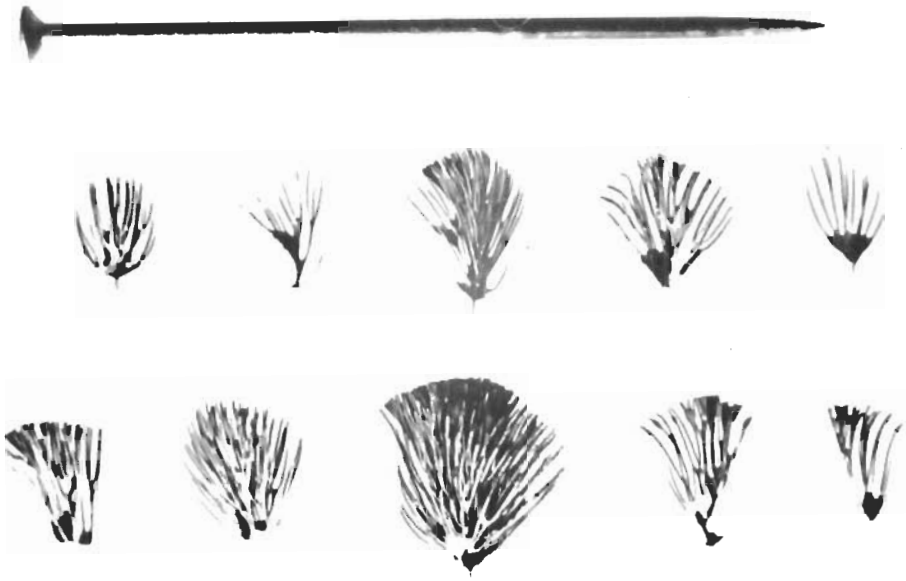
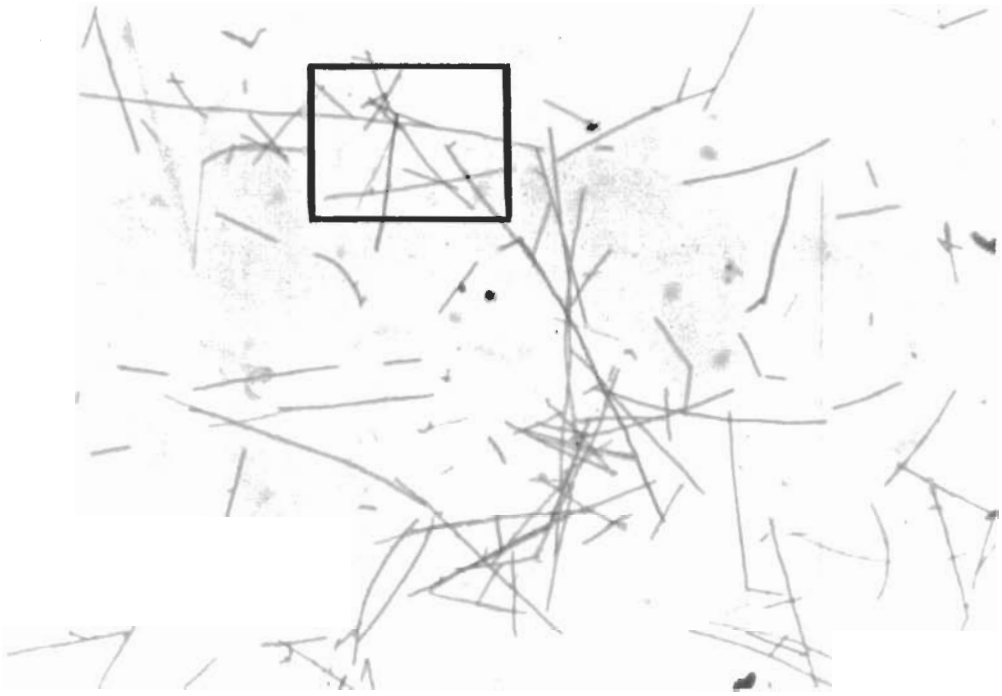


Figure 7 "BUSH" FORM OF SILICON METAL FOUND TO DEPOSIT IN AREA A OF REACTION TUBE -3.5 X MAG.



