

AD-A067 225

CHEMETAL CORP PACOIMA CALIF
INVESTIGATION OF THE CNTD MECHANISM AND ITS EFFECT ON MICROSTRU--ETC(U)
SEP 78 R A HOLZL

N00019-77-C-0395

F/G 11/2

NL

UNCLASSIFIED

1 OF 1
AD
A067225



END
DATE
FILMED
6-79
DDC

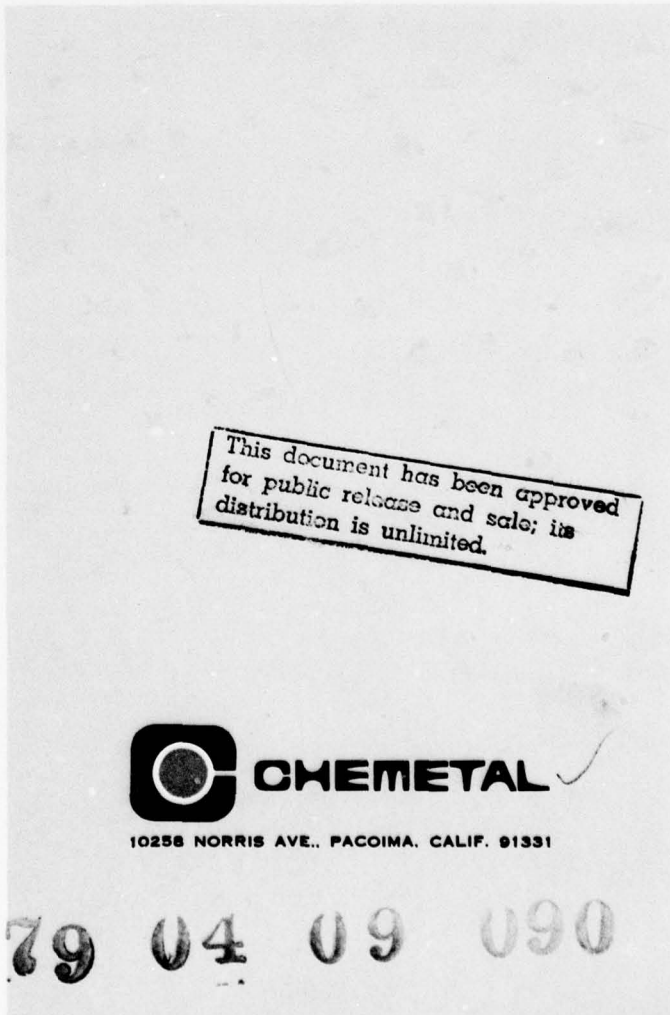
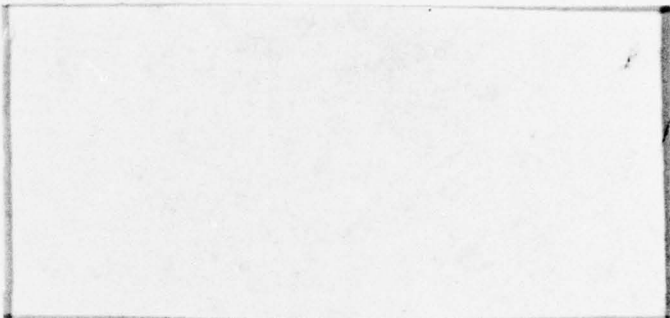
A067225

DDC FILE COPY

LEVEL ~~II~~

10

DDC
RECEIVED
APR 10 1979
C



This document has been approved
for public release and sale; its
distribution is unlimited.

 CHEMETAL

10258 NORRIS AVE., PACOIMA, CALIF. 91331

79 04 09 090

10

DDC
RECEIVED
APR 10 1979
C

AD A0 67225

DDC FILE COPY

U.S. NAVAL AIR SYSTEMS COMMAND
WASHINGTON, D.C.

Contract No. N00019-77-C-0395
Final Report

SEPTEMBER 1978

This document has been approved for public release and sale; its distribution is unlimited.

⑥ INVESTIGATION OF THE CNTD MECHANISM AND ITS EFFECT
ON MICROSTRUCTURE AND PROPERTIES OF SILICON NITRIDE

⑨ Summary Report (Final)

July 1978 to July 1979 ✓

Contract No. N00019-77-C-0395 ✓

⑮ Prepared for

U.S. Naval Air Systems Command

Washington, D.C.

⑪ Sep 78

⑫ 39p.

Prepared by

⑩ Robert A. Holzl

CHEMETAL CORP. ✓

Pacoima, California 91331

Approved for public release; distribution unlimited

409 801

byg

TABLE OF CONTENTS

| | <u>PAGE</u> |
|--|-------------|
| I. INTRODUCTION | 1 |
| II. EXPERIMENTAL EQUIPMENT AND PROCEDURES | 2 |
| III. CHEMISTRY OF SILICON NITRIDE | 4 |
| IV. EXPERIMENTAL RESULTS: PROCESS EVALUATION AND DISCUSSION | 5 |
| V. CONCLUSIONS | 11 |
| VI. RECOMMENDATIONS | 12 |
| VII. APPENDIX: ASSOCIATED STUDIES | 13 |
| VIII. REFERENCES | 16 |

| | |
|------------------------------------|---|
| ACCESSION for | |
| NTIS | White Section <input checked="" type="checkbox"/> |
| DDC | Buff Section <input type="checkbox"/> |
| UNANNOUNCED | <input type="checkbox"/> |
| JUSTIFICATION | |
| BY | |
| INSTRUMENTATION/AVAILABILITY ROOMS | |
| Dist. | SERIAL |
| A | |

LIST OF ILLUSTRATIONS

| <u>FIGURE</u> | | <u>PAGE</u> |
|---------------|--|-------------|
| 1. | Schematic Si_3N_4 System | 17 |
| 2. | Line Diagram for Si_3N_4 System | 18 |
| 3. | Pressure Temperature Diagram for $\text{SiCl}_4/\text{NH}_3$ System Showing Various Types of Deposits at high total Pressure | 19 |
| 4. | Pressure Temperature Diagram for $\text{SiCl}_4/\text{NH}_3$ System Showing the Effect of Hydrocarbon Addition on the Nature of the Deposit. | 20 |
| 5. | X-Ray Diffraction Patterns | 21 |
| 6.a. | S.E.M. Surface Topography Amorphous Deposit | 21 |
| 6.b. | S.E.M. Surface Topography Coarse Crystalline Deposit | 22 |
| 7.a. | S.E.M. Fractured Surface Hybrid Material | 23 |
| 7.b. | S.E.M. Fractured Surface Hybrid Material | 23 |
| 8. | S.E.M. Fractured Surface Hybrid Material | 24 |
| 9.a. | S.E.M. Fractured Surface Amorphous Material | 25 |
| 9.b. | S.E.M. Higher Mag. of Figure 9.a. | 25 |
| 10.a. | S.E.M. Surface Topography of Crystalline Deposit | 26 |
| 10.b. | S.E.M. Fractured Surface Crystalline Deposit | 26 |
| 11.a. | S.E.M. Fractured Surface Needlelike Grains | 27 |
| 11.b. | S.E.M. Higher Mag. of 11.a. | 27 |
| 12.a. | S.E.M. Cross Section Growth Similar to Figure 11.a. | 28 |
| 12.b. | S.E.M. Fractured Surface Broken Up Needlelike Grain | 28 |
| 13.a. | S.E.M. Surface Topography of Crystalline Deposit | 29 |
| 13.b. | S.E.M. High Temperature Whisker Formation | 29 |
| 14. | Photomicrograph of Fracture Toughness Measurement | 30 |

LIST OF TABLES

| | <u>PAGE</u> |
|---|-------------|
| I SUMMARY OF REPRESENTATIVE DEPOSITION CONDITIONS | 31 |
| II SUMMARY OF PHYSICAL AND MICROSTRUCTURAL PROPERTIES | 32 |

I INTRODUCTION

Silicon carbide and silicon nitride have been recognized as prime candidate materials for numerous high temperature applications, based on their properties such as oxidation resistance, chemical stability, creep resistance, strength, and thermal shock resistance. As a result, a number of different consolidation techniques are being investigated for potential use. Ceramics produced by CVD are thought to have considerable potential in these applications in offering greater purity and density than ceramics produced by more conventional consolidation techniques.

At Chemetal, an advanced state of the art CVD process, called Controlled Nucleation Thermochemical Deposition has been developed. The influence of the process on the microstructures is readily apparent. The characteristics of the resultant deposit are quite different in that the columnar crystal growth, which is typical of CVD, is interrupted so as to provide instead a fine grained non-columnar deposit. This program was directed toward achieving a better understanding of the mechanism of the CNTD process as it relates to silicon nitride deposition.

It is usually considered that a most desirable structure for a brittle ceramic would be one having minimum flaw size, minimum flaw population and minimum grain size. These characteristics are believed to be influential in establishing good mechanical strength for a material.

During the course of this program the effect of deposition conditions on the resultant flexural stress, hardness, and fracture toughness of deposited silicon nitride was investigated.

II EXPERIMENTAL EQUIPMENT AND PROCESS PROCEDURES

The experiments on this program used a typical laboratory scale CVD reactor. The deposition chamber was an air cooled quartz chamber of 75mm diameter. Most of the tests used two resistant heated tungsten wires of 0.5mm diameter x 152mm long as substrates.

