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DEVELOPMENT AND EVALUATION OF DIE AND CONTAINER MATERIALS

Second Quarterly Progress Report, January 1—March 31, 1978

By
R. R. Wills
D. E. Niesz

April 15, 1978

Work Performed Under Contract No. NAS-7-100-954876

Battelle Columbus Laboratories
Columbus, Ohio

MASTER

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SECOND QUARTERLY PROGRESS REPORT

(Covering the Period January 1, 1978, to March 31, 1978)

on

DEVELOPMENT AND EVALUATION OF DIE AND CONTAINER MATERIALS

JPL Contract No. 954876
Silicon Sheet Task
Low Cost Silicon Solar Array Project

to

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

April 15, 1978

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, under NASA Contract NAS7-100 for the U. S. Department of Energy, Division of Solar Energy.

The JPL Low-Cost Silicon Solar Array Project is funded by DOE and forms part of the DOE Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays.

by

R. R. Wills, Principal Investigator, and D. E. Niesz, Program Manager

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Columbus, Ohio 43201

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ABSTRACT

Initial samples of four silicon aluminum oxynitride (Sialons) ceramics have been prepared from commercial Si_3N_4, Al_2O_3, AlN, and SiO_2 powders by hot pressing at 1750 C. $Si_{1.9}Al_{0.1}N_{1.9}O_{1.1}$, $Si_{1.8}Al_{0.2}N_{1.8}O_{1.2}$, and $Si_{3.6}Al_{2.4}N_{5.6}O_{2.4}$ Sialons were densified to $\geq$90 percent theoretical density, but $Si_{5.4}Al_{0.6}N_{7.4}O_{0.6}$ Sialon could be pressed only to 72 percent theoretical density. None of these materials are single-phase materials; one group of samples contains an unidentified Sialon phase, while the other group contains significant amounts of free elemental silicon. Chlorine in the Si_3N_4 powder and free aluminum in the AlN powder are responsible for these effects.

Initial evaluation of these materials in contact with molten silicon at 1450 C indicates that chemical reaction is occurring. Thin string-like precipitates found in the silicon after reaction with $Si_{3.6}Al_{2.4}N_{5.6}O_{2.4}$ Sialon are considered to be due to the presence of a second phase in the material. Electron probe analysis of silicon in contact with a $Si_{1.8}Al_{0.2}N_{1.8}O_{1.2}$ sample did not detect aluminum in the silicon, but two reaction zones were found at the interface.

Solution thermodynamics studies show that beryllium oxide is much more resistant to attack than aluminum oxide. Fifteen weight percent aluminum dissolved in molten silicon compared with 5000 ppm beryllium. The Henry's Law Constants for oxygen, beryllium, and aluminum at concentrations $\leq$5000 ppm have been determined.

ACKNOWLEDGMENT

The authors gratefully acknowledge the capable assistance of the following individuals in the performance of the work and preparation of this report. Mr. I. Sekercioglu, Mr. M. F. Browning, Mr. W. J. Wilson, Dr. C. A. Alexander, Mr. J. A. Ogden, Mr. A. J. Roese, Mr. P. V. Johnson, Mrs. E. T. Clark, Mrs. D. M. Knight, Dr. J. M. Blocher, Jr., Mr. J. S. Fippin, Mr. R. J. Garrett, Dr. R. W. Kidd, Mr. D. C. Landon, and Mr. K. Newton.

DEVELOPMENT AND EVALUATION OF DIE AND CONTAINER MATERIALS

by

R. R. Wills and D. E. Niesz

INTRODUCTION

The JPL Low Cost Silicon Solar Array Project has been established with the goal of decreasing the cost of solar photovoltaic arrays for electrical power generation. Methods of producing silicon sheet for solar cells are under active development as one of several tasks designed to achieve this objective. In the crystal-growing processes a refractory crucible is required to hold the molten silicon, while in the ribbon processes an additional refractory shaping die is needed to enable silicon ribbon to be produced. In several ribbon processes the high-temperature materials are a limiting factor in the development of the technique.

The objective of this study is to develop and evaluate refractory die and container materials. The performance targets for the die and container materials are given in the statement of work as:

(a) The material must be mechanically stable to temperatures greater than the melting point of silicon (1412 C). Thus, it must not melt or undergo other destructive phase changes below this temperature.

(b) Materials in contact with molten silicon must be dimensionally stable, to 0.5 mil over a 24-hour period in case of dies. This is necessary to maintain dimensional control of the processed silicon strip, and is to include erosion, corrosion, or growth of surface reaction products. With container materials, acceptable reaction rates will be controlled by permissible impurity level.

(c) The die and container material must not excessively contaminate silicon processed through it. Present indications suggest that 10^{15} atoms/cm^3 is an upper limit for general impurities. Exceptions to this are: aluminum, phosphorus, boron, arsenic, and gallium, which may be present 1 or 2 orders of magnitude higher, and carbon, oxygen, and nitrogen, which may be present in amounts dictated by erosion rates (approximately 10^{19} atoms/cm^3). However, revision of these numbers may occur as knowledge of the specific effects of these elements is developed. For example, there are indications that structural imperfections result from carbon levels greater than 1 x 10^{18} atoms/cm^3.

(d) The process or processes developed must be amenable to the fabrication of dies and containers with close tolerances and of varying geometries.

(e) The die to be produced and evaluated on this program shall be capable of producing and maintaining a capillary column of silicon 1 to 3 cm wide x 0.01 cm thick to a height of at least 2.5 cm. Experience with other materials has indicated that a contact angle of less than 80 degrees is required.

This study has been initiated to attempt to meet these requirements. The general approach involves the determination of the solution thermodynamics of several refractory materials in contact with molten silicon, together with the development and assessment of silicon metal oxynitride ceramics.

Four silicon aluminum oxynitride (Sialon) materials will initially be fabricated and assessed as potential dies and containers. These materials are based on two solid solutions of general formulae:

$Si_{6-x}Al_xN_{8-x}O_x$ where $x \leq 4.2$ at 1760 C

$Si_{2-x}Al_xN_{2-x}O_{1+x}$ where $x \leq 0.4$ at 1760 C.

The first material, frequently called β'-Sialon, is a solid solution between β-Si_3N_4 and Al_2O_3, AlN. The second material referred to as O'-Sialon is a solid solution between Si_2N_2O and Al_2O_3.

These materials will be prepared by the following reactions:

(1) $Si_3N_4 + AlN + Al_2O_3 \rightarrow$ β' Sialon

(2) $Si_3N_4 + Al_2O_3 + SiO_2 \rightarrow$ O' Sialon.

In the first 3 months, commercial high-purity Si_3N_4, Al_2O_3, and SiO_2 powders were obtained and analyzed, and mass spectrometric studies of molten silicon in contact with SiO_2 were completed. Initial work on the preparation of high purity ultrafine AlN powder by a chemical vapor deposition process was also performed.

TECHNICAL DISCUSSION OF RESULTS THIS QUARTER

Preparation and Characterization of Powders

Preparation of Aluminum Nitride Powder

The objective of this task is to develop a process for preparing high-purity submicron AlN powder that can be used in the preparation of β' Sialons. The overall processing approach employs chemical vapor deposition techniques. During this quarter the effort directed toward preparation of AlN powder by reaction of ammonia with aluminum monochloride was brought to a conclusion without arriving at a practical process for preparing quantities of pure material in powder form. Gas-phase nucleation, as required to form powder in a free-space reactor, was less favorable than surface nucleation in the various systems evaluated.

The work on the AlN phase having been concluded, this second quarterly report provides a summary which, for completeness, includes the preparation of AlN by reaction of ammonia with aluminum trichloride as described in the previous quarterly report, together with a description of this quarter's work on the aluminum monochloride approach.

A review of literature and BCL experience suggests that the most promising candidate systems for preparing a high-purity submicron AlN powder are:

(1) $AlCl_3(g) + 1/2N_2(g)* + 3/2H_2(g) \xrightarrow{1000\ C} AlN(s) + 3HCl(g)$

$\Delta G = +6.15$ kcal/mole

(2) $AlF_3(g) + 1/2N_2(g)* + 3/2H_2(g) \xrightarrow{1000\ C} AlN(s) + 3HF(g)$

$\Delta G = +25.04$ kcal/mole

(3) $AlCl(g) + 1/2N_2(g)* + 2/3H_2(g) \xrightarrow{1200\ C} AlN(s) + HCl(g)$

$+ H_2(g)$ $\Delta G = -24.02$ kcal/mole.

Thermodynamically, the most favored reaction of the above is Reaction (3). However, because of the higher reaction temperature and the inherent complications of the system, it was decided to initially investigate one of the first two specimens. In view of the thermodynamic advantage, the chloride system [Reaction (1)] was chosen.

---

* NH_3 is used as the reactant to take advantage kinetically of atomic hydrogen; however, $N_2 + H_2$ are the predominant equilibrium species.

Since, thermodynamically, the $AlCl_3$ reaction [Reaction (1) above] is not especially favorable, it was desirable to use NH_3 in considerable excess (4 to 18 times) of that required stoichiometrically. Experiments were performed under these conditions at 1000 C in a free-space reactor system (Figure 1). Two separate gas streams were introduced into a 6.5-cm-diameter by 45-cm-long chamber. One of these streams was an unprecracked* mixture of NH_3 and H_2 and the other was the reaction product ($AlCl_3$) formed in the chamber in which aluminum was hydrochlorinated at ∿600 C. The powder formed in the main reaction chamber maintained at the desired temperature with a wire-wound furnace was entrained in a reaction-product gas stream which exhausted into a glass trap and then into two electostatic precipitators. The system was isolated from the atmosphere by means of an oil-filled trap.