240 X MAG.

1450 X MAG.

Figure 8 SHORT, STUBBY NEEDLE-LIKE GROWTH OF SiC TYPICAL OF FORMATION IN AREA B

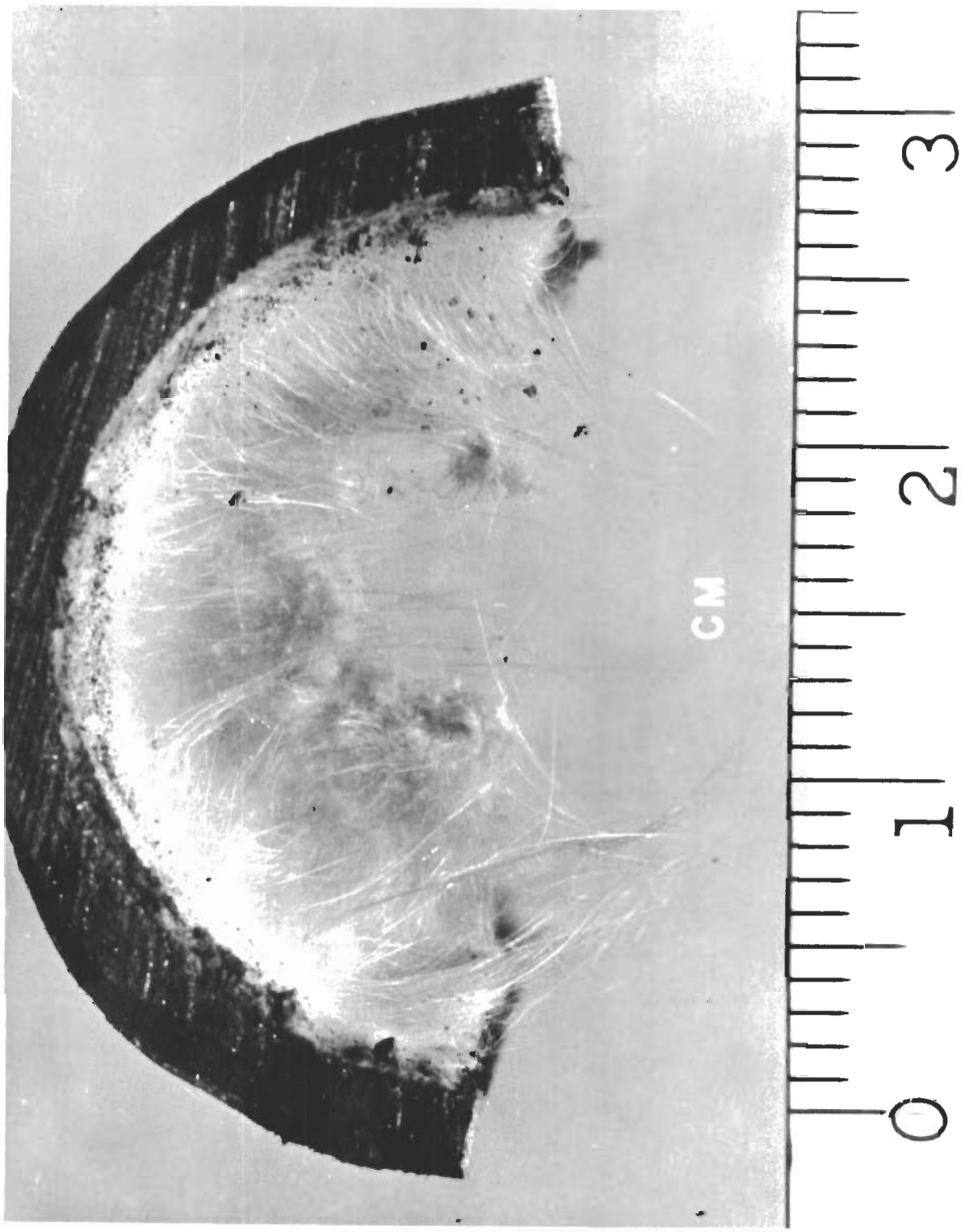
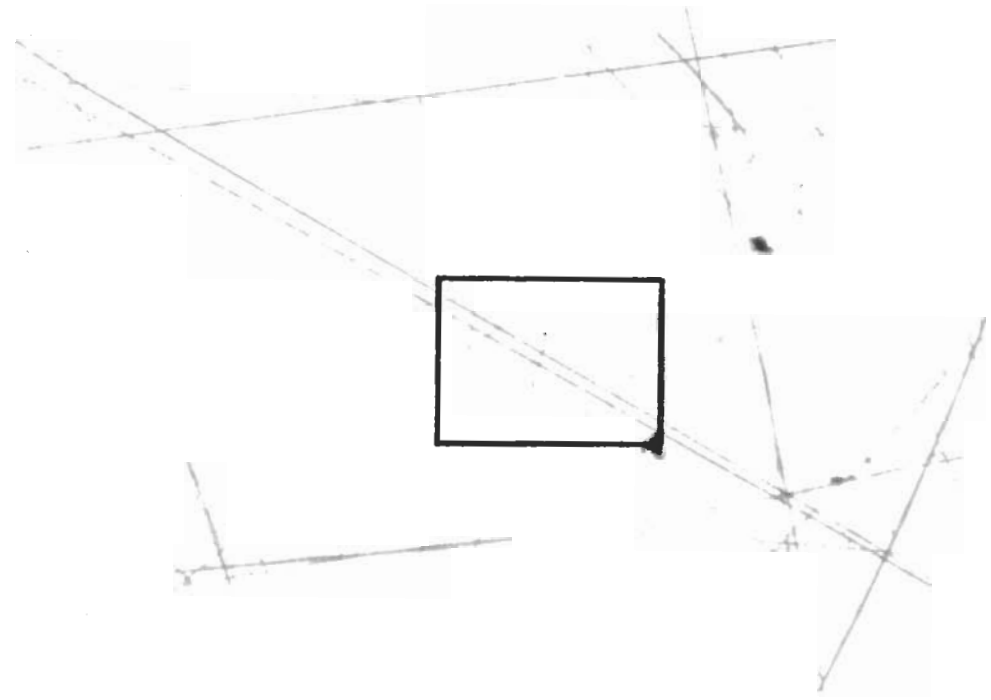
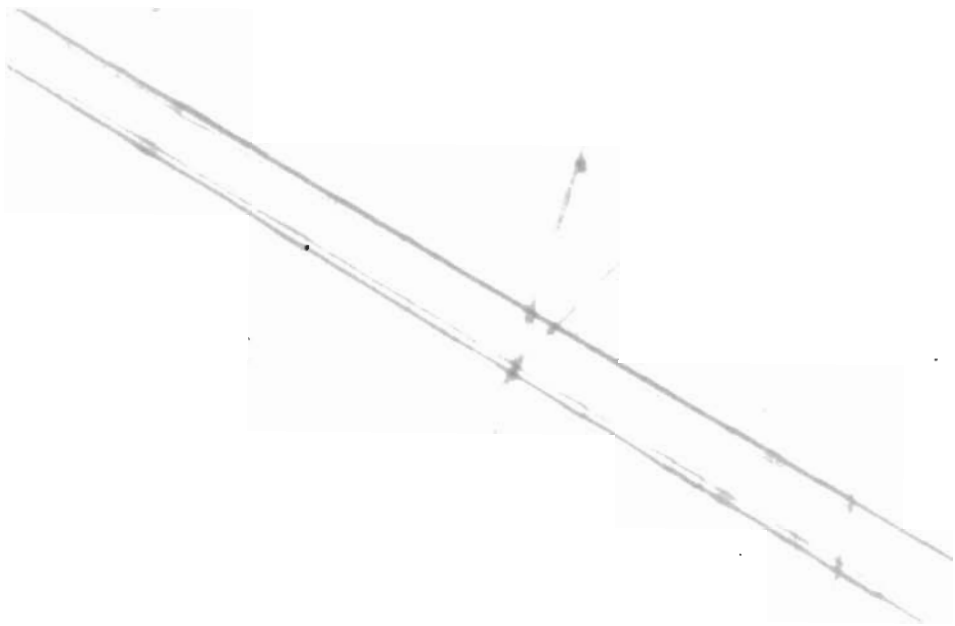