Additional tests were conducted using graphite substrates of an expansion coefficient the same as that of the silicon nitride. These graphite substrates were either 25mm diameter x 38mm long rods or 2.0mm diameter by 152mm graphite rods. An external resistance heater was used to regulate the preheat temperature of the reactant stream. This temperature was monitored by a thermocouple immersed in the stream 13mm above the substrate. Substrate temperatures were measured by a micro optical pyrometer. The over-all system is depicted in Figures 1 and 2.

During the course of this one year program more than 200 experimental runs were conducted.

For the majority of the runs silicon tetrachloride was used as a source of silicon. The SiCl_4 was dispensed into the system using nitrogen as a carrier gas in a conventional bubbler arrangement. Metering of the SiCl_4 was effected by measuring the flow of the dry carrier by an electronic mass flow meter, measuring the flow of the combined stream exiting the bubbler and determining the SiCl_4 by difference.

In all cases the source of nitrogen was ammonia. Hydrogen gas was also used in the system. These gases were metered through standard borosilicate

glass rotometers with pressure gauges and needle type valves for maintaining constant metering pressure.

Earlier work conducted at Chemetal and confirmed by other investigators has indicated that a considerable problem for silicon nitride deposition is related to the generation of solid particles in the gas stream. Not only are there considerable amounts of partially decomposed intermediates but also copious quantities of ammonium chloride. These products tend to collect on chamber walls and in exhaust lines. Not only do they impair the flow but they make optical temperature measurements difficult. In order to minimize these problems certain general procedures were adopted for the experiments.

- . Combined partial pressures of the reactants were kept below 80 torr.
- . Ammonia and silicon chloride were introduced into the reaction chambers separately and mixed near the part.
- . Substantial dilution with an inert gas was employed.
- . Inlet gases were preheated as high as 700°C to minimize certain of the low temperature reactions.
- . Certain foreign species such as hydrocarbons were introduced in an attempt to influence intermediate reactions.

Tables I and II summarize the results of various mechanical and

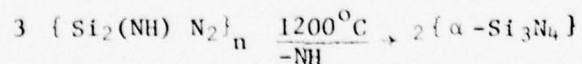
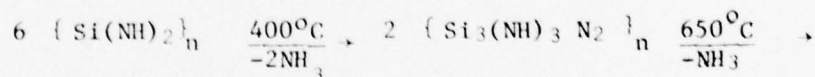
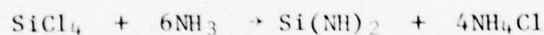
metallographic tests conducted on these typical deposits.

III. CHEMISTRY OF SILICON NITRIDE DEPOSITION

Amorphous silicon nitride for semiconductor applications has been made by CVD for a number of years, but it has not been until recently that attention has been directed towards making dense, crack free, free standing or coated bodies of crystalline CVD silicon nitride.

As experienced by various investigators of silicon nitride, this process is more complicated than most other CVD processes due to the fact that a series of solid intermediate complexes form immediately upon mixing the SiCl_4 and NH_3 . This is in contrast to other CVD systems where a gas phase reaction or decomposition of the reactive species takes place directly.

According to Nihara and Hirai¹ the sequence of steps proceeds in the following manner:



It could thus be deduced that these intermediate imides such as $\text{Si}(\text{NH})_2$ have important bearing on the morphology and character of the deposit. Billy² has suggested that the formation of three dimensional polymeric species based on monomer $\text{Si}(\text{NH})_2$ may account for varying crystallite sizes

or the presence of random large crystals in certain deposits. Such a supposition is not inconsistent with the theory of CNTD in which it is believed that deposition occurs via an intermediate compound. It has been hypothesized that an apparently extremely low vapor pressure polymeric liquid may be deposited which subsequently is thermochemically converted to the final product.³ As a result even at high temperatures which favor crystallization, a vitreous material may be formed.

At Chemetal, efforts have been directed towards controlling the formation of Si(NH) nuclei in such a manner that they deposit and crystallize on the substrate before having sufficient time to grow in the gas stream. It is expected that the ultimate crystal size will be smaller if the size of the imide precursor nuclei can be reduced.

IV. EXPERIMENTAL RESULTS: PROCESS EVALUATION AND DISCUSSION

The following deposition parameters and conditions were studied with the intention of controlling the microstructure of the deposit. Tables I and II give some typical deposition parameters and refer to Figures 6 through 13 which show the microstructure encountered.

1. Effect of Total Pressure: Runs were conducted at various pressures from 20 torr to 500 torr. Smooth regular crystalline deposits were obtained in the range 40-60 torr. At higher pressures deposits tended to be coherent but amorphous in nature. This effect might be explained by correlating the increase in pressure with an increase in the frequency with which gaseous imide species collide and grow, and they, in turn, deposit on the substrate at a rate faster than the rate at which crystallization can take place.

Low pressure (< 30 torr) was rather difficult to maintain because of the adverse effect of solid by-products in the exhaust. At higher pressures, around 400-500 torr, rate of deposition was quite high (250-300 microns/hr), as compared to rates at 30 torr of approximately 100 to 150 microns/hr. Essentially our results compared well with tests conducted by Nihara and Hirai¹ on the effects of total pressure on the CVD of Si_3N_4 .

2. Part Temperature: This is the single most influential parameter controlling the phase of the deposit. Irrespective of other parameters, relatively fine grained crystalline deposits were obtained at 1380°C and -40 torr pressure whereas, at higher temperatures, the deposit tended to be coarse columnar and at temperatures below 1250°C all deposits were amorphous. Between 1250°C and 1380°C the deposit tended to be either amorphous or crystalline or a mixture of both depending on other process parameters involved, i.e. $\text{SiCl}_4/\text{NH}_3$ partial pressure, gas preheat temperature and total pressure.

Figure 3 shows the combined effect of total pressure and part temperature on the morphology of Si_3N_4 . At both high temperature ~1600°K (~1327°C) and pressures (~400mm/Hg) a mixture of amorphous and crystalline deposits is obtained. Crystalline deposits are favored at low pressures, and for a particular range of temperature and pressure it is possible to get fine columnar deposit and/or coherent banded amorphous deposit, as designated by the shaded area. At temperatures >1650°K (>1377°C) deposits were rough and whiskers were obtained. Most of the work was concentrated

in the shaded area of Figure 3 because those deposits consistently yielded good strengths.

3. Gas Preheat Temperature: Work done at Chemetal on CNTD silicon carbide⁸ pointed out the considerable influence of gas preheat temperature on the properties of resultant deposits. During the present work on CNTD silicon nitride it does not appear that gas temperature has such an influential effect. Most of the runs, nonetheless, entailed heating the incoming gases for the purpose of i) limiting the formation of low temperature powdery precursor species, ii) improving circulation of gases in the reaction chamber thereby making the gaseous concentration more homogeneous over the length of the chamber. Too high a gas preheat temperature (>700°C) tended to favor formation of amorphous deposits, possibly due to increased rate of collision among the precursor species, excessive rate of deposition, and inadequate conversion to crystalline Si₃N₄.

4. SiCl₄/NH₃ System: The literature (1 thru 6) shows that various reactant gas ratios have been used. Clarke & Popper⁴, for example, used SiCl₄/NH₃ between 1:1 and 1:15. In our work it was preferred to use low ammonia concentrations because it was found that precursor imide formation was minimized making it easier to check temperatures and observe the deposition run through the quartz chamber. Additionally, lower ammonia concentrations tended to slow down the deposition rate (yielding more homogeneous deposits.) Finally, lower ammonia concentrations promote conditions for amorphous deposits near which, it was hoped grain refinement would take place. Mixture ratios were

between 1:1 and 15:1. At high $\text{SiCl}_4/\text{NH}_3$ ratios the deposit favored more crystalline formation, resulting in a rate which was rather low (125 to 200 microns/hr). Deposits exhibited different colors, the majority ranging from brown to black, indicating the possible presence of free silicon. At near 1:1 ratios, the rate was as high as 350 microns/hr. Those few runs conducted with $\text{SiCl}_4:\text{NH}_3$ ratios $>1:1$ tended to produce amorphous deposits, varying from vitreous to powdery and poorly consolidated. At such ratios an abundance of intermediate powdery products collected on the walls of the reaction chamber.

5. $\text{SiHCl}_3/\text{NH}_3$ System: The decomposition of SiHCl_3 takes place more readily than SiCl_4 . For this reason the $\text{SiHCl}_3/\text{NH}_3$ system gave higher rates of deposition using the same parameters as in the $\text{SiCl}_4/\text{NH}_3$ system. At a part temperature of 1420°C , a rate of 350 microns/hr. was achieved. This system tended to produce amorphous deposits at those temperatures at which crystalline deposits would be expected with $\text{SiCl}_4/\text{NH}_3$ system.
6. Hydrocarbon Additions: Propane was used in initial experiments on the effect of hydrocarbon additions to the deposition system. Such additions apparently "laundered" the deposits and produced virtually clear, transparent material. The morphology and structure were different from deposits made without hydrocarbon additions in that the grain sizes were smaller. Further, the grain growth was in a form of fine dense needles rather than a coarse columnar structure. The deposition reactor was notably free of powdery byproducts, enhancing pyrometric measurements, and reducing exhaust line clogging. The deposition rate typically was low (200 microns/hr), which facilitated better control of the process. X-ray diffraction showed these deposits to be $\alpha\text{Si}_3\text{N}_4$ without any evidence

of free silicon or SiC. Stoichiometry measurements indicated near perfect stoichiometry, in fact better than that achieved in earlier tests. Rupture moduli increased, with strengths over 500 MPa consistently attained and some samples exhibiting strengths of over 1000 MPa.