A considerable quantity of white submicron powder was prepared by this technique in the equipment described, but it was determined that the powder collected was primarily NH_4Cl and $AlCl_3$. This was based mainly on the fact that most of the powder, 90 percent, could be vaporized at 1200 C. It was tentatively concluded that the product probably contained AlN and some Al_2O_3, but in view of the small AlN yield and the inherent difficulty of separating it from the relatively large quantity of chlorides present, it was decided to explore a modification of the technique before expending funds on a more exhaustive analysis of the product.

To improve the yield and reduce the excessive quantity of NH_4Cl in the product, the coating system was modified to ensure that the NH_3 was completely cracked immediately before being introduced into the main reaction chamber. This has the potential of providing nitrogen in the most active form and minimizing the formation of NH_4Cl by limiting the availability of NH_3 to only the small amount that escaped uncracked.

In preparation for the above-described approach to forming AlN, experiments were performed to provide minimum conditions for cracking NH_3 so that the time between cracking and introduction into the

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* Mixture was heated (>600 C) to prevent cooling of reaction chamber but not sufficiently to result in appreciable cracking.

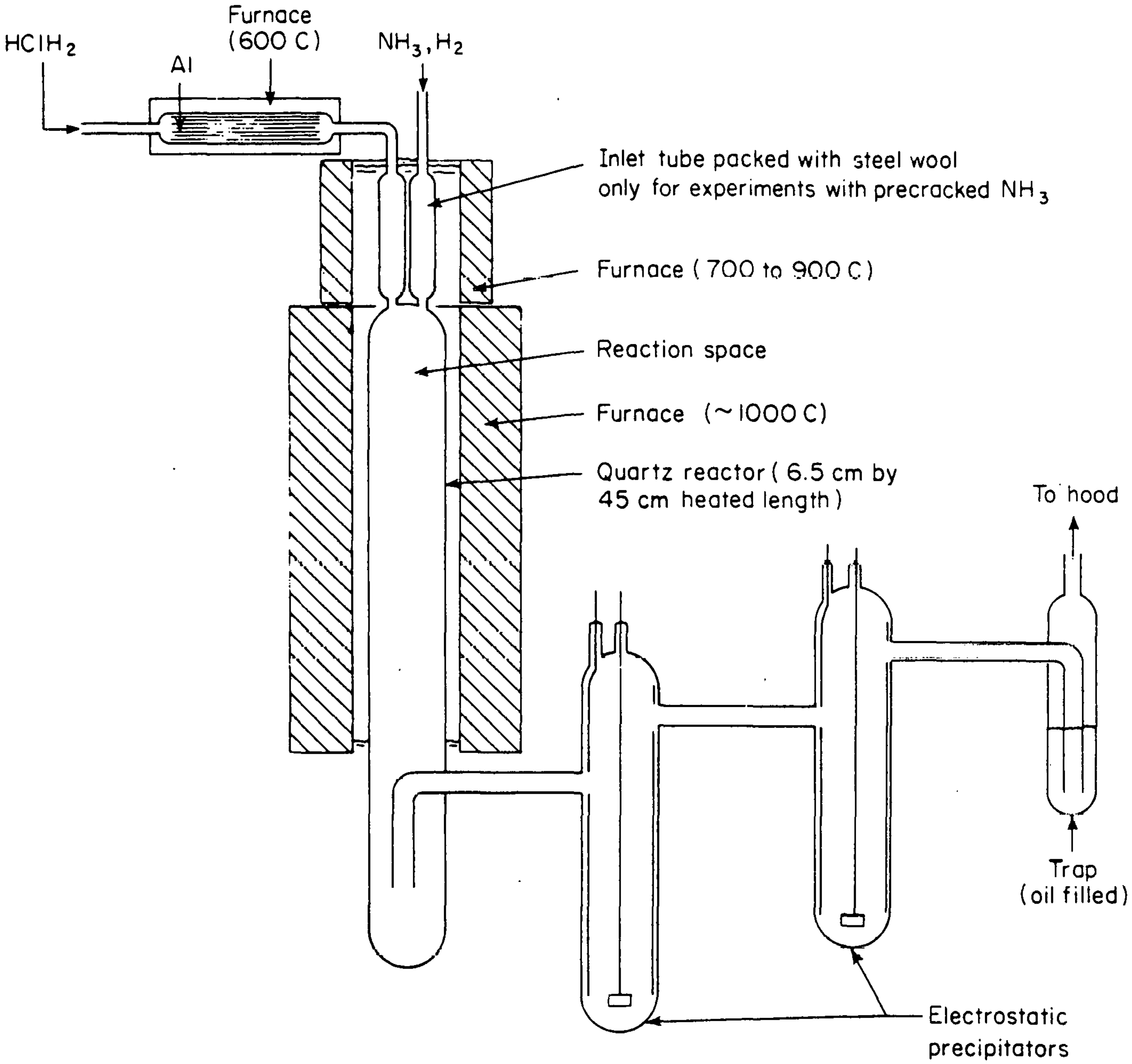


FIGURE 1. APPARATUS FOR INVESTIGATING $AlCl_3 + NH_3$ REACTION FOR PREPARATION OF AlN

reaction chamber could be minimized. This should maximize the availability of active nitrogen by minimizing time for conversion to molecular nitrogen. It was determined that a gas flow of 290 cm^3/minute (NH_3/Ar of $\sim$5) in a quartz cracker (10-cm diameter by 28 cm long) filled with steel wool and maintained at a temperature of 800 C, NH_3 was completely (>99 percent) dissociated.

The powder-forming system used in the initial work was modified to provide an NH_3 cracker adjacent to the main reaction chamber. A preheater temperature of 700 to 900 C was used with a reaction-chamber temperature of 1000 C. Other portions of the system were identical to those used earlier for reacting ammonia without precracking.

The product from the most promising run with the first system (i.e., with uncracked ammonia) was evaluated by heating slowly to 450 C and holding for 4 hours in an inert gas stream. The residue was then heated to 1200 C for 3 hours to increase the crystallite size for X-ray diffraction studies. The final residue represented about 8 percent of the initial sample. The residue gave poor X-ray patterns, which indicated that it was not highly crystalline, and only weak patterns for corundum (Al_2O_3) and delta Al_2O_3 could be identified. This result does not prove that AlN was not present, only that it was not in a crystalline form. However, the analysis does indicate a disappointingly low yield.

This ratio of reactants (NH_3/$AlCl_3$) for the run in which the above product was prepared was 18. This ratio was varied from 18 down to 4 without significant change in results. A product from the second variation of the aluminum trichloride reaction (i.e., with precracked ammonia) at a NH_3/$AlCl_3$ ratio of 3 was evaluated in a similar fashion. To promote a further increase in crystallite size, this product was heated in argon to 1400 C. Since only 2 weight percent of the sample remained, the residue was not examined by X-ray diffraction studies. The results of the second approach seem to confirm the results of the initial experiments in that the formation of adequate quantities of AlN by reaction of NH_3 with $AlCl_3$ would probably be time consuming because of low yields and would require considerable development to optimize.

In view of the low yield obtained in the above work involving the use of $AlCl_3$, attention was turned to an alternative approach for the preparation of AlN involving reaction of NH_3 (or possibly N_2) with AlCl. The following are the simplified reactions:

$$(1) \quad Al + HCl \xrightarrow{1200\ C} \underset{\sim 75\%}{AlCl} + \underset{\sim 25\%}{AlCl_3} + H_2$$

(The reaction is not balanced in view of the varying ratio of products with temperature.*)

$$(2) \quad 1/2N_2^{**} + 3/2\ H_2 + AlCl(g) \xrightarrow{1000\ C} AlN(s) + HcL(g)$$

$H_2(g)$ $\Delta G = 24.02$ kcal/mole.

It should be noted that thermodynamically this reaction is much more favorable than that involving $AlCl_3$ discussed earlier. It was deferred to second consideration, however, because of higher temperatures and the handling of molten aluminum make for more complicated apparatus and slower experimental turnaround time.

The AlN powder-forming system (Figure 2), assembled for evaluating AlCl as a precursor, consisted of a vertically oriented quartz chamber (9-cm diameter by 90 cm long) enclosing a graphite crucible. The top portion of this crucible was used for reacting NH_3 with AlCl, and the bottom for forming the AlCl by hydrochlorination of molten aluminum. Both portions were heated to ∿1200 C inductively. The residue and powder handling portion of this system was essentially the same as that used in the earlier work.

---

* $HCl(g) + Al(\ell)$ excess $\xrightarrow{1\ atm}$

Composition of product vapor in mole percent at temperatures shown:

	1027 C	1127 C	1227 C
$AlCl(g)$	21.6	38.86	55.20
$AlCl_3(g)$	26.97	16.58	6.78
$H_2(g)$	51.26	44.31	37.73
$HCl(g)$	0.17	0.25	0.29

** Although $NH_3(g)$ was used in the feed stream to take kinetic advantage of atomic nitrogen, N_2 and H_2 are the equilibrium species which must be so stated if the ΔG comparisons are to have meaning.