Figure 9 TYPICAL FORMATION OF "COTTON-LIKE" SiC WHISKERS IN AREA C BY THE GASEOUS REACTANT PROCESS

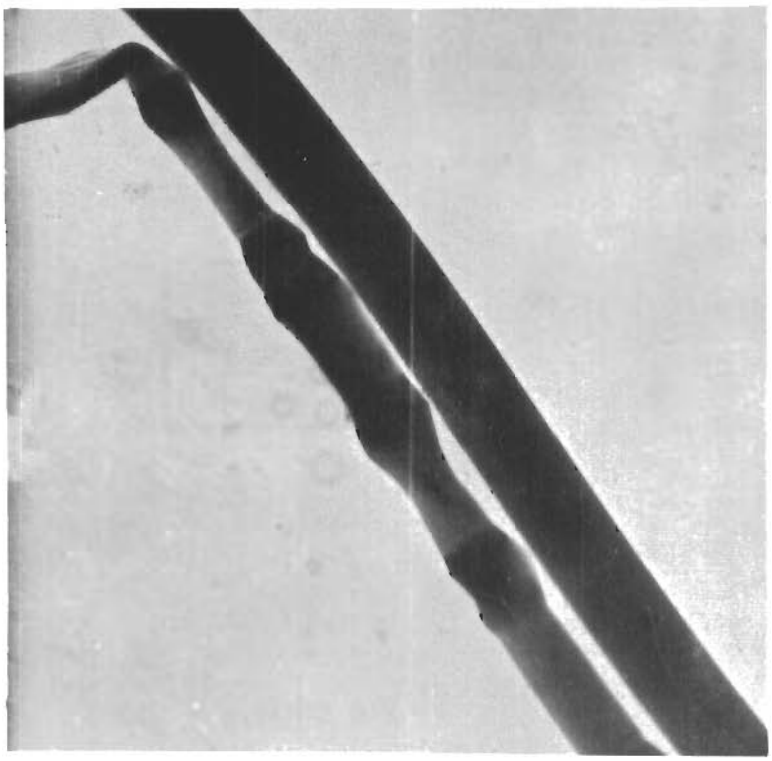


210 X MAG.

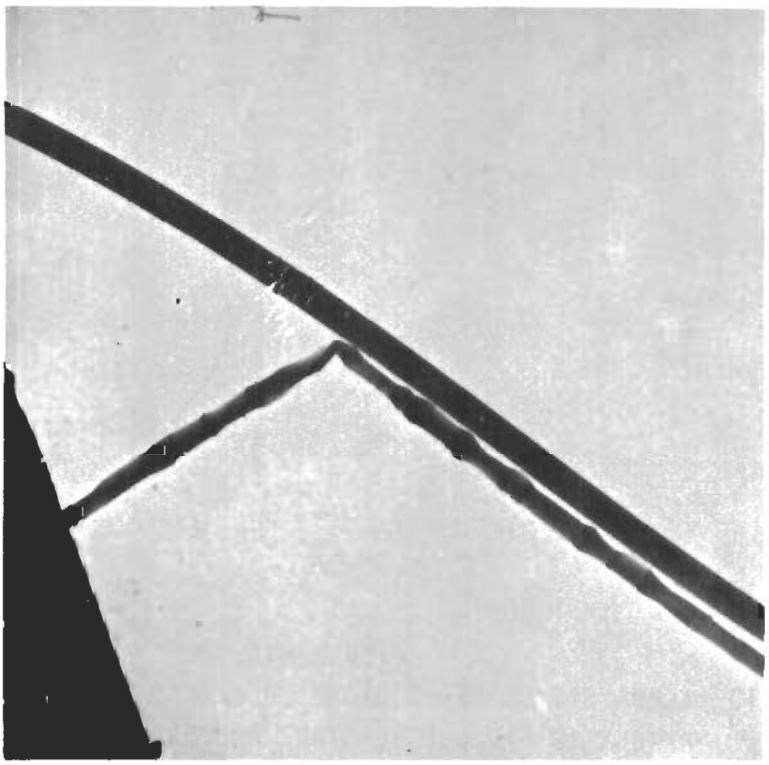


1450 X MAG.

Figure 10 ALPHA SiC WHISKERS GROWN IN AREA C OF REACTION TUBE BY THE PYROLYTIC GASEOUS REACTANT PROCESS



(b) 20,000 X MAG.