Some preliminary study of possible changes in chemistry as a result of propane addition has been made. One assumption is that propane may serve the function of removing any possible traces of oxygen present in the system, and may thereby influence the deposition mechanism. Such an assumption may be belied however by other work at Chemetal, in which attempts to make siliconoxynitride by CO additions were unsuccessful, producing instead very pure Si_3N_4 . Formations of intermediate complex compounds cannot be ruled out. Further investigation of this possibility is planned.

Figure 4 shows schematically the effect of propane on the morphology of the deposit. It has been observed to broaden the band in which high strength fine grained Si_3N_4 exists. Investigations with other hydrocarbons are scheduled to be conducted in the coming year.

7. Stoichiometry Measurements: Measurements were carried out on a Tracor Northern Energy Dispersive X-ray Spectrometer, at the University of Southern California. A review of Table II indicates most of the samples to be near stoichiometric. Run #539 was an exception, which deposit was 24 weight percent deficient in silicon. As indicated, Run #539 produced an amorphous deposit, which might be assumed to contain unconverted intermediate species.

V. PROPERTY CHARACTERIZATION

Table II briefly summarizes the physical properties of some typical deposits. The following descriptions indicate equipment and procedures used.

1. X-ray Diffraction: A G.E. X-ray Diffractometer was used for this analysis. CuK_α with a Ni filter was used. The time constant was 2, with range of 1000 C.P.S. Most of the deposits showed some preferred orientation which varied with deposition conditions. All crystalline X-ray peaks obtained match with ASTM card 9-250 for a hexagonal Si_3N_4 , however intensities varied considerably. See Figure 5 for a comparison of diffractometry data on runs #289, 495, 504, and 539.
2. Scanning Electron Microscopy: A Cambridge Stereo Scan S4-10 was used for SEM. Figures 6 through 14 show typical morphologies of amorphous and crystalline Si_3N_4 deposited under different conditions.
3. Rupture Strength: Room temperature modulus of rupture measurements were carried out on a Comten 3 point bend test machine. The span used was 14.3 mm. Specimens were approximately 1.8 mm diameter x 50.0 mm long deposited on 0.5 mm diameter tungsten wire.
4. Microhardness: Using a Leitz Microhardness tester, typical hardnesses were determined to be in the range of 2500-3200 $\text{Kg/mm}^2\text{HV}_{500}$. Isolated values over 3800 $\text{kg/mm}^2\text{HV}_{500}$ were recorded.
5. Fracture Toughness Measurements: The critical stress intensity factor K_{Ic} was deduced from the indentation fracture information obtained

from use of a Leitz microhardness indenter by measuring the crack extension which occurs from the corners of a Vickers diamond impression ¹⁰. Typical values for critical stress intensity factors for various deposits of Si₃N₄ have been summarized in Table I. Values as high as 6.9 MPa√m have been achieved with typical values averaging 4.5 MPa√m. See Figure 14 for a micrograph of a typical indent.

6. Oxidation Resistance: Oxidation tests were carried out at Stanford Research Institute by Dr. D. D. Cubicciotti, and Dr. K. L. Lau under SRI's contract No. F44620-76-C-0116 with AFOSR. These tests were conducted at 1450°C for four hours. The weight gained was measured to be 0.099 mg/sq. cm.

V. CONCLUSIONS

1. Fine grained alpha silicon nitride of near total transparency with a composition close to stoichiometric can be made.
2. Rupture strengths of 550 MPa combined with fracture toughness values from 3-5 MPa√m and hardness values between 2500 and 3500 HV₅₀₀ can be regularly achieved.
3. Higher rupture strengths and fracture toughness values (circa 1000 MPa and 7.0 MPa√m) appear to be obtainable.
4. Substrate temperature and total pressure have the most significant influence on the type of deposit produced, i.e. crystalline or amorphous.

5. Measurable improvement in high temperature oxidation behavior versus hot pressed silicon nitride may be anticipated.
6. Small partial pressure additions of hydrocarbons to the reactant stream can influence the microstructure of the deposit, i.e. grain size and morphology.
7. A fine grain structure approaching the structure of CNTD materials has been achieved. However, additional work is required to refine grain size while maintaining acceptable cohesive strength in such deposits. It is possible that this will be accomplished by deposition at higher temperatures along with compensatory changes in other deposition parameters.

VI. RECOMMENDATIONS FOR FUTURE WORK

Considerable progress has been made, as a result of the work conducted on this program, on the refinement of the grains in chemically vapor deposited alpha silicon nitride. It has been demonstrated that the mechanical properties can be improved by reducing the grain size of the deposit. It was interesting to note that some deposits were translucent approaching transparency. Fracture toughness values, hardness, and oxidation resistance of the deposits all appear favorable. In light of these results the following future work is recommended:

1. Experiments to further refine grain size beyond that shown in Fig. 11 and 12 should be continued with particular emphasis on those conditions which produce submicron grains. Adjustments in the chemical system

should be made, which will allow such submicron grains to be formed at more elevated temperatures, thereby to produce the CNTD structure.

2. An effort should be made to characterize and improve the translucent deposits observed during the current project. Even though mechanical properties may not be optimized, there is clear potential for development of a material for use in E/O applications.
3. The effect of dilute concentrations of additive species in the reactant gas stream should be assessed as a method for grain refinement.
4. Alternate nitrogen-containing reactants should be investigated.
5. Uniformity of deposits of silicon nitride on more extended surfaces should be investigated.
6. A rigorous study of residual stresses in the deposited material and their relationship to fracture toughness and room temperature and high temperature strength should be considered.

VII. APPENDIX: ASSOCIATED STUDIES

Work is being conducted at Chemetal on silicon based ceramics for various applications. Considerable effort has been devoted to understanding the CNTD mechanism as it applies to silicon carbide under contract to the Air Force Office of Scientific Research. Insight into CNTD silicon nitride has been gained as a result of these investigations since the reactant systems are similar in certain respects.

Investigations of CNTD silicon nitride have impacted work conducted for NASA-JPL on the low cost silicon solar cells program. Silicon nitride, silicon carbide, aluminum nitride, and mixtures of Sialon materials are being evaluated for use as die and container materials for fabrication of silicon solar cells. Initial tests indicate that CNTD silicon nitride and silicon carbide are very stable in contact with molten silicon.

Recently, a program to study methods for applying uniform silicon nitride deposits on complex shapes was initiated under contract to the Air Force Materials Laboratory. It is anticipated that in conjunction with the continued study of the mechanism of CNTD silicon nitride important advances will be made.

Some distribution to the U.S. Technical Community of the information generated directly and indirectly from this program has already taken place. A brief reference to the results was made in the September, 1977 meeting of the Electrochemical Society in the following paper:

"Grain Refinement by Thermochemical Means," R.A. Holzl³

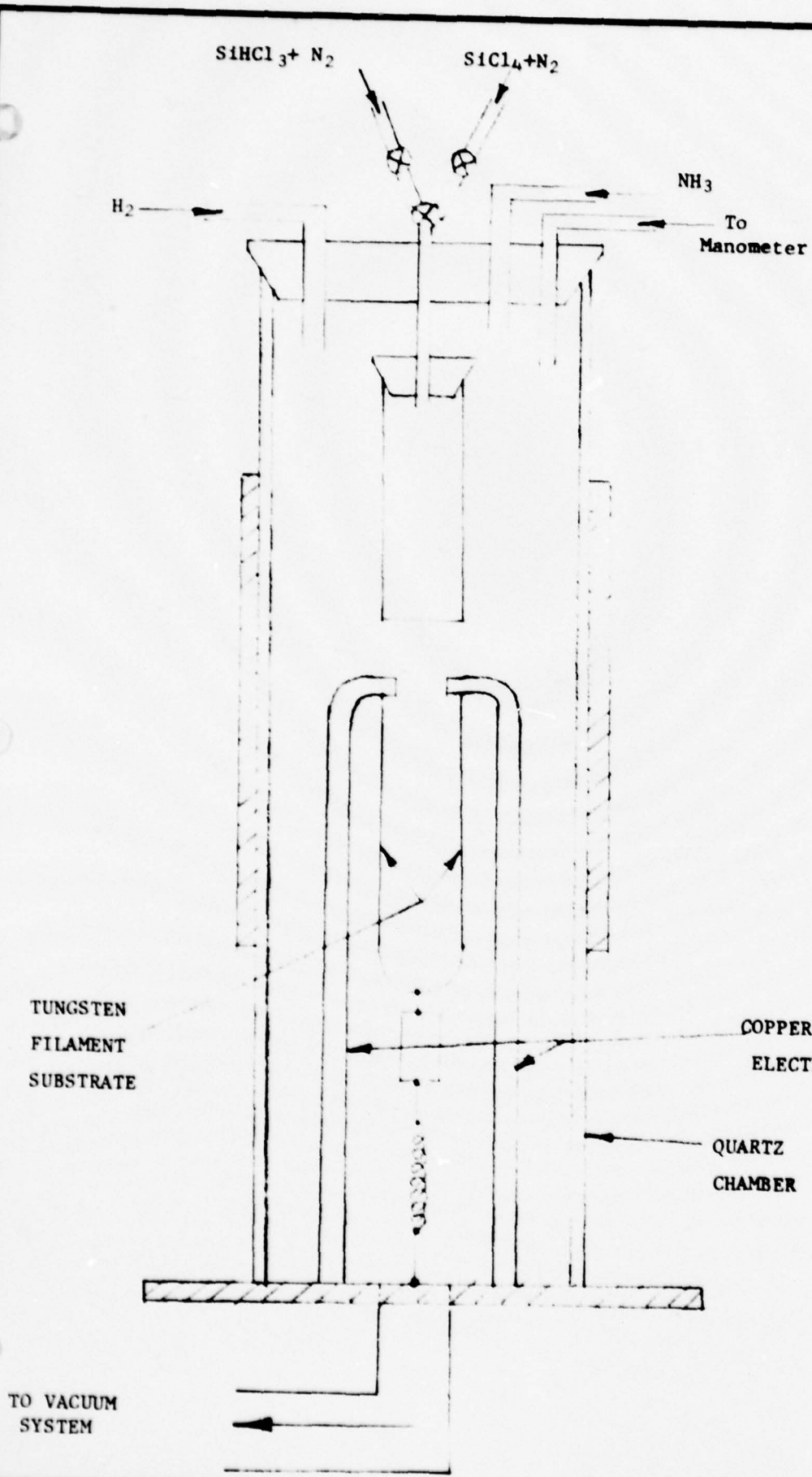
In addition, a review of outside laboratory evaluation of silicon carbide specimens produced in part on the AFOSR program was presented at The American Ceramic Society 80th Annual Meeting and Exposition, May, 1978, Detroit, Michigan in the following paper:

"Characterization and Properties of Controlled Nucleation Thermochemical-Deposited SiC," S. Dutta, NASA-Lewis; R. Rice, NRL; H. Graham, AFML; M. Mendiratta, Systems Research Lab.

Additional information presentation is planned for a paper to be given at:
The American Ceramic Society Regional Meeting, October, 1978 in San Diego, CA
entitled:

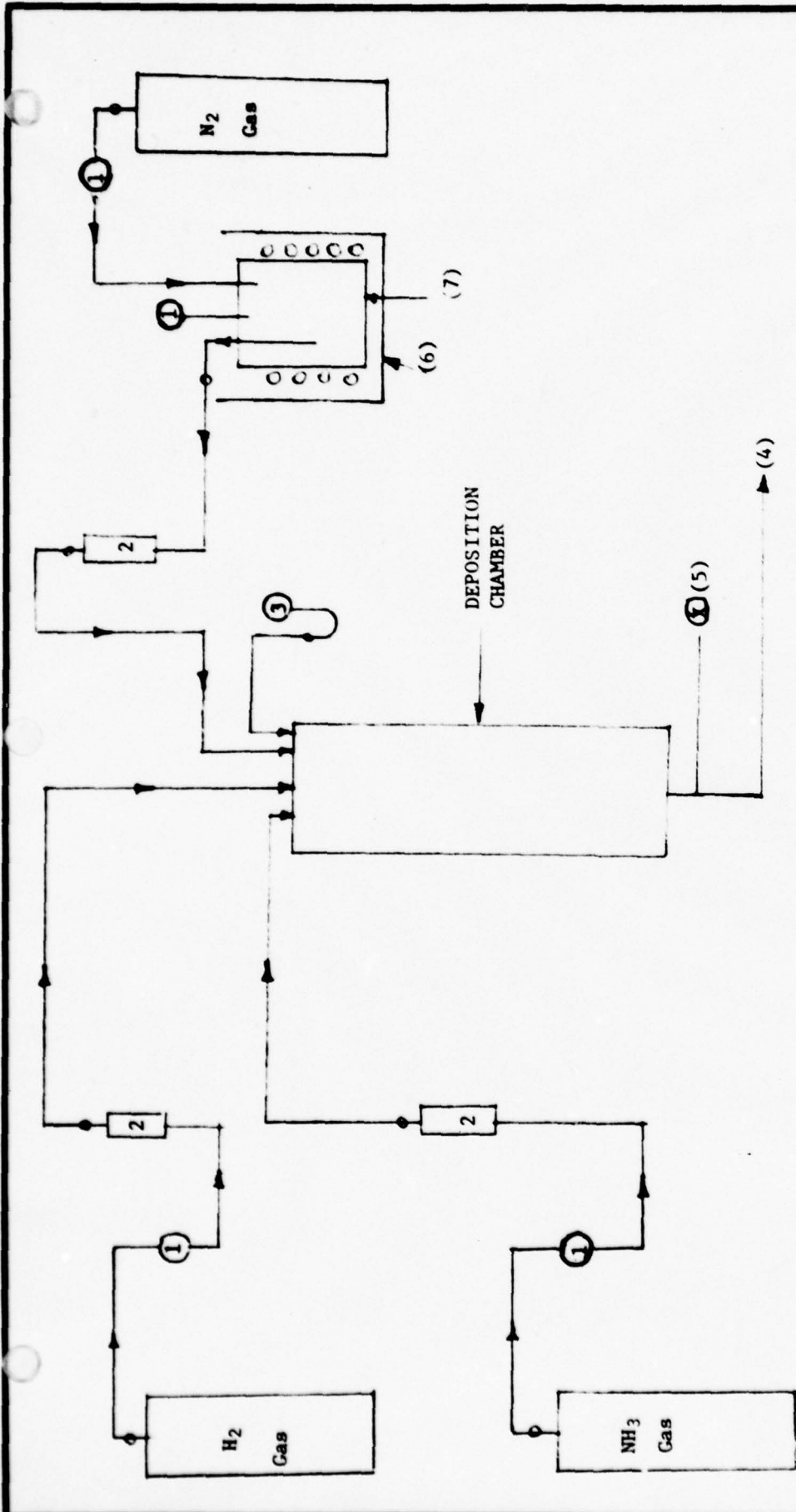
"Fabrication of Ceramics by Controlled Nucleation Thermochemical
Deposition (CNTD)," R.A. Holzl and B. G. Zealear.

1. K. Nihara and T. Hirai, J. Mat. Sci., 12 (1977), 1243-1252.
2. M. Billy, Bull. Soc. Chim. (France), 1960, 1653-54.
3. R. A. Holzl, "Grain Refinement by Thermochemical Means' Proceedings of the Sixth International Conference on Chemical Vapor Deposition 1977, Proceedings Volume 77-5, the Electrochemical Society, Inc. P.O. Box 2071, Princeton, N. J. 08540.
4. A.O. Airey, S. Clarke and P. Popper, Trans. Brit. Ceram. Soc., 22, 1973, 305-320.
5. J. J. Gebhardt, R. A. Tanzilli, and T. A. Harris, J. Electrochem. Soc., 123, (10), 1976, 1578-83.
6. K. S. Mazdidasni and C. M. Cooke, J. Amer. Ceramic Society, 55, (8), P. 431 (1972).
7. C.V.D. of Si_3N_4 , Summary Report, General Electric Document #775DR2257.
8. Investigation of CNTD Mechanism and Its Effect on Microstructural Properties, Robert A. Holzl, Chemetal Corp., CA 91331. AFOSR Contract F49620-77-C-0086.
9. Svante Prockazka and Charles Greskovich, (579) Ceramic Society Bulletin, June, 1978.
10. A. G. Evans and E. A. Charles, J. Amer. Ceramic Society 59 (7-8), 371, (1976.)



| REVISIONS | | FIGURE 1 SCHEMATIC Si_3N_4 SYSTEM | | CHEMETAL CORPORATION | |
|-----------|------|--|-------|----------------------|----------|
| NO. | DATE | BY | SCALE | DRAWN BY | MATERIAL |
| 1 | | | | SAM | |
| 2 | | | | CHK'D | |
| 3 | | | | | |
| 4 | | | | | |
| 5 | | | | | |

| | |
|-------------|-----------------|
| DATE | 7/31/78 |
| APP'D | |
| DRAWING NO. | C/F 4-14 (9-78) |



- (1) Pressure Gauges
- (2) Flowmeter
- (3) Manometer
- (4) Exhaust Pump
- (5) Pressure Regulator
- (6) Constant Temp. Bath
- (7) SiCl₄ Reservoir

| REVISIONS | | FIGURE 2 LINE DIAGRAM FOR Si ₃ N ₄ SYSTEM | | | |
|-----------|------|--|-------|----------|--|
| NO | DATE | BY | SCALE | MATERIAL | |
| 1 | | | | | |
| 2 | | | | | |
| 3 | | | | | |
| 4 | | | | | |
| 5 | | | | | |

| | | | |
|-----------------|--|-----------------|--------------------------------|
| DRAWN BY SAM | | SCALE | MATERIAL |
| CHK'D | | DATE 7-31-78 | DRAWING NO. C/F 4-15 (9-78) |
| TRACED | | APP'D | |