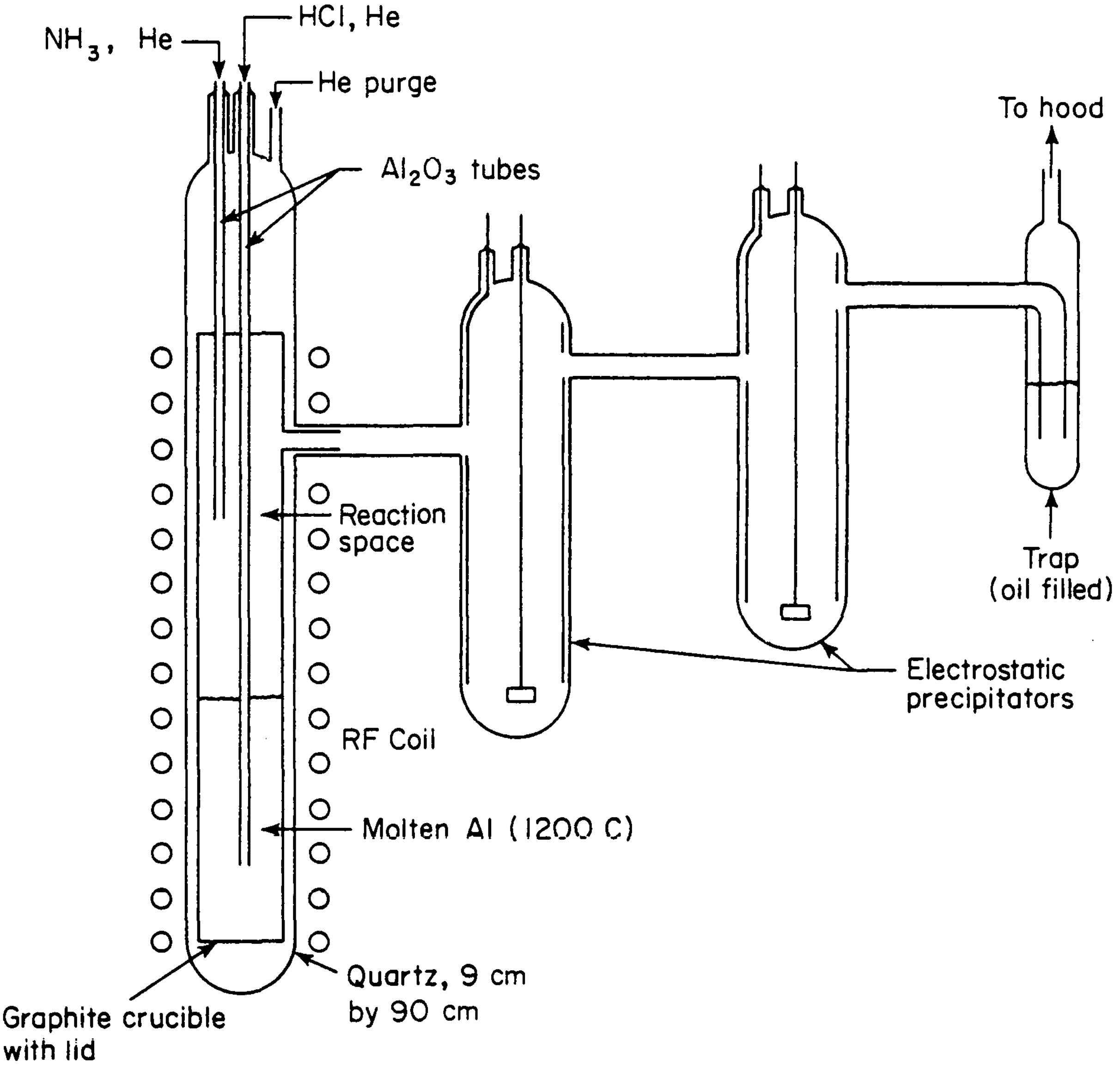


FIGURE 2. APPARATUS FOR INVESTIGATING AlCl + NH_3 REACTION FOR PREPARATION OF AlN

The quantity and gray color of the powder collected in the electrostatic precipitator suggested that $AlCl_3$ and aluminum were formed by the disproportionation of the AlCl. Vaporization and oxidation evaluation of the powder showed a maximum possible AlN content of less than 10 percent of a yield of less than 1 g/hr mixed with finely divided aluminum and large quantities of $AlCl_3$. It was concluded that in this system AlCl was being formed but the NH_3 + AlCl reaction was not proceeding as anticipated. Initially it was suspected that cooling of the reactant mixture by insufficiently heated NH_3 was a major contributor to the poor reaction efficiency, but this was not confirmed in later experiments.

The major coating parameters evaluated using the AlCl apparatus were:

(1) 1175 to 1300 C coating temperature

(2) Use of nitrogen gas or ammonia

(3) Injection of N_2 or NH_3

  (a) Into heated free space above aluminum as shown in Figure 2

  (b) Beneath the surface of liquid aluminum either mixed with HCl stream or through a separate tube

  (c) Through inductively heated graphite preheater (1300 C) into free space above liquid aluminum.

Neither the variation in temperature nor, as was anticipated, the choice of N_2 versus NH_3 made any discernible difference, so results discussed below involve only Item (3), the mode of injecting the nitrogen component.

Injecting NH_3 into the free space above the aluminum pool provided an operable system in which runs could be continued for at least 4 hours. Comparison of HCl input from Al consumed verified the formation of AlCl at roughly the level expected at 1227 C. Therefore, both reactants were injected into the melt through the same tube to provide maximum preheating and reaction. In less than 1 hour the injection tubes were immobilized by formation of precipitate in the aluminum before becoming plugged. Appearance of the cooled ingot showed open gas passages and extensive formation of large yellow crystals and some white powder. The plug in the gas inlet tube could not be drilled and the ingot was cut only with great difficulty.

The white powder was assumed to be AlN but was too limited in quantity to identify more positively. The hexagonal translucent yellow crystals were thought to be aluminum carbide but were not identifiable by X-ray beyond being a complicated spinel-type material. The limited amount of powder collected downstream was similar to that described before. Similar results were obtained when N_2 and HCl were injected into the aluminum melt through separate tubes.

Addition of nitrogen into the reactor free space through a graphite-packed preheater at 1300 C was the final attempt to promote gas-phase nucleation of AlN. The results were almost identical to those discussed above, which indicated that preheating is probably not the major factor controlling this reaction.

Further investigation of the preparation of AlN has been deferred pending an evaluation of the suitability of a product obtained from a commercial source.

Characterization of Powders

1. Silica - As mentioned in the previous quarterly report, a new SiO_2 powder has been obtained and characterized because the Cabosil EH-5 grade powder was extremely difficult to handle and disperse in the hexane milling medium. This new -325 mesh powder was purchased from Atomergic Chemetal Company of New York. Storage and handling procedures were the same as described previously.

The chemical and physical characteristics of this powder are given in Table 1 and Figures 3 through 6. In particular, it should be noted that the major metallic impurities, Na (100 ppm), Al (100 ppm),

TABLE 1. MASS SPECTROGRAPHIC ANALYSIS OF ATOMERGIC CO'S SiO_2 POWDER (ppm)

Li	0.2	Ag	<0.2
Be	<0.002	Cd	<0.2
B	2	In	<0.4
F	0.1	Sn	0.2
Na	100	Sb	<0.1
Mg	≤20	Te	<0.3
Al	100	I	<0.2
Si	Major	Cs	<0.1
P	3	Ba	4
S	1	La	1
Cl	20	Ce	<1
K	20	Pr	<0.2
Ca	60	Nd	<0.4
Sc	<0.1	Sm	<0.2
Ti	20	Eu	<0.1
V	0.5	Gd	<0.3
Cr	<1	Tb	<0.06
Mn	<1	Dy	<0.6
Fe	30	Ho	<0.2
Co	<1	Er	<0.4
Ni	<2	Tm	<0.06
Cu	≤2	Yb	<0.1
Zn	<2	Lu	<0.06
Ga	1	Hf	<0.5
Ge	<0.03	Ta	<3
As	≤0.3	W	<0.1
Se	<0.05	Re	<0.06
Br	0.1	Os	<0.07
Rb	<0.4	Ir	<0.1
Sr	5	Pt	<0.1
Y	2	Au	<0.03
Zr	3	Hg	<0.1
Nb	<0.2	Tl	<0.04
Mo	2	Pb	2
Ru	<0.1	Bi	<0.04
Rh	<0.06	Th	<0.1
Pd	<3	U	<0.1