(a) 12,000 X MAG.

Figure 11 BANDED AND UNBANDED ALPHA SiC WHISKERS GROWN IN AREA C OF REACTION TUBE

SUMMARY AND RECOMMENDATIONS

Silicon carbide whiskers were prepared by pyrolysis and reaction of methyltrichlorosilane with hydrogen at furnace controller temperatures in the range from 1375-1450°C. The best results were achieved under the following conditions:

Flow rate of CH_3SiCl_3	3.43×10^{-4} moles/min
Flow rate of hydrogen carrier gas	20 cm^3/min
Flow rate of excess hydrogen	1000 cm^3/min.
Reaction Time	5 hours
Furnace controller temperature	1400°C
Reaction temperature	about 1260°C

The whiskers grown by this process were identified as alpha (hexagonal) silicon carbide. The specific gravity of this form ranges from 3.214 to 3.217.

The whiskers grow in a very limited region of the reaction tube. The length of this region probably indicates that the whiskers grow only in a small range of temperatures. In addition, the quality and quantity appears to be quite sensitive to flow rate, ratio of gaseous reactants, reaction temperature and reaction time. In Run 13, under the conditions listed above, dense growths of whiskers 1.2 - 1.5 centimeters in length and 2 to 5 microns in diameter were observed. The length of the longest whisker was 5 centimeters.

The tensile properties of the SiC whiskers were measured in a modified analytical balance. The results on whiskers from 2.0 to 4.5 microns in diameter indicate that the strength usually ranges from 100,000 to 500,000 psi, although one whisker had a strength of 1,600,000 psi. SiC whiskers deformed elastically up to 1.1%. No plastic deformation was observed. Rupture occurs in typical brittle fashion.

The following additional research is recommended:

A. Expansion of capacity for growing silicon carbide whiskers. Investigation of methods for growing longer whiskers.

B. Investigation of the use of silicon carbide whiskers in mat form as high temperature thermal insulation.

C. Investigation of the use of silicon carbide whiskers as a reinforcing material in composites.

Expansion of capacity for growing silicon carbide whiskers is largely a matter of increasing the volume of the region in which the conditions for whisker growth prevail. The larger reaction chamber and larger quantities of reactants may also aid in growing longer whiskers. The lengths of the ordinary whiskers produced in the above experiments were a large fraction of the diameter of the reaction tube. The five centimeter whisker was almost twice as long as the diameter of the reaction tube.

Several properties of silicon carbide whiskers make them attractive for a variety of potential uses. Among these properties are the following:

(1) High strength - The strength of these whiskers is in the same range as the strength of glass fibers. Due to increased hardness and corrosion resistance compared to glass fibers, the usable strength of the whiskers may exceed that of the glass fibers.

(2) High modulus of elasticity - The results of these experiments indicate that the modulus of elasticity of the silicon carbide whiskers can be much larger than that of fiber glass. Utilization of a high modulus reinforcing material can aid greatly in stiffening structures made of reinforced plastics or ceramics.

(3) Low specific gravity - The elements, silicon and carbon, have low atomic weight so that the specific gravity of this material is low relative to many possible alternative materials.

(4) High index of refraction - This property will cause scattering of thermal radiation and, therefore, will reduce the total heat transfer through a composite material and for materials in mat form will effectively insulate against radiant heat transmission.

(5) Stable decomposition products - In an oxidizing atmosphere silicon carbide decomposes at the surface to form SiO_2 glass which protects against further oxidation. In a reducing atmosphere it decomposes leaving graphite.