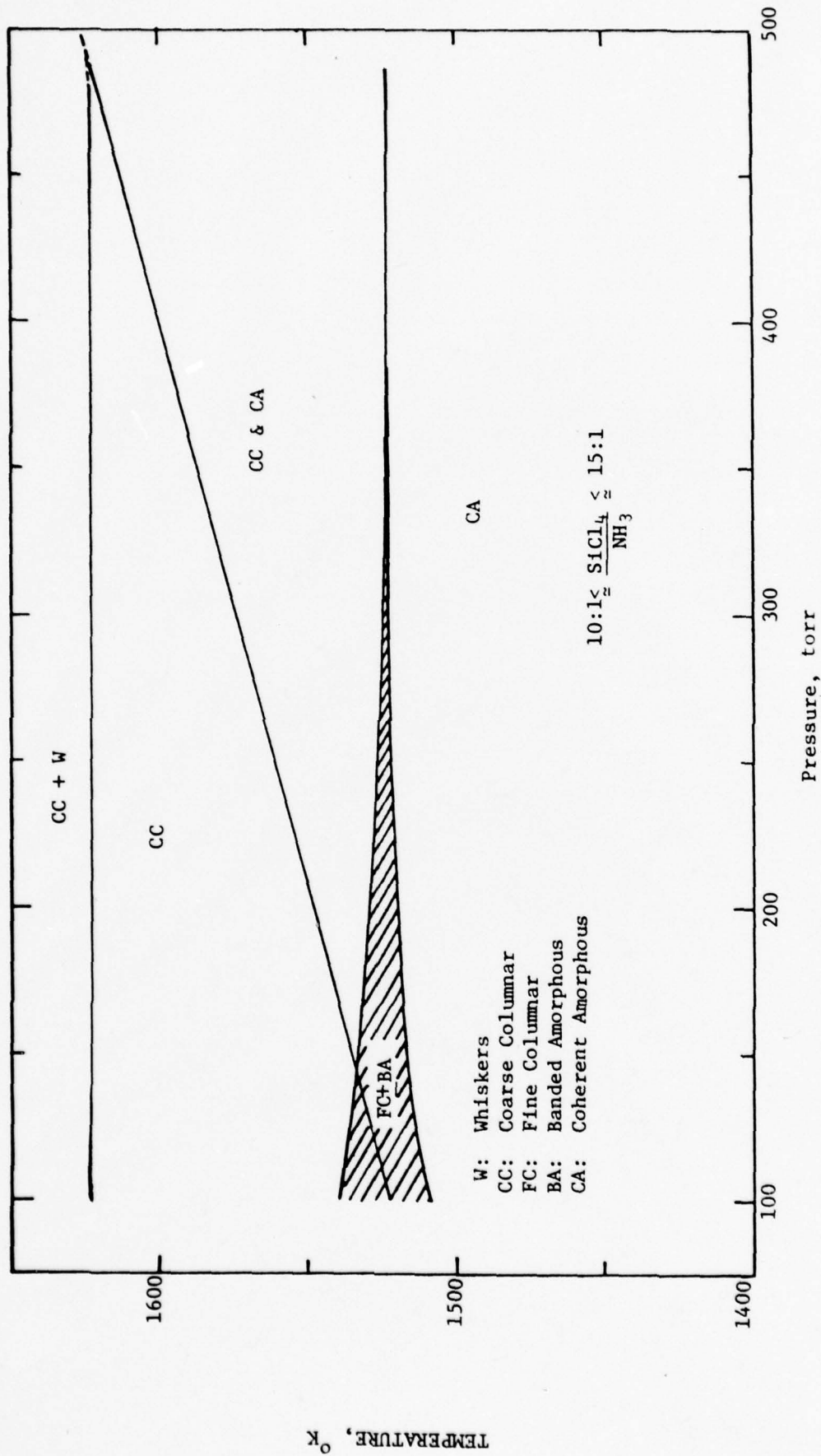


Figure 3 Pressure-temperature diagram for $SiCl_4/NH_3$ system showing various types of deposits formed at high total pressure.

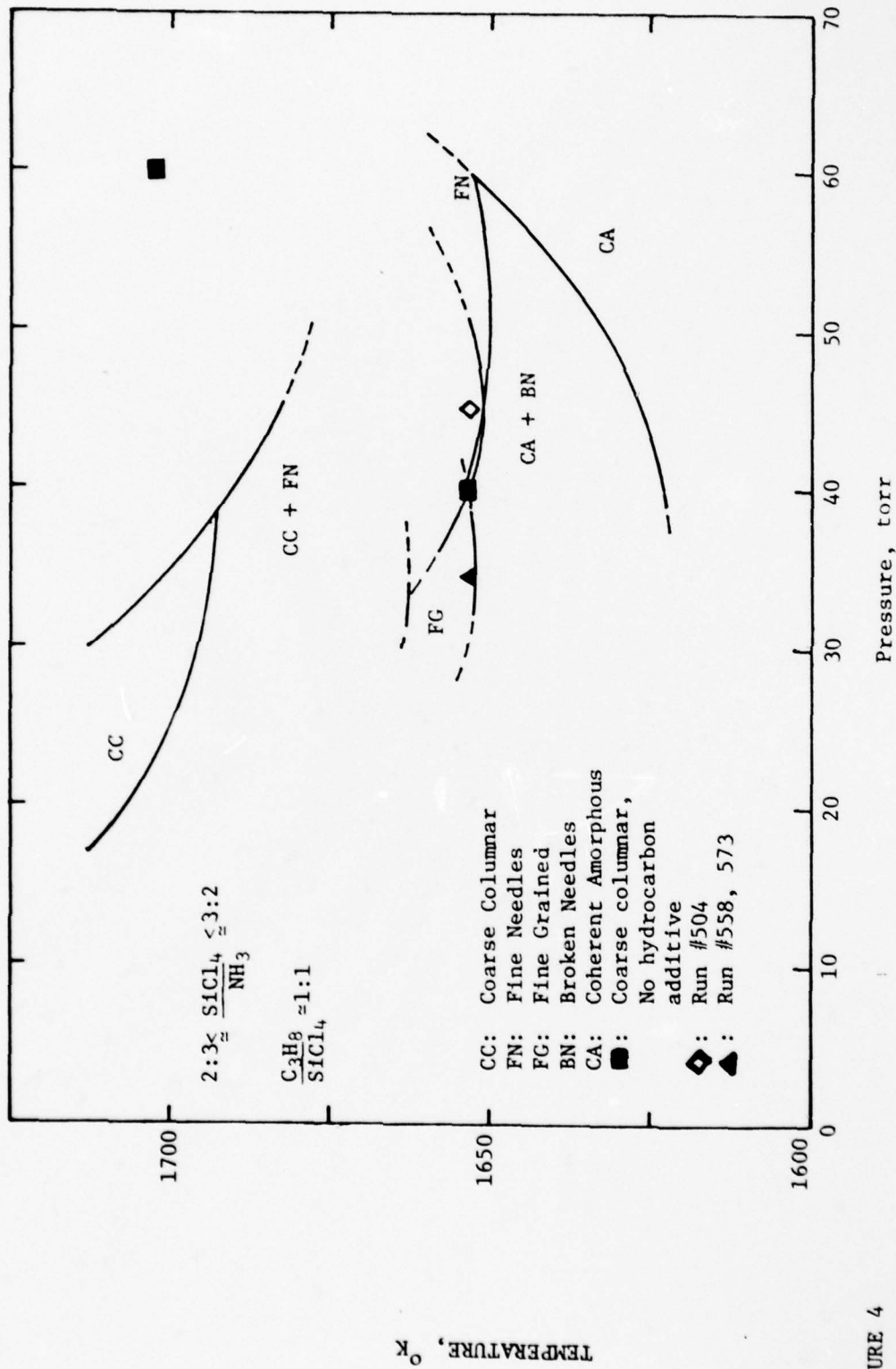
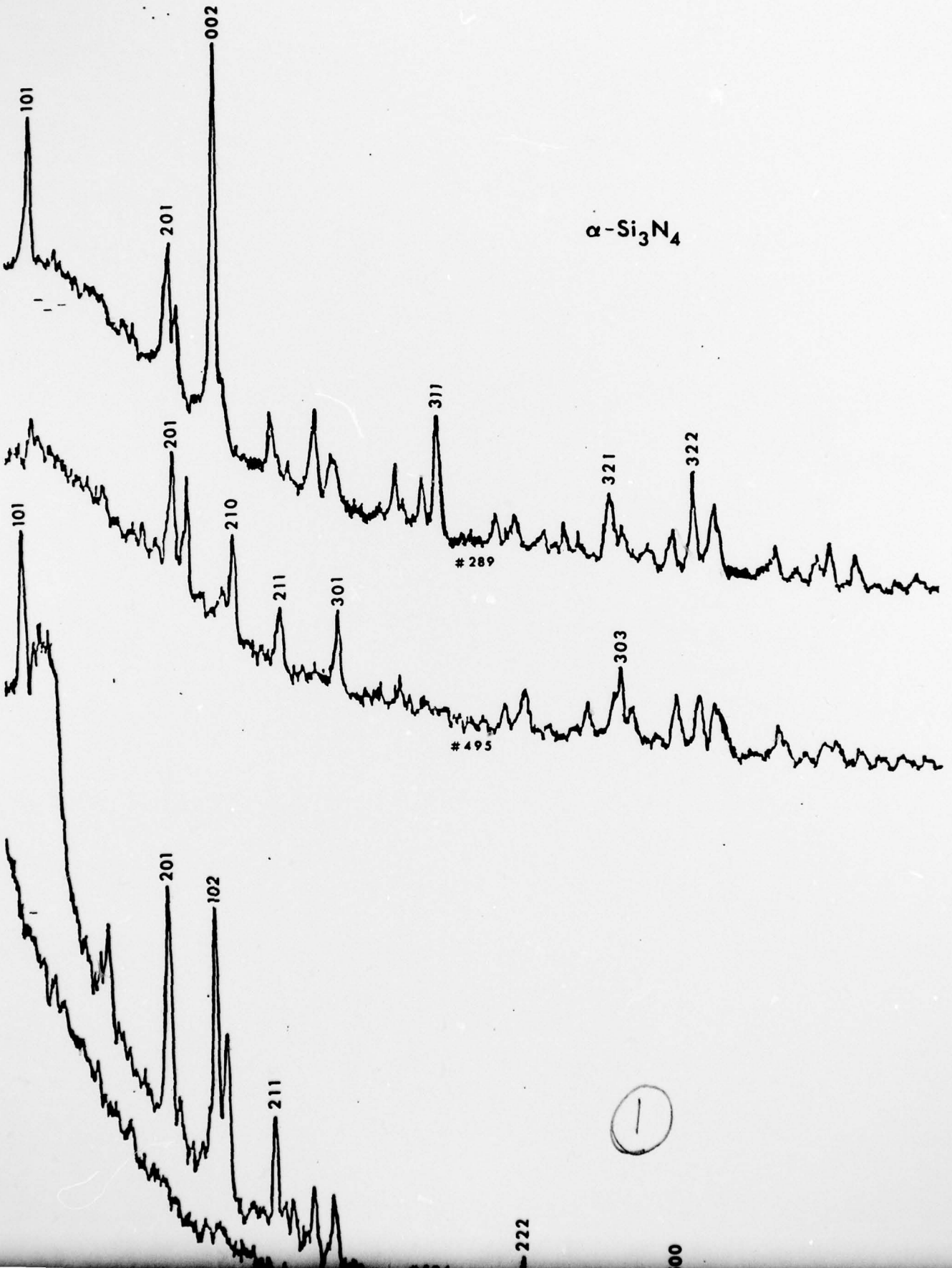
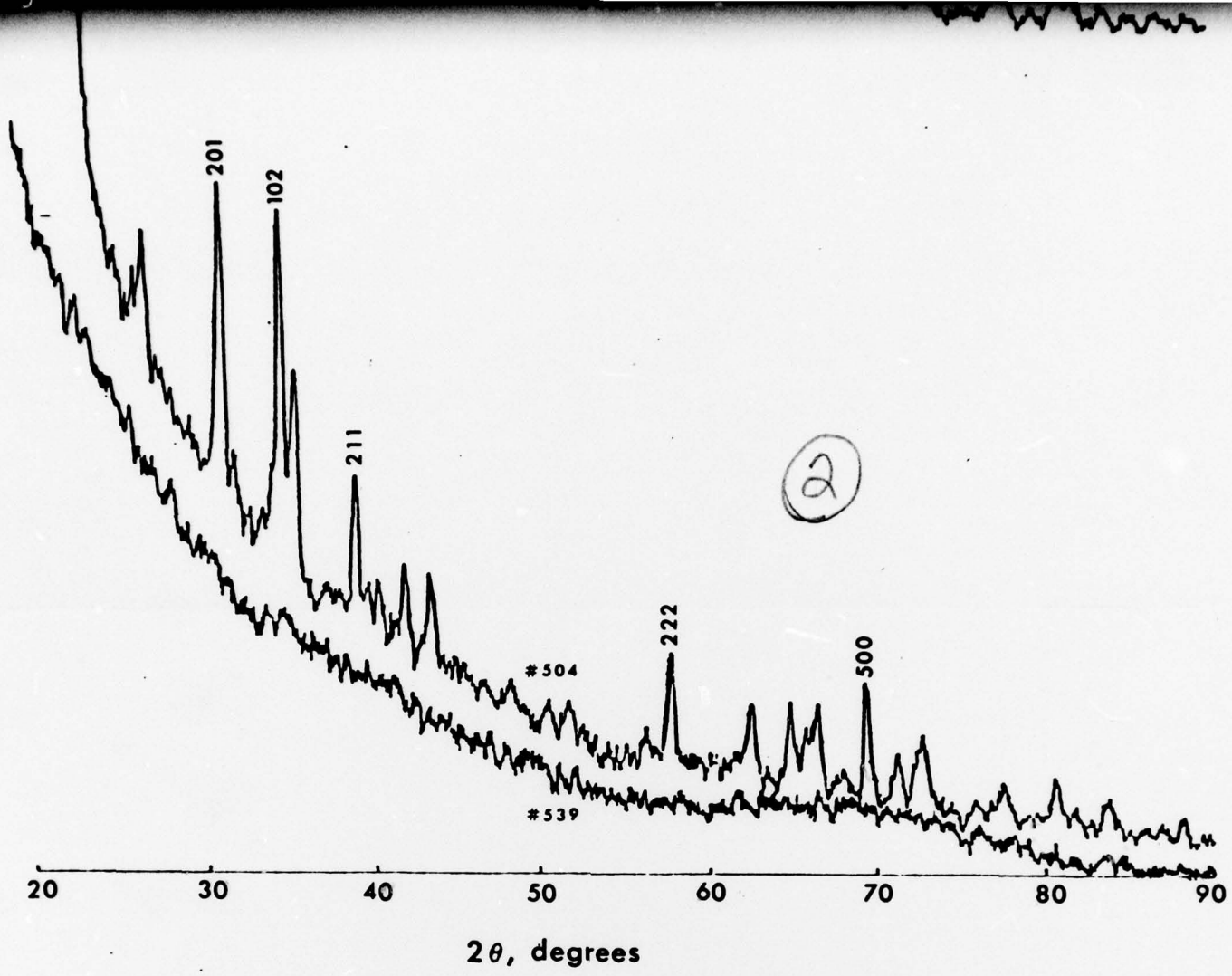