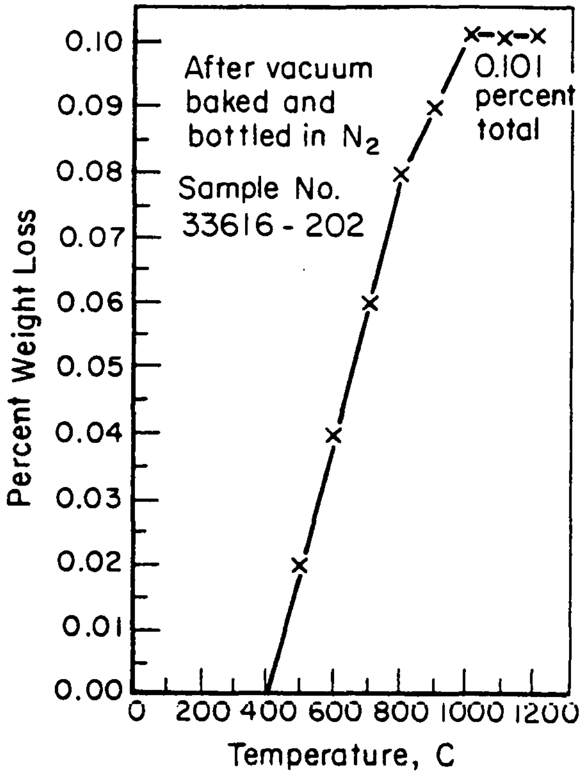


FIGURE 3. THERMOGRAVIMETRIC ANALYSIS OF ATOMERGIC SiO_2 POWDER

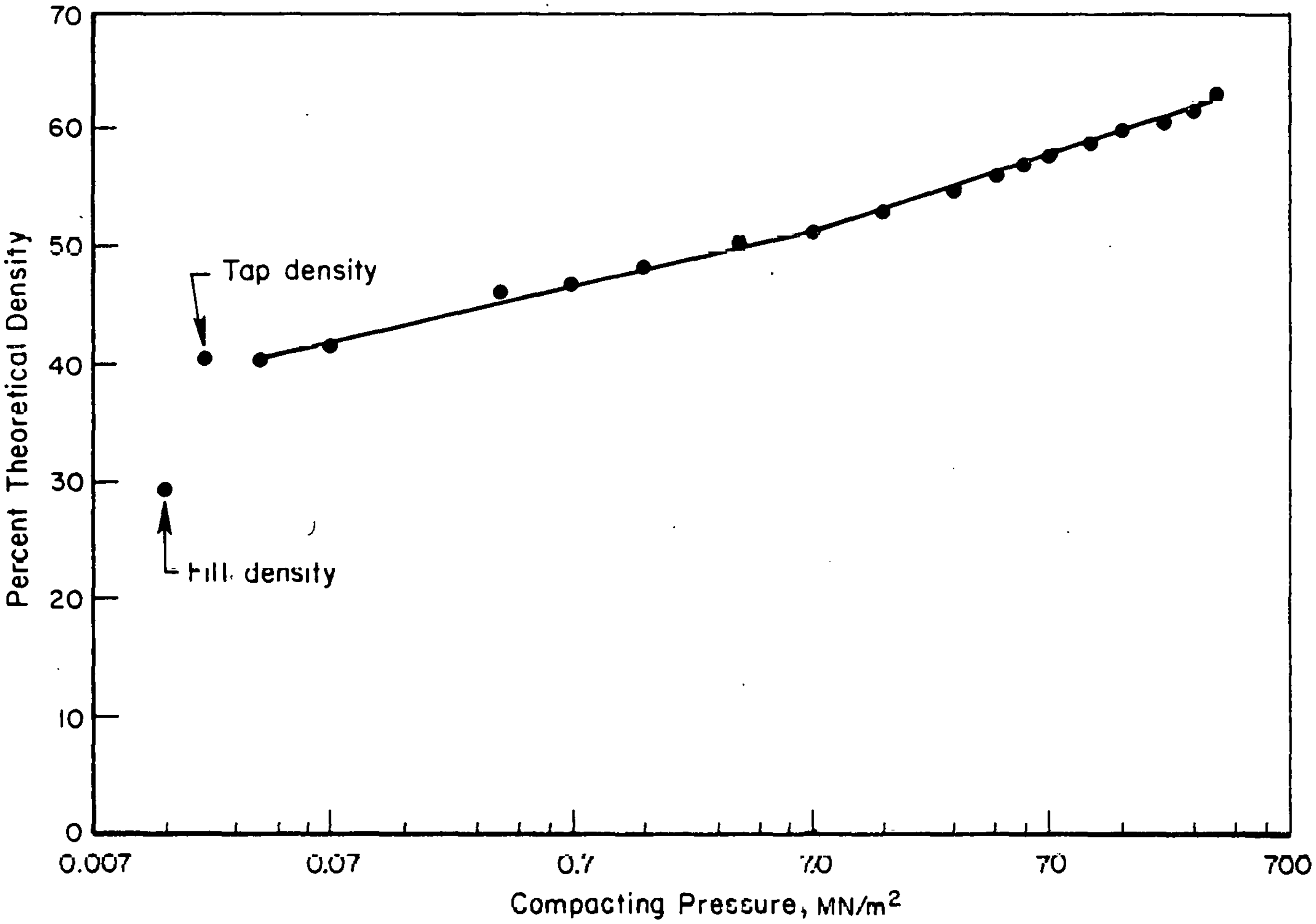


FIGURE 4. COMPACTION CURVE FOR ATOMERGIC SiO_2 POWDER

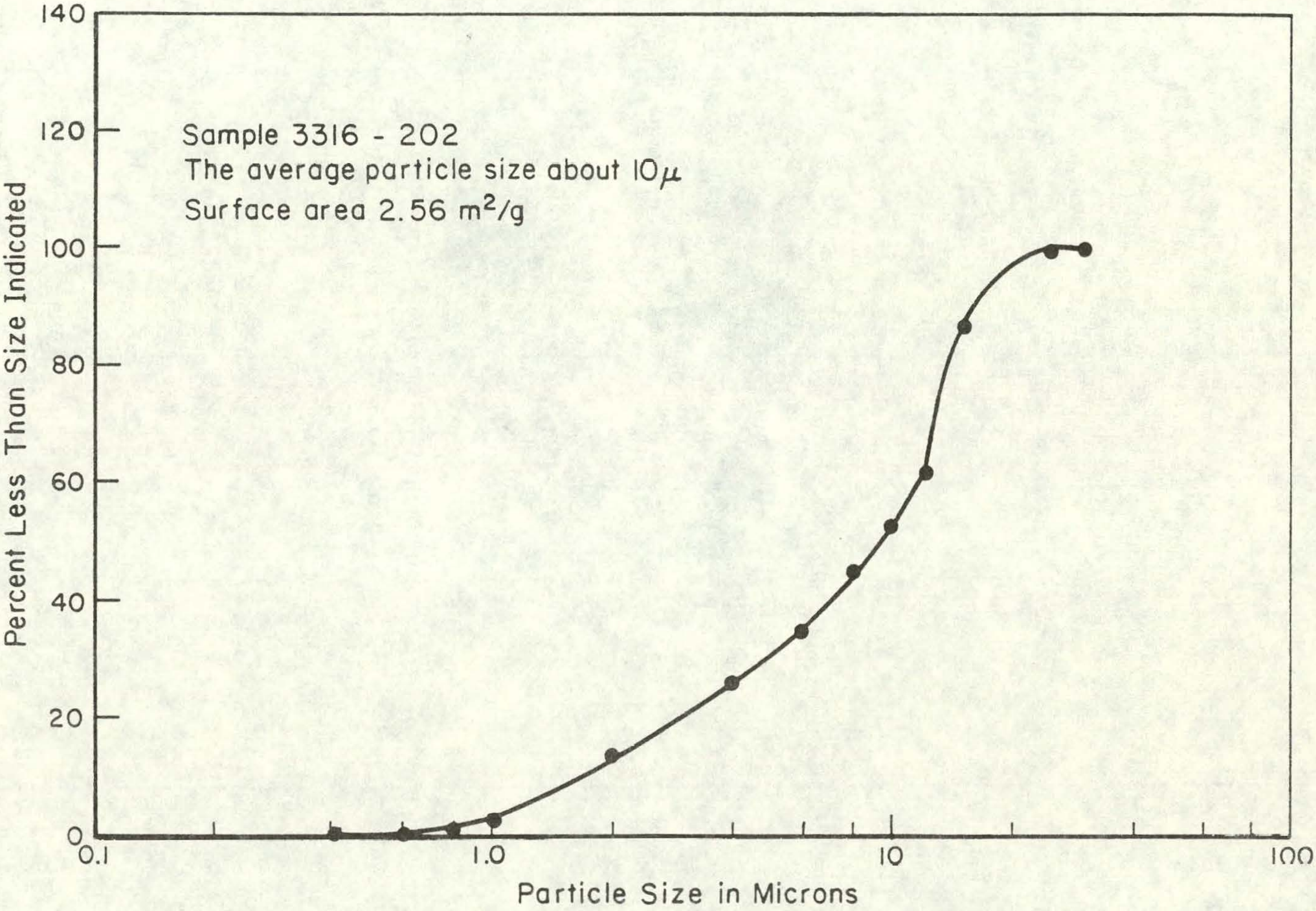
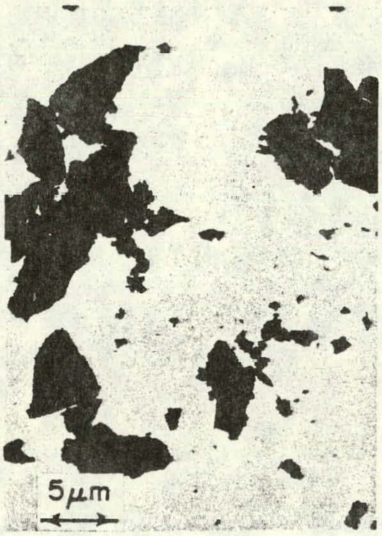


FIGURE 5. PARTICLE SIZE DISTRIBUTION OF SiO_2 POWDER



J-5
(x2000)

FIGURE 6. SHARP EDGED IRREGULAR S_iO_2 PARTICLES

Ca (60 ppm), and Fe (30 ppm) are present in slightly higher concentrations than in the Cabosil EH-5 grade powder.