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TABLE I

EXPERIMENTS USING SILICON TETRACHLORIDE, TOLUENE AND HYDROGEN

Run No.	$SiCl_4$ (mole/min.)	$SiCl_4$ H_2 flow (cm^3/min.)	Toluene (mole/min.)	Toluene H_2 flow (cm^3/min.)	Ratio Moles $SiCl_4$: $C_6H_5CH_3$	Total H_2 flow cm^3/min.	Time of Reaction (hrs.)	Furnace Temp. °C	Excess H_2 cm^3/min.	Observations
1	1.66×10^{-3}	75	2.30×10^{-4}	30	7.2:1	1105	1.25	1483	1000	No SiC crystals, unidentified white powder on exit side.
2	1.62×10^{-3}	75	3.03×10^{-4}	30	5.4:1	1105	2.00	1450	1000	No SiC Crystals, unidentified white powder on exit side.
3	1.63×10^{-3}	75	9.50×10^{-5}	30	17.1:1	1105	4.00	1400	1000	No SiC crystals, Si metal deposit on mullite tube at entry to hot zone.

TABLE I (Cont'd.)

EXPERIMENTS USING SILICON TETROCHLORIDE, TOLUENE AND HYDROGEN - cont'd

Run No.	$SiCl_4$ (mole/min.)	H_2 flow (cm^3/min.)	$C_6H_5CH_3$ (mole/min.)	H_2 flow cm^3/min.)	Ratio Moles $SiCl_4$: $C_6H_5CH_3$	Total H_2 flow cm^3/min.	Time of Reaction (hrs.)	Furnace Temp. °C	Excess H_2 cm^3/min.	Observations
4	1.61×10^{-3}	75	8.47×10^{-5}	30	19.0:1	1105	3.00	1475	1000	No SiC crystals, Si metal deposit on mullite tube at entry to hot zone.
5	1.15×10^{-3}	75	5.33×10^{-5}	30	21.6:1	1105	4.40	1450	1000	No SiC crystals, Si metal deposit on mullite tube. White powder on exit side.
6	1.52×10^{-3}	75	3.61×10^{-5}	30	42.1:1	605 500 N_2	1.00	1450	500 500 N_2	No SiC crystals, Si metal deposit on mullite tube. White powder on exit side.

TABLE I (Cont'd.)

EXPERIMENTS USING SILICON TETROCHLORIDE, TOLUENE AND HYDROGEN - cont'd

Run No.	(mole/min.)	H_2 flow (cm^3/min.)	(mole/min.)	H_2 flow (cm /min.)	Ratio Moles $SiCl_4$: $C_6H_5CH_3$	Total H_2 Flow cm^3/min.	Time of Reaction (hrs.)	Furnace Temp. °C	Excess H_2 cm^3/min.	Observations
7	1.33×10^{-3}	75	7.10×10^{-5}	30	18.8:1	1005 100 N_2	4.35	1450	900 100 N_2	No SiC crystals, Si metal deposit on mullite tube. White powder on exit side.
8	2.55×10^{-3}	150	1.13×10^{-4}	60	22.5:1	1710	4.00	1475	1500	No SiC crystals. Heavy deposit of Si metal on entry side of mullite tube.
9*	2.26×10^{-3}	150	7.70×10^{-5}	60	29.4:1	710	4.00	1475	500	No SiC crystals

* Granulated zinc added to the system-- placed just forward of the reaction zone.

TABLE II

EXPERIMENTS USING METHYLTRICHLOROSILANE, TOLUENE AND HYDROGEN

Run No.	CH_3SiCl_3 (mole/min.)	H_2 flow (cm^3/min.	Toluene (mole/min.)	H_2 flow (cm^3/min.)	Moles CH_3SiCl_3 $C_6H_5CH_3$	Total H_2 flow cm^3/min.	Time of Reaction (hrs.)	Temp. °C	Excess H_2 cm^3/min.	Obser. vations
10	3.11×10^{-3}	320	---	---	---	1320	3.5	1455	1000	No SiC crystals. Unusual growth of Si crystals on entry to hot zone.
11	4.44×10^{-4}	30	---	---	---	1330	4.5	1455	1300	αSiC whiskers and short stubby SiC needles formed on exit of graphite tube. Si metal on entry side
12	3.42×10^{-4}	20	---	---	---	1320	4.5	1425	1300	αSiC whiskers and short stubby SiC needles formed on exit of graphite tube also some whiskers formed at entrance.