FIGURE 4

Pressure-temperature diagram for $\text{SiCl}_4/\text{NH}_3$ system showing the effect of hydrocarbon addition on the nature of deposit.

FIGURE 5





2θ , degrees



FIGURE 6.a. MAG. 70X
SURFACE TOPOGRAPHY OF AN AMORPHOUS DEPOSIT, CRACKS CAN BE SEEN.

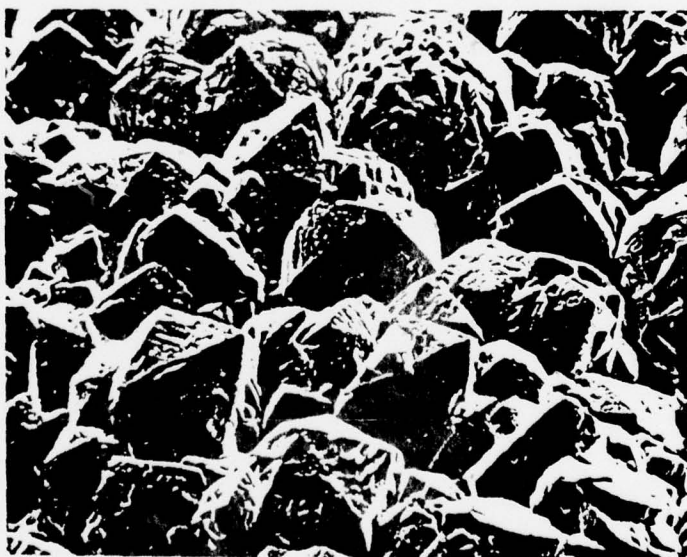


FIGURE 6.b. MAG. 26X
CRYSTALLINE DEPOSITS WITH ROUGH BOTRYOIDAL SURFACE. SMALL CRYSTALLITE GROWTH ON SOME BOTRYOIDS CAN BE SEEN.

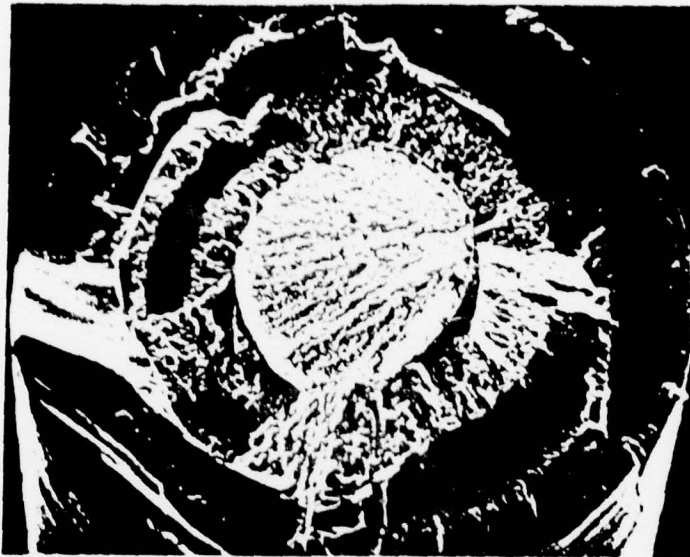


FIGURE 7.a. Run #553 MAG. 75X

CROSS SECTION OF A LAYERED DEPOSIT, HAVING A GLOSSY APPEARING OUTER REGION.

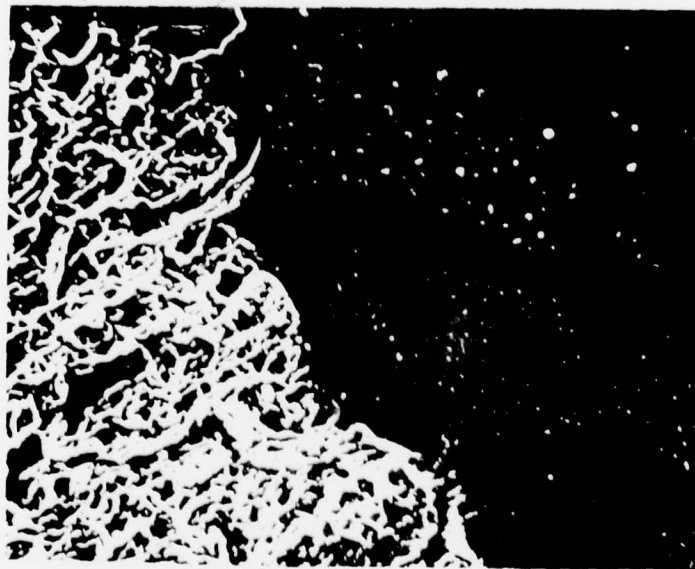


FIGURE 7.b. MAG. 730X

A MAGNIFIED VIEW OF THE ABOVE FIGURE SHOWING TRANSITION REGION.