2. Aluminum Nitride - As discussed earlier in this report, efforts to produce an ultrafine high-purity AlN powder at Battelle have not progressed as originally anticipated. Consequently, to prevent delays in the initial assessment of β' Sialons, commercial AlN powder was obtained from Atomergic Chemetal Company of New York. Handling, storage, and characterization procedures were again similar to those described in the first quarterly report.

The physical and chemical aspects of this powder are shown in Figures 7 through 10 and Table 2. The concentrations of metallic impurities (see Table 2) are considerably higher than those found in the Si_3N_4, Al_2O_3, and SiO_2 powders, major impurities being Na (200 ppm), Si (200 ppm), Cr (200 ppm), Fe (200 ppm), Co (300 ppm), Ni (60 ppm), Mo (50 ppm), and W (150 ppm). These impurity levels may prove to be unacceptably high, but this will not be known until extensive evaluation of the β' Sialons in contact with molten silicon has been completed. This powder also contains appreciable amounts of oxygen (1.9 percent) and carbon (525 ppm) and is also thought to contain ∿8 percent of free aluminum since its nitrogen content (29.47 percent) is considerably below the theoretical value (34.16 weight percent). As discussed later, this free aluminum metal gives rise to multiphase samples of β' Sialon.

This batch of AlN powder has been returned to the supplier, Atomergic Chemetal Company, who has agreed to provide another batch of powder containing no free aluminum