TABLE II (Cont'd.)

EXPERIMENTS USING METHYLTRICHLOROSILANE, TOLUENE AND HYDROGEN

Run No.	CH_3SiCl_3 (mole/min.)	H_2 flow (cm^3/min.)	Toluene (mole/min.)	H_2 flow (cm^3/min.)	Ratio Moles CH_3SiCl_3 / $C_6H_5CH_3$	Total H_2 flow cm^3/min.	Time of Reaction (hrs.)	Temp. °C	Excess H_2 cm^3/min.	Observations
13	3.43×10^{-4}	20	---	---	---	1020	5.0	1400	1000	Large growth of αSiC whiskers & short stubby SiC needles. Whiskers 1.2 to 1.5 cm long.
14	3.01×10^{-4}	20	---	---	---	1320	6.0	1455	1300	αSiC whiskers and short stubby SiC needles. Unusual growth of Si metal on entry side.
15	4.77×10^{-4}	20	---	---	---	520	5.0	1375	500	αSiC whiskers and short stubby SiC needles. Unusual growth of Si metal on entry side.

TABLE II (Cont'd.)

EXPERIMENTS USING METHYLTRICHLOROSILANE, TOLUENE AND HYDROGEN

Run No.	CH_3SiCl_3 (mole/min.)	H_2 flow (cm^3/min.)	Toluene (mole/min.)	H_2 flow (cm^3/min.)	Ratio Moles CH_3SiCl_3 $C_6H_5CH_3$	Total H_2 flow cm^3/min.	Time of Reaction (hrs.)	Temp. °C	Excess H_2 cm^3/min	Observations
16	4.20×10^{-4}	30	---	---	---	1030	7.5	1400	1000	αSiC whiskers and short stubby SiC needles. Growth of Si metal on entry side.
17	2.52×10^{-4}	20	---	---	---	1020	7.0	1400	1000	αSiC whiskers and short stubby SiC needles.
18	4.45×10^{-4}	30	4.74×10^{-5}	30	9.4:1	1060	6.5	1400	1000	αSiC whiskers and short stubby SiC needles.

TABLE III

RESULTS OF TENSILE MEASUREMENTS ON SiC WHISKERS

(Whiskers 1.2-1.5 cm in length from Run 13)

Whisker Diameter (μ)	Observed Strain %	Tensile Strength		Elastic Modulus	
		(dyn cm.$^{-2}$)	(lb.in.$^{-2}$)	(dyn cm.$^{-2}$)	(lb.in.$^{-2}$)
2.2	--	1.14×10^{11}	1,650,000	---	---
4.5	--	6.90×10^{9}	100,400	---	---
2.7	0.69	3.08×10^{10}	447,000	4.31×10^{12}	62.5×10^{6}
2.5	0.71	6.96×10^{9}	101,300	8.76×10^{11}	12.7×10^{6}
3.5	0.99	2.18×10^{10}	316,000	1.93×10^{12}	28.0×10^{6}
3.7	0.81	9.51×10^{9}	138,200	1.06×10^{12}	15.4×10^{6}
2.5	0.60	1.58×10^{10}	230,000	2.65×10^{12}	38.4×10^{6}
2.25	--	1.49×10^{10}	216,000*	2.88×10^{12}	41.8×10^{6}
2.8	1.10	2.74×10^{10}	397,000	2.47×10^{12}	35.8×10^{6}
4.4	0.96	2.41×10^{10}	350,000	2.49×10^{12}	36.1×10^{6}
3.0	0.41	3.44×10^{10}	499,000	8.50×10^{12}	123.3×10^{6}
2.5	0.49	1.96×10^{10}	284,000	4.04×10^{12}	58.6×10^{6}

* Specimen pulled out of cement--no rupture strength recorded.