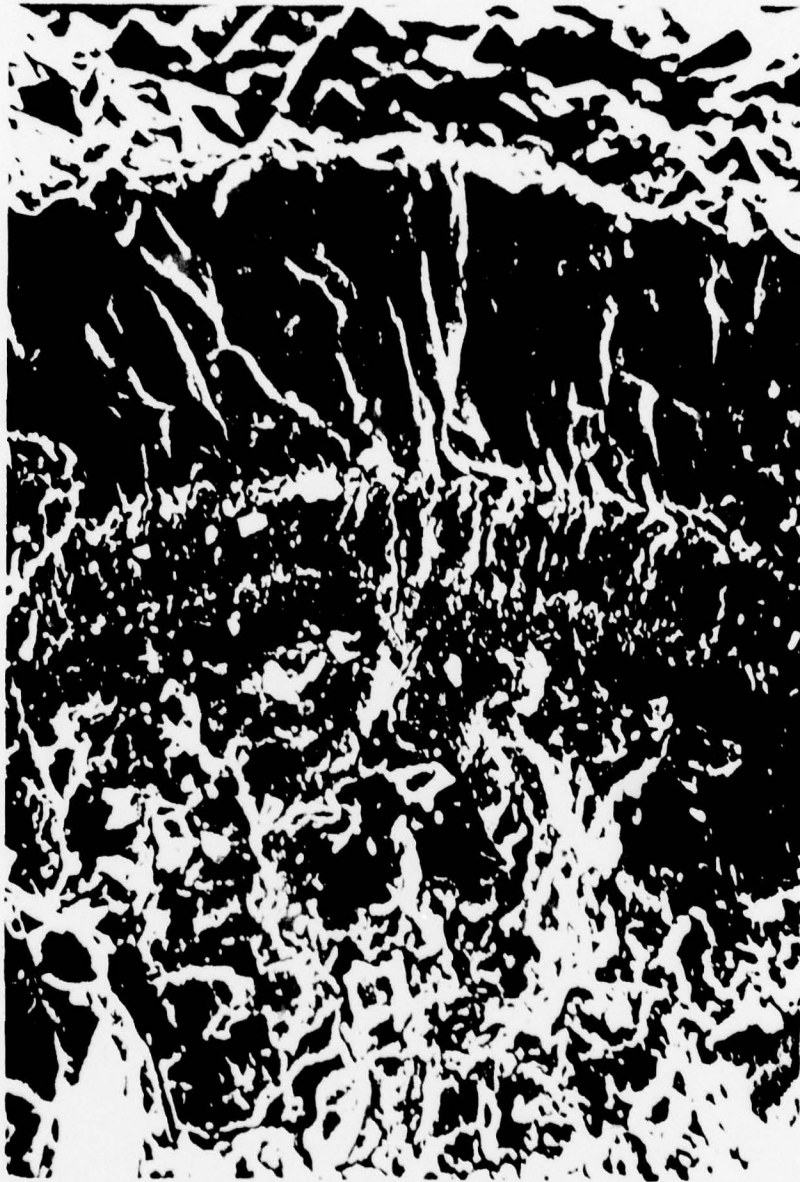


FIGURE 8 .

MAG. 1850X

CROSS SECTIONAL VIEW OF A DEPOSIT SHOWING AMORPHOUS TYPE OF GROWTH ON I.D. WITH A TRANSITION ZONE IN BETWEEN AND A COLUMNAR TYPE GROWTH, ON THE O.D.

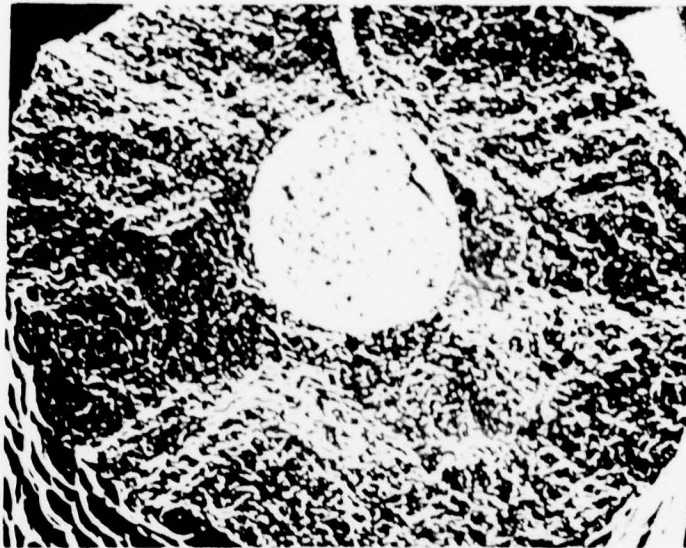


FIGURE 9.a. Run #539 MAG. 66X

CROSS SECTIONAL VIEW OF AN AMORPHOUS DEPOSIT. SURFACE IS BOTRYOIDAL.

FIGURE 9.b. MAG. 1625X

MAGNIFIED VIEW OF ABOVE FIGURE, SHOWING BIG BLOCKY LOOKING AMORPHOUS STRUCTURE.

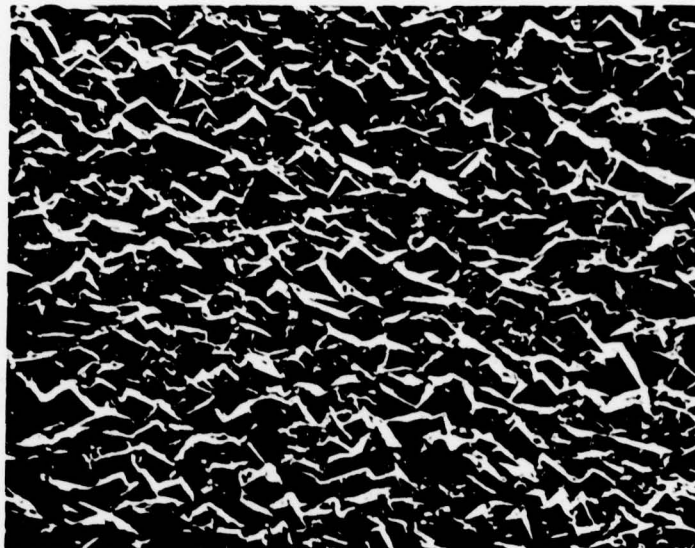


FIGURE 10.a. Run #256 MAG. 260X
SURFACE TOPOGRAPHY OF A CRYSTALLINE DEPOSIT.

FIGURE 10.b. MAG. 630X
CROSS SECTIONAL VIEW OF THE ABOVE DEPOSIT SHOWING LONG COLUMNAR GROWTH.

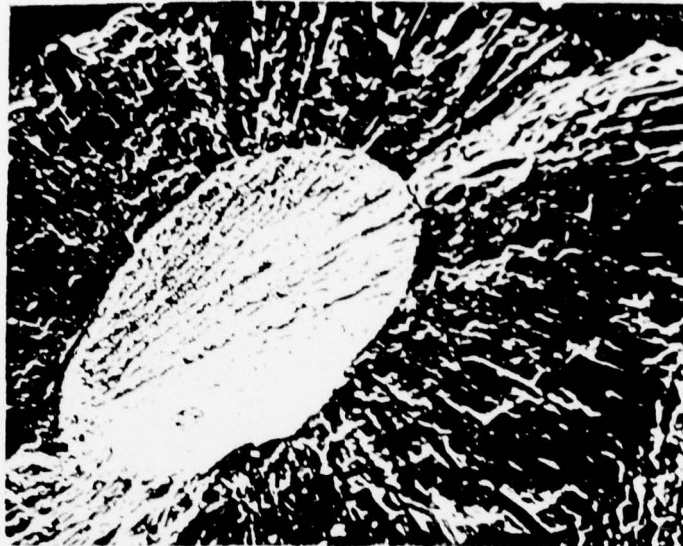


FIGURE 11.a. Run #504 MAG. 125X

CROSS SECTIONAL VIEW SHOWING FINE NEEDLE LIKE GROWTH PATTERN.



FIGURE 11.b. MAG. 625X

HIGHER MAGNIFICATION OF THE ABOVE FIGURE SHOWING CLEARLY NEEDLE TYPE CRYSTALLITES RADIATING OUT. CRYSTAL SIZE IS CONSIDERABLY SMALLER THAN THAT OF COLUMNAR GROWTH OF RUN #256. (REFER TO FIGURE 10).