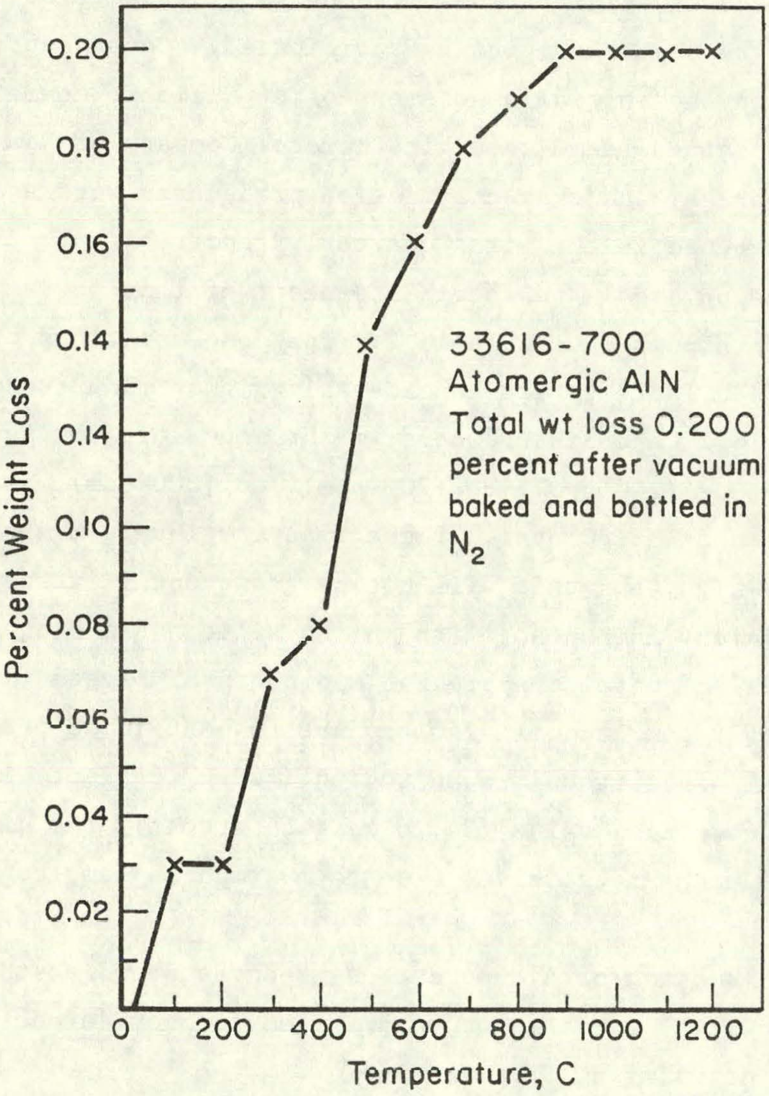


FIGURE 7. THERMOGRAVIMETRIC ANALYSIS OF ATOMERGIC AlN

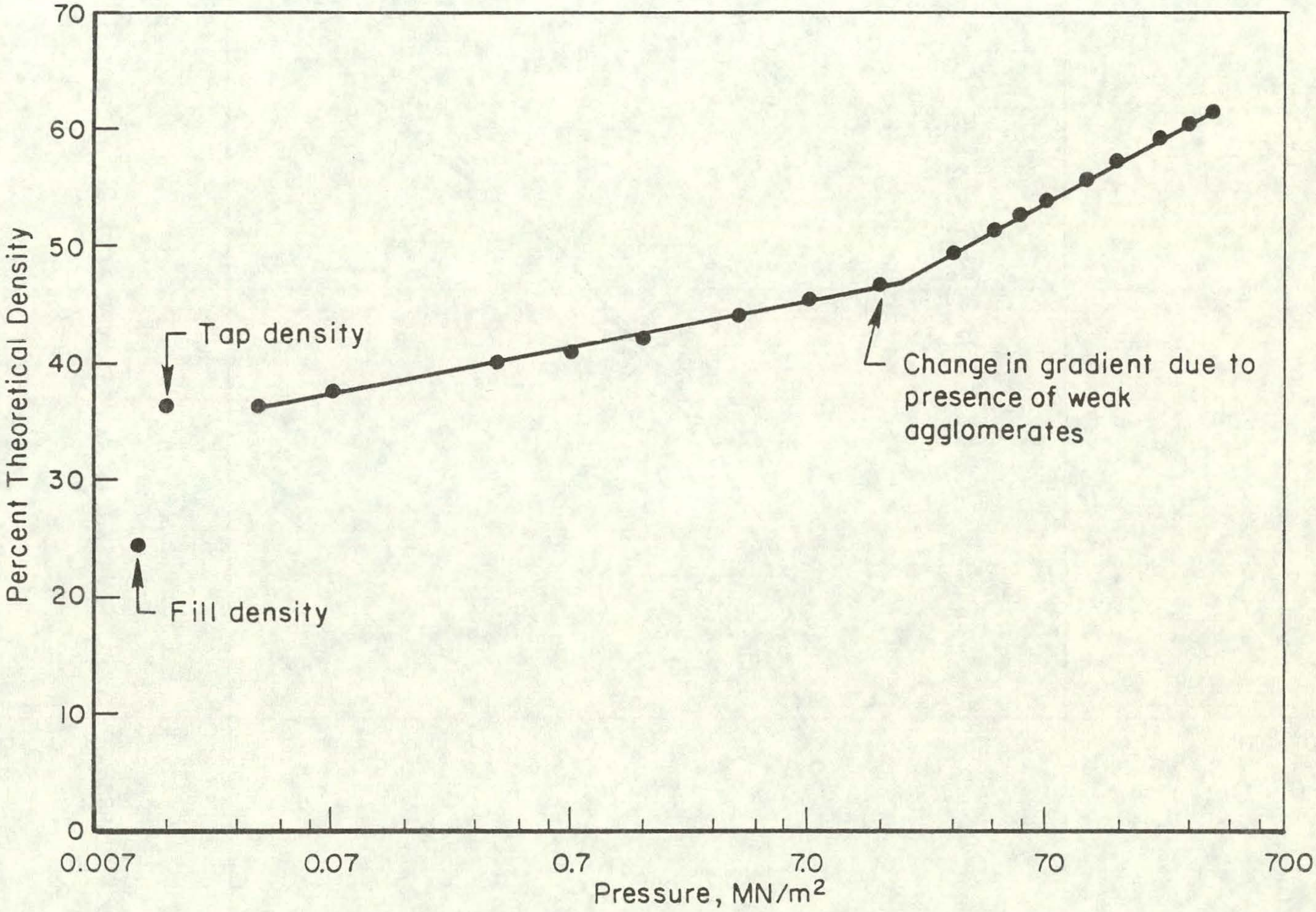


FIGURE 8. COMPACTION CURVE OF ATOMERGIC AlN POWDER

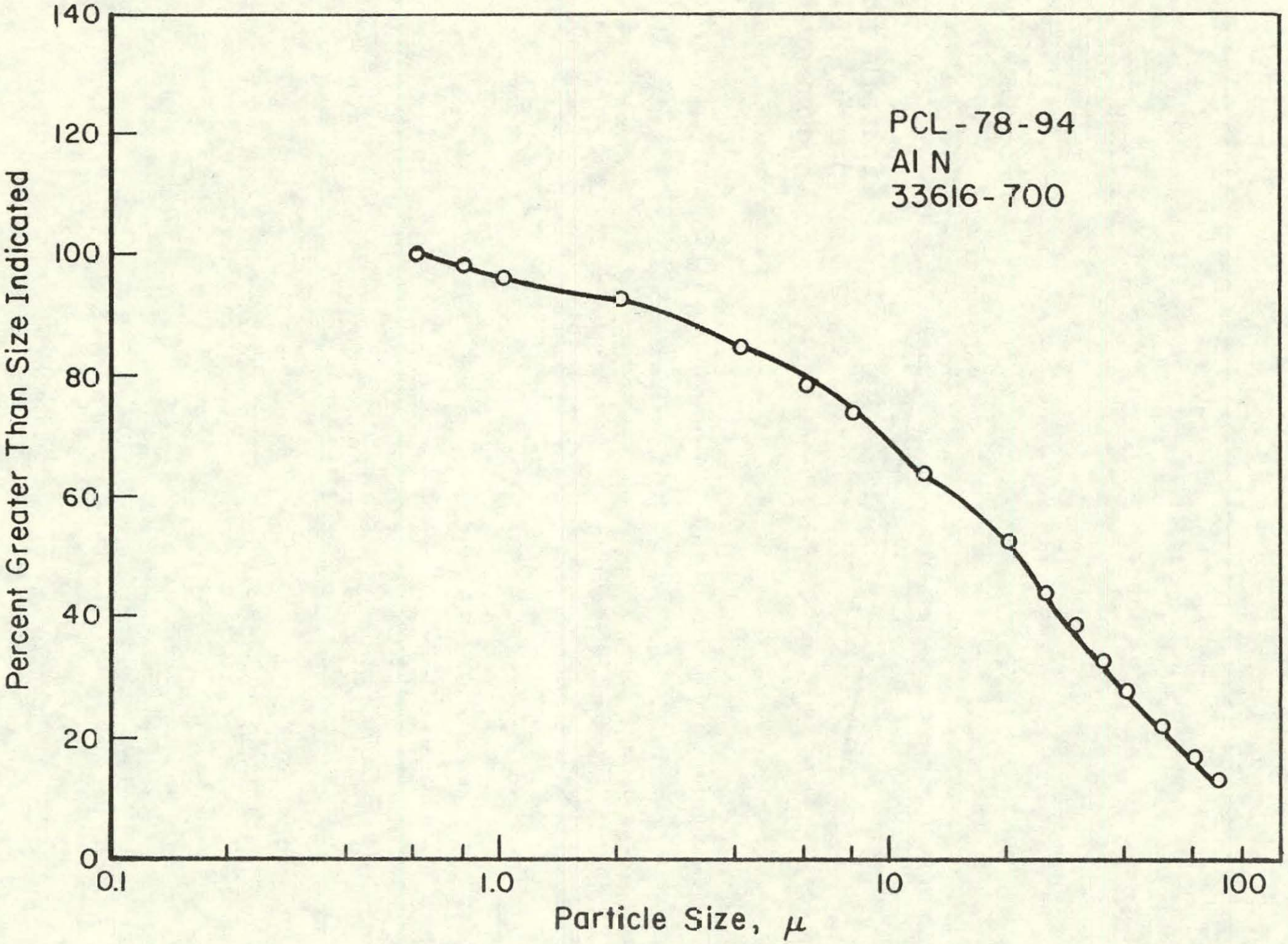
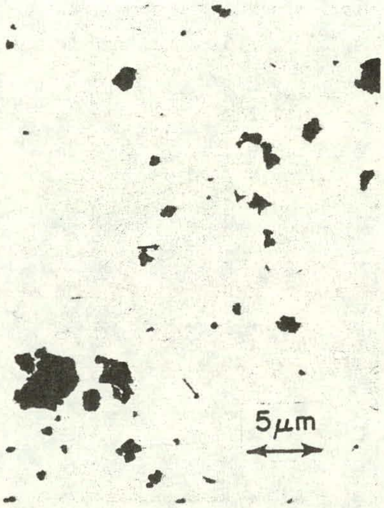


FIGURE 9. PARTICLE SIZE DISTRIBUTION OF ATOMERGIC AlN POWDER



AlN J3
(x2000)

FIGURE 10. TRANSMISSION ELECTRON MICROGRAPH OF ATOMERGIC AlN POWDER

TABLE 2. MASS SPECTROGRAPHIC ANALYSIS OF ATOMERGIC CO'S AlN POWDER (ppm)

Li	0.04	Ag	<0.1
Be	<0.002	Cd	<0.1
B	1	In	<0.06
F	≤0.05	Sn	0.6
Na	200	Sb	<0.2
Mg	10	Te	<0.1
Al	Major	I	<0.03
Si	200	Cs	<0.1
P	0.2	Ba	0.1
S	4	La	<0.03
Cl	40	Ce	<0.1
K	5	Pr	<0.04
Ca	6	Nd	<0.1
Sc	<0.1	Sm	<0.2
Ti	20	Eu	<0.1
V	5	Gd	<0.2
Cr	200	Tb	<0.04
Mn	10	Dy	<0.2
Fe	200	Ho	<0.04
Co	300	Er	<0.1
Ni	60	Tm	<0.04
Cu	10	Yb	<0.1
Zn	<0.3	Lu	<0.4
Ga	≤2	Hf	<0.2
Ge	<0.3	Ta	<0.2
As	<0.1	W	150
Se	<1	Re	<0.1
Br	<0.1	Os	<0.1
Rb	<0.3	Ir	<0.1
Sr	<0.06	Pt	<0.2
Y	<0.04	Au	<0.05
Zr	2	Hg	<0.2
Nb	<0.2	Ti	<0.07
Mo	50	Pb	1
Ru	<0.2	Bi	<0.05
Rh	<0.1	Th	<0.06
Pd	<0.2	U	<0.3

Fabrication and Characterization of Silicon Aluminum Oxynitrides

Milling Procedure

All milling operations were carried out in new high purity 1 gallon Al_2O_3 ball mills using high density, high purity balls (1.87 cm diameter) from Coors Porcelain Company. The interior surfaces of the mills were rough and many of the balls had sharp edges. Some of the balls were pink in color, the remainder being a dull white. In order to clean and prepare these ball mills, the following procedure was used.

Each mill was charged with 5 kg of the Al_2O_3 balls and run for 72 hours at 72 rpm with 500 g of -60 mesh Al_2O_3 and 1000 cm^3 of water. The mills and Al_2O_3 balls were subsequently cleaned in distilled water and vacuum dried at 150 C. The Al_2O_3 balls which still showed chipping or inhomogeneities were rejected.

The impurity pickup during milling was checked by milling a 150-g batch consisting of 105.41 g of Si_3N_4, 36.96 g of SiO_2, and 7.63 g of Al_2O_3. This mixture, which corresponds to the Sialon $Si_{1.9}Al_{0.1}N_{1.9}O_{1.1}$, was milled for 24 hours in 1000 cm^3 of n-hexane* using 3000 g of the white Coors Al_2O_3 balls. Samples were drawn after 4 hours, 8 hours, and 24 hours and analyzed for Si, Al, O, N, and metallic impurities. The mass spectrographic analyses of these three samples are shown in Table 3. Comparison of these data with the data for the starting powders themselves indicates some increases in the concentration levels of Mg, S, Cl, Ca, Ti, Mo, and Ba. These increases, however, do not always increase with milling time, as might be expected. The chloride content, in particular, shows a wide variation, from 1200 ppm to 1 percent, probably because of variations in chloride content of the Si_3N_4 itself. The overall metallic impurity concentration for the material milled for 4 hours is approximately 160 ppm.

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* "Nanograde" Hexane supplied by American Hospital Supply Company.

TABLE 3. MASS SPECTROGRAPHIC ANALYSES OF MILLED Si_3N_4, Al_2O_3, AND SiO_2 MIXTURES (ppm)

Element	After 4 Hours	After 8 Hours	After 24 Hours
Li	0.1	<0.003	0.1
Be	<0.002	<0.002	<0.002
B	0.06	0.06	0.06
F	0.5	2	0.5
Na	4	20	10
Mg	≤10	≤40	100
Al	Major	Major	Major
Si	Major	Major	Major
P	15	15	20
S	10	30	10
Cl	1200	12	7000
K	0.2	0.2	0.7
Ca	40	6	40
Sc	<0.1	<0.1	<0.1
Ti	<6	≤20	≤20
V	<0.2	<0.2	<0.5
Cr	<1	<1	<1
Mn	<1	<1	<1
Fe	3	3	5
Co	<1	<0.3	<0.5
Ni	<2	<2	<2
Cu	2	1	<2
Zn	<2	<2	<2
Ga	2	4	10
Ge	<0.03	<0.03	<0.03
As	<0.01	0.01	<0.01
Se	<0.05	<0.05	<0.05
Br	3	5	3
Rb	<0.4	<0.4	<0.4
Sr	0.2	0.2	2
Y	0.05	0.5	0.3
Zr	<1	<0.2	<1
Nb	<0.2	<0.2	<0.2
Mo	60	40	20
Ru	<0.3	<0.1	<0.2

TABLE 3. (Continued)

Element	After 4 Hours	After 8 Hours	After 24 Hours
Rh	<0.2	<0.1	<0.1
Pd	<2	<0.4	<0.4
Ag	<1	<0.1	<0.2
Cd	<1	<0.4	<0.4
In	<0.4	<0.4	<0.4
Sn	0.8	0.2	0.2
Sb	<0.1	<0.1	<0.1
Te	<0.1	<0.1	<0.2
I	<0.1	<0.04	<0.04
Cs	<0.2	<0.1	<0.06
Ba	4	2	6
La	0.1	0.02	0.02
Ce	<0.05	<0.05	<0.1
Pr	<0.1	<0.05	<0.03
Nd	<0.2	<0.2	<0.1
Sm	<0.2	<0.2	<0.2
Eu	<0.3	<0.1	<0.1
Gd	<0.2	<0.2	<0.1
Tb	<0.06	<0.06	<0.06
Dy	<0.3	<0.1	<0.6
Ho	<0.3	<0.06	<0.03
Er	<0.4	<0.2	<0.1
Tm	<0.3	<0.1	<0.06
Yb	<0.2	<0.1	<0.2
Lu	<0.06	<0.06	<0.2
Hf	<0.3	<0.1	<0.1
Ta	<1	<1	<1
W	<0.1	<0.1	<0.1
Re	<0.1	<0.1	<0.06
Os	<0.1	<0.07	<0.07
Ir	<0.3	<0.1	<0.1
Pt	<0.3	<0.1	<0.1
Au	<0.1	<0.1	<0.03
Hg	<0.2	<0.1	<0.1
Tl	<0.07	<0.04	<0.04
Pb	<0.1	0.2	<0.2
Bi	<0.07	<0.04	<0.04
Th	<0.1	<0.1	<0.1
U	<0.1	<0.1	<0.1

Table 4 shows the Si, Al, O, and N contents of this mixture after 4 hours and 24 hours milling. Si and Al were determined by gravimetric analysis, and O and N by inert gas fusion at Leco Corporation. Considerable difficulty was experienced in dissolving the silicon from the Si_3N_4; consequently, we do not have a high degree of confidence in the values given in the table. The table shows that some nitrogen loss occurs with increasing time, and mainly for this reason 4 hours was chosen as the optimum milling time.

Hot Pressing Trials and Materials Characterization

Hot pressing trials were performed with all four Sialons, $Si_{1.9}Al_{0.1}N_{1.9}O_{1.1}$, $Si_{1.8}Al_{0.2}N_{1.8}O_{1.2}$, $Si_{5.4}Al_{0.6}N_{7.4}O_{0.6}$, and $Si_{3.6}Al_{2.4}N_{5.6}O_{2.4}$. The compositions of these materials, in terms of their Si, Al, O, and N contents, are given in Table 5. In preparing these materials, allowances were made for the oxygen content of the Si_3N_4 powder and the weight losses exhibited by these powders, according to the thermogravimetric analysis data.

Powder batches (500 g) were milled in 1400 cm^3 of hexane for 4 hours using 4000 g of Al_2O_3 balls, and subsequently vacuum dried at 190 C over a 24-hour period. The oven was then back filled with nitrogen prior to separating the powder from the balls by sieving through a -70 mesh screen. Separated powder was vacuum dried and stored under nitrogen in sealed jars. 18-g powder samples were cold pressed at 56 MN/m^2 (8,000 psi) in a 1-inch steel die prior to being loaded into the graphite die set. A protective boron nitride layer was used to prevent reaction with the graphite punch, plug, and die set during hot pressing.

Hot-pressing trials were performed both in vacuum and under atmospheric nitrogen, the final temperature and pressure conditions being 1750 C and 70 MN/m^2 (10,000 psi). All samples exhibited substantial fuming of vapors at 1450 C to 1580 C, the temperature range in which

TABLE 4. SILICON, ALUMINUM, NITROGEN, AND OXYGEN CONTENTS OF A Si_3N_4-Al_2O_3-SiO_2 MIXTURE AFTER MILLING FOR 4 HOURS AND 24 HOURS*

	Si	Al	O	N
Initial Composition	53.22	2.70	17.54	26.54
After 4 Hours Milling	nd	nd	17.53	24.24
After 24 Hours Milling	50.5	2.75	18.94	22.57

* Values shown are in weight percent.

nd = not determined.

TABLE 5. COMPOSITIONS OF THE SIALONS IN TERMS OF THEIR SILICON, ALUMINUM, NITROGEN, AND OXYGEN CONTENTS*

Composition	Si	Al	N	O
$Si_{1.9}Al_{0.1}N_{1.9}O_{1.1}$	53.22	2.70	26.54	17.54
$S_{1.8}Al_{0.2}N_{1.8}O_{1.2}$	50.37	5.38	25.12	19.13
$Si_{5.4}Al_{0.6}N_{7.4}O_{0.6}$	53.95	5.76	36.87	3.41
$Si_{3.6}Al_{2.4}N_{5.6}O_{2.4}$	35.76	22.92	27.74	13.58

* Values given are in weight percent.

densification began. Severe condensation of the volatile species occurred on the pyrometer window during hot pressing under nitrogen to the extent that temperature readings were not considered meaningful. A thermocouple has recently been inserted into the graphite die wall to overcome this problem.

Weight losses on the samples ranged from 8 percent to 25 percent, and in one sample of $Si_{5.4}Al_{0.6}N_{7.4}O_{0.6}$ β' Sialon large amounts of free silicon were noticed. Table 6 summarizes the densities and weight losses of all four materials hot pressed in atmospheric nitrogen. Assuming that the theoretical densities of these Sialons are identical to those of Si_3N_4 (3.18 g/cm^3) and Si_2N_2O (3.1 g/cm^3), all the materials except for $Si_{5.4}Al_{0.6}N_{7.4}O_{0.6}$ β' Sialon have densities $\geq$90 percent of theoretical.

Table 7 lists the impurities in a hot-pressed $Si_{1.8}Al_{0.2}N_{1.8}O_{1.2}$ sample. Total impurities are approximately 160 ppm ignoring the iron which was probably picked up during sample crushing. Particularly noticeable is the sharp drop in chlorine content, which indicates that chlorine or chlorine-containing compounds are the volatile species observed during hot pressing. This problem of fuming can largely be overcome by using Sylvania Company's SN502 grade of Si_3N_4 powder, and this powder will be used in future processing iterations.

Samples of $Si_{1.8}Al_{0.2}N_{1.8}O_{1.2}$ and $S_{1.9}Al_{0.1}N_{1.9}O_{1.1}$ Sialons were analyzed for their Si, Al, O, and N contents. Oxygen and nitrogen contents were determined by inert gas fusion, and silicon and aluminum by an X-ray fluorescence method using mixtures of Si_3N_4, Al_2O_3, and SiO_2 as standards. In this method of calibration a curve of Al/Si counts versus (weight percent Al)/(weight percent Si) was prepared, and the Al and Si concentrations were determined of silicon and aluminum. Table 8 shows that the compositions of the Sialons have changed slightly during hot pressing, becoming marginally richer in silicon and aluminum while losing some oxygen and nitrogen. It appears from these data that the volatile species observed during hot pressing were

TABLE 6. DENSITIES AND WEIGHT LOSSES OF SIALONS HOT PRESSED IN ATMOSPHERIC NITROGEN

Sample	Density, g/cm^3	% Theoretical Density*	Weight Loss, %
$Si_{5.4}Al_{0.6}N_{7.4}O_{0.6}$	2.30	72.0	8.7
$Si_{3.6}Al_{2.4}N_{5.6}O_{2.4}$	3.13	98.4	8.5
$Si_{1.9}Al_{0.1}N_{1.9}O_{1.1}$	2.79	90.0	8.1
$S_{1.8}Al_{0.2}N_{1.8}O_{1.2}$	2.81	90.6	8.2

* Assuming the theoretical densities of β' Sialon and O' Sialon are identical to those of Si_3N_4 and Si_2N_2O. The actual theoretical densities are slightly lower so the numbers in Column 2 are on the low side.

TABLE 7. IMPURITIES IN TYPICAL HOT PRESSED O' SIALON (ppm)

Li	0.1	Ag	<0.1
Be	0.002	Cd	<0.2
B	20	In	<0.04
F	<0.1	Sn	<0.2
Na	40	Sb	<0.1
Mg	10	Te	<0.2
Al	Major	I	<0.06
Si	Major	Cs	<0.07
P	0.5	Ba	6
S	3	La	<0.1
Cl	10	Ce	0.1
K	10	Pr	<0.04
Ca	20	Nd	<0.2
Sc	<0.7	Sm	<0.2
Ti	10	Eu	<0.05
V	0.3	Gd	<0.1
Cr	3	Tb	<0.03
Mn	1	Dy	<0.2
Fe	100*	Ho	<0.03
Co	0.3	Er	<0.1
Ni	0.2	Tm	<0.1
Cu	2	Yb	<0.1
Zn	<4	Lu	<0.03
Ga	<9	Hf	<0.1
Ge	<1	Ta	<0.2
As	<0.03	W	0.1
Se	<1	Re	<0.05
Br	<0.2	Os	<0.06
Rb	<0.1	Ir	<0.2
Sr	1	Pt	<0.1
Y	1	Au	<0.03
Zr	3	Hg	<0.1
Nb	<0.2	Tl	<0.1
Mo	10	Pb	<0.2
Ru	<0.3	Bi	<0.04
Rh	<0.06	Th	<0.04
Pd	<0.2	U	<10

* Picked up during sample preparation.

TABLE 8. COMPOSITIONS OF HOT PRESSED $Si_{1.8}Al_{0.2}N_{1.8}O_{1.2}$ AND $Si_{1.9}Al_{0.1}N_{1.9}O_{1.1}$ SIALONS

	Si	Al	O	N
Initial Compositions				
$Si_{1.9}Al_{0.1}N_{1.9}O_{1.1}$	53.2	2.70	17.54	26.5
$Si_{1.8}Al_{0.2}N_{1.8}O_{1.2}$	50.37	5.38	19.13	25.12
Final Compositions After Hot Pressing				
$Si_{1.9}Al_{0.1}N_{1.9}O_{1.1}$	55.8	2.9	16.60	24.70
$S_{1.8}Al_{0.2}N_{1.8}O_{1.2}$	53.31	5.81	18.08	22.80
Final Compositions After Hot Pressing in Atmospheric Nitrogen				
$Si_{1.9}Al_{0.1}N_{1.9}O_{1.1}$	nd	nd	17.81	24.80
$S_{1.8}Al_{0.2}N_{1.8}O_{1.2}$	nd	nd	18.26	24.15

* Values given are in weight percent.

nd = not determined.

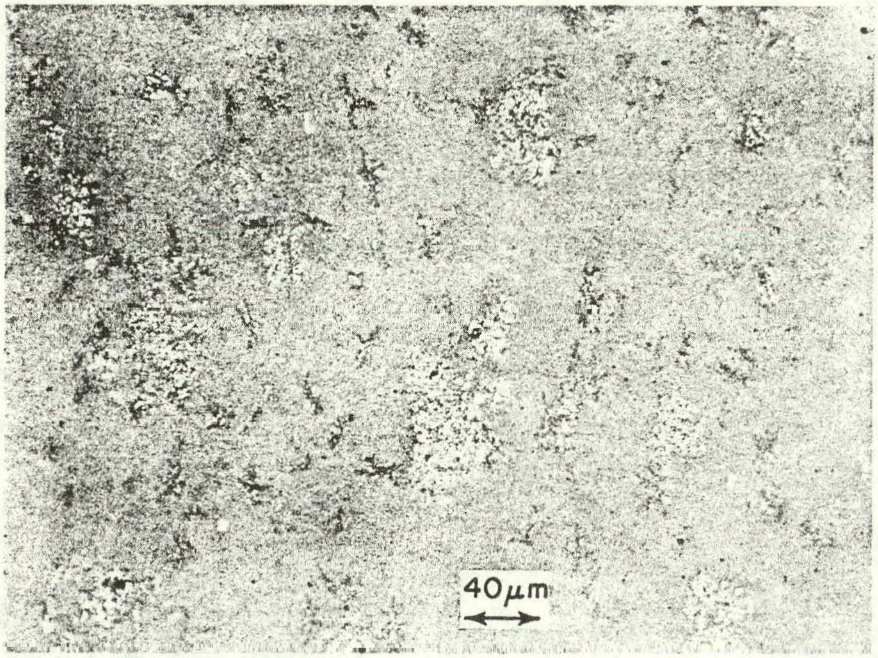
largely oxygen and nitrogen, but since chlorine is also evolved it is likely that the vapor consists of oxides of nitrogen and chlorine.

X-ray diffraction analysis of all the Sialon samples shows that they are not single-phase materials; additional peaks, however, could not be unequivocally assigned to any other one phase in the Si-Al-O-N system. Figures 11 and 12 are typical photomicrographs of O' and β' materials. The white phase in Figure 11 is elemental silicon, which probably results from partial decomposition of the Si_3N_4 during hot pressing. In contrast, the β' Sialon samples contain very little elemental silicon, but a major second phase (the dark 20 to 40 μm grains in Figure 12) is present. Semi-quantitative analysis with an electron microprobe analyzer showed that the Si/Al ratio of this phase is 0.75 (the matrix has the expected ratio of 1.5). Its presence in the β' Sialon samples is probably a direct result of the 8 percent free aluminum in the AlN powder.

Compatibility with Molten Silicon

Initial studies with $Si_{1.8}Al_{0.2}N_{1.8}O_{1.2}$ and $Si_{3.6}Al_{2.4}$-$N_{5.6}O_{2.4}$ Sialons have been completed. Sample surfaces were polished to 3 μ diamond finish, and cleaned in acetone, prior to being held in contact with molten silicon in an argon atmosphere at 1450 C for 1 hour.

Figure 13 shows that wetting occurred in both instances, and in the case of $Si_{1.8}Al_{0.2}N_{1.8}O_{1.2}$ Sialon (labeled 13 in the figure) the silicon has also covered most of the side of the specimen and appears to have infiltrated it. Transverse sections of the silicon ceramic interface show thin string-like precipitates (see Figures 14 and 15) in the silicon next to the multiphase $Si_{3.6}Al_{2.4}N_{5.6}O_{2.4}$ sample. These precipitates are an aluminum-rich material according to electron probe analysis. The unidentified second phase in this Sialon material is probably responsible for precipitate formation, but further experimentation with a single-phase $Si_{3.6}Al_{2.4}N_{5.6}O_{2.4}$ β' Sialon is needed to verify this hypothesis.



4J712

FIGURE 11. TYPICAL MICROGRAPH OF $Si_{1.8}Al_{0.2}N_{1.8}O_{1.2}$ SIALON SAMPLE CONTAINING ELEMENTAL SILICON

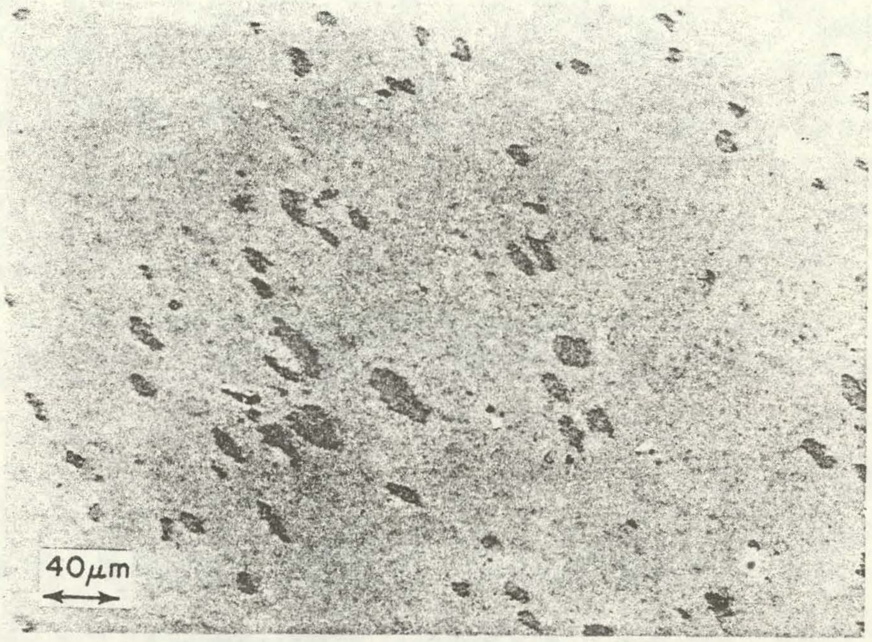


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FIGURE 12. OPTICAL MICROGRAPH OF $Si_{3.6}Al_{2.4}N_{5.6}O_{2.4}$ SIALON SAMPLE CONTAINING LARGE SECOND PHASE GRAINS

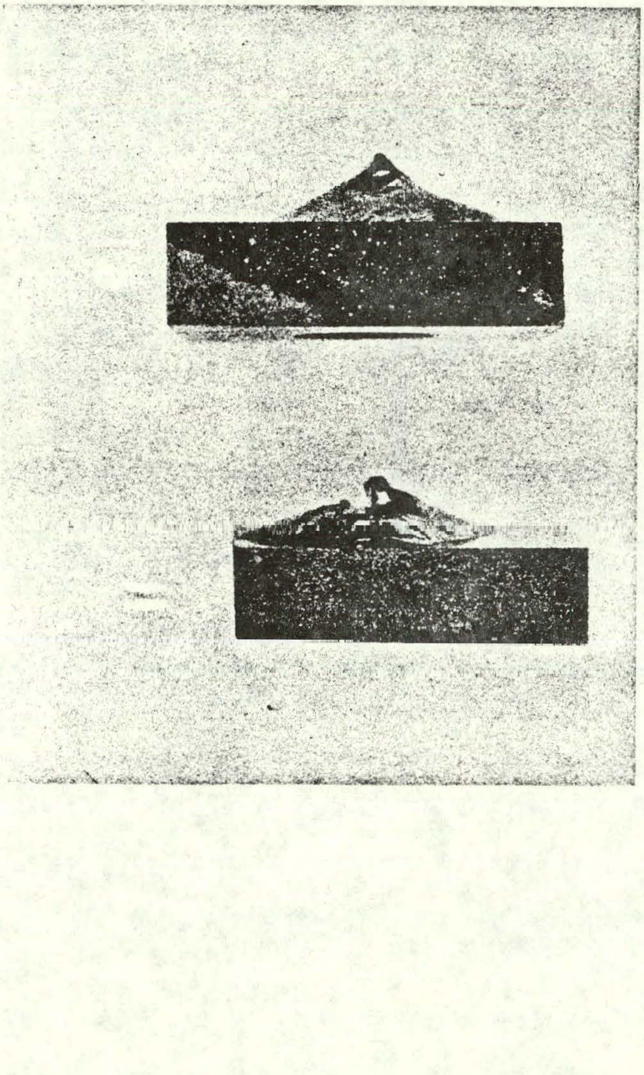