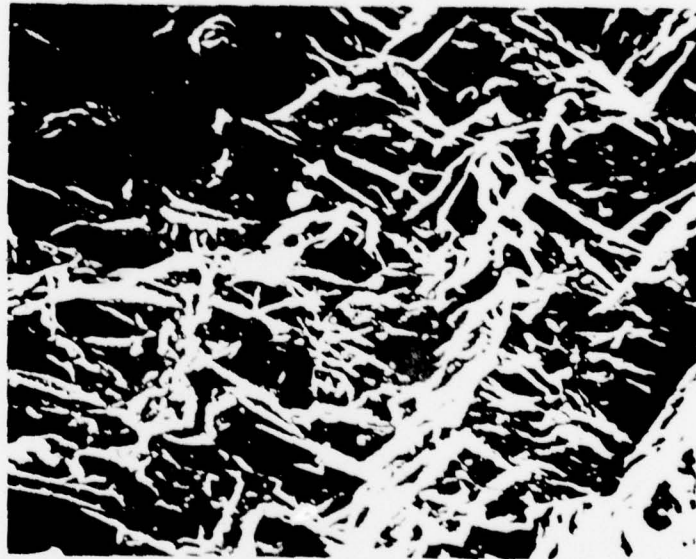
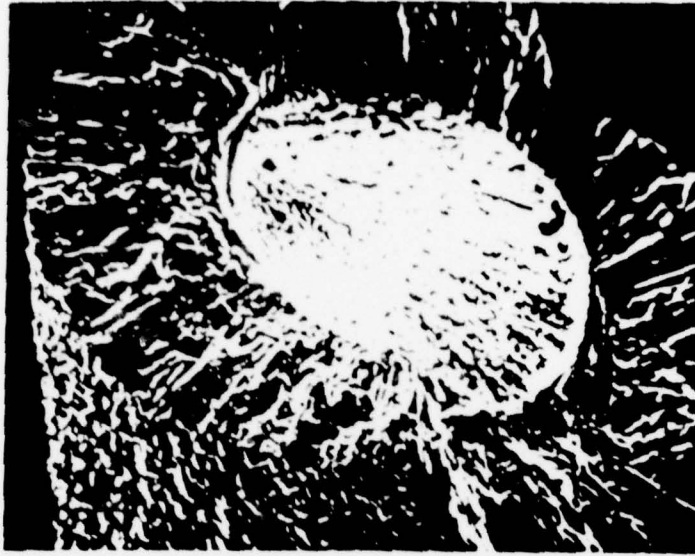


FIGURE 12.a. Run #573 MAG. 115X

CROSS SECTIONAL VIEW SHOWING SIMILAR NEEDLE TYPE OF GROWTH AS IN FIGURE 11.a.

FIGURE 12.b. MAG. 1040X

HIGHER MAGNIFICATION OF ABOVE FIGURE SHOWING NEEDLE GROWTH IS INTERRUPTED, TO GIVE A BROKEN UP NEEDLE APPEARANCE.



FIGURE 13.a. MAG. 1600X

SURFACE TOPOGRAPHY OF A TYPICAL CRYSTALLINE DEPOSIT WITHOUT ANY HYDROCARBON ADDITIONS.



FIGURE 13.b. MAG. 250X

LONG WHISKER LIKE HEXAGONAL CRYSTALLINE GROWTH. TYPICAL OF A HIGH TEMPERATURE DEPOSIT. ($\sim 1500^{\circ}\text{C}$)

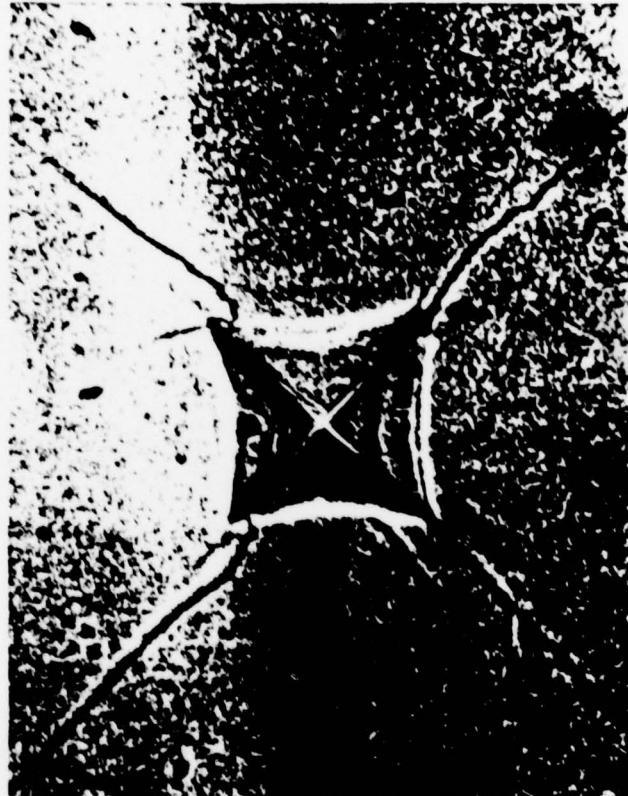


FIGURE 14.

FRACTURE TOUGHNESS MEASUREMENT BY INDENTATION.

TABLE I SUMMARY DATA OF SOME TYPICAL RUNS SHOWING FLOW CONDITIONS AND TYPE OF DEPOSITS OBTAINED

| FIG. # | * RUN # | PRESS. TORR | PART T °K | Gas T °K | Ar | SILICON SOURCE | NH ₃ | H ₂ | C ₂ H ₂ | COMMENTS |
|--------|---------|-------------|-----------|----------|---------|------------------------|-----------------|----------------|-------------------------------|---|
| 10.a. | 256 | 62 | 1653 | 873 | 1500 cc | SiCl ₄ 140 | 150 cc | 800 cc | - | Blue smooth crystalline deposit: cross section has columnar grains. |
| 10.b. | | | | | | | | | | |
| - | 276 | 80 | 1653 | 873 | 1500 cc | SiCl ₄ 140 | 150 cc | 800 cc | - | Smooth crystalline deposit. Cross section is columnar. |
| - | 289 | 55 | 1700 | 873 | 1500 cc | SiCl ₄ 140 | 150 cc | 800 cc | - | Smooth bluish crystalline deposit with columnar growth |
| 11.a. | 504 | 45 | 1653 | 573 | 1500 cc | SiCl ₄ 140 | 150 cc | 800 cc | 190 cc | Very smooth translucent white deposit. Cross section has thin columns, looks like thin needles radiating out. |
| 11.b. | | | | | | | | | | |
| 9.a. | 539 | 60 | 1653 | 1023 | 1500 cc | SiHCl ₃ 162 | 68 cc | 800 cc | 300 cc | Black Botryoidal deposit. Cross section has big equiaxed amorphous structure. |
| 9.b. | | | | | | | | | | |
| 7.a. | 553 | 40 | 1623 | 898 | 2000 cc | SiHCl ₃ 162 | 35 cc | 800 cc | - | Deposit is yellow crystalline having columnar growth, top 1" of deposit is smooth white fine grained. Cross section shows smooth glassy appearance with amorphous layer on I.D. |
| 7.b. | | | | | | | | | | |
| - | 558 | 35 | 1653 | 573 | 1500 cc | SiCl ₄ 140 | 85 cc | 800 cc | 214 cc | Smooth white deposit. Cross section has fine columnar grains. |
| 12.a. | 573 | 35 | 1653 | 838 | 2000 cc | SiCl ₄ 280 | 175 cc | 2500 cc | 330 cc | Smooth deposit. Cross section shows few of the columnar broken up grains. |
| 12.b. | | | | | | | | | | |

TABLE I SUMMARY DATA OF SOME TYPICAL RUNS SHOWING FLOW CONDITIONS AND TYPE OF DEPOSITS OBTAINED

Continued

| FIG. # | Run # | PRESS TORR | PART T °K | GAS T °K | AR | SILICON SOURCE | NH ₃ | H ₂ | C ₃ H ₈ | COMMENTS |
|--------|-------|---------------|--------------|-------------|------|--------------------------|-----------------|----------------|-------------------------------|---|
| 13.b. | 249 | 60 | 1773 | 873 | 2000 | 280 SiCl ₄ | 175 | 800 | — | Long hexagonal whisker growth. Typical of high temperature characteristic. |
| 6.b. | 288 | 60 | 1573 | 873 | 1500 | 280 SiCl ₄ | 175 | 800 | — | Surface has rounded botryoids and numerous, small crystals sticking out from surface of the botryoids. |

* NOTE Run numbering system is chronological for a given experimental station. Thus, run numbers do not start from 1 at the beginning of a program nor end with that program.

TABLE II SUMMARY DATA OF PROPERTY EVALUATION OF TYPICAL DEPOSITS

| FIG. # | * RUN # | EDA | HARDNESS HV _{5.0} VHN Kg/mm ² | FRACTURE TOUGHNESS K _{IC} MPa√m | M.O.R. MPa | X-RAY DIFFRACTION | MORPHOLOGY |
|--------|---------|--------------------|--|--|--------------------|---|--|
| 6.a. | 504 | 0.08% excess Si | 2940 | 3.5 | 614 1076 642 | αSi ₃ N ₄ | V. smooth translucent deposit. Cross section has dense fine columnar grains. |
| 6.b. | | | | | | | |
| -- | 558 | 0.75% less Si | 2610 | 4.7 | ≈ 482 | αSi ₃ N ₄ | V. smooth white deposit. Cross section had fine columnar grains. |
| 7.a. | 553 | - | 2360 | 3.7 | 345 421 | αSi ₃ N ₄ + amorphous | Smooth white deposit - cross section is columnar. Top 1" is fine grained and glassy fracture with amorphous deposit on ID. |
| 7.b. | | | | | | | |
| -- | 289 | 2.5% less Si | 2834 | 2.9 | 310 | αSi ₃ N ₄ | Deposit - dark in color is crystalline. Cross section is big columnar grains. |
| 9.a. | 539 | **24% less Si | 2300 | - | - | Amorphous | Black botryoidal deposit is smooth. Cross section has big shiny blocky amorphous structure. |
| 9.b. | | | | | | | |

* See Note, Table I

** The deficiency in Si is discussed in the discussion of results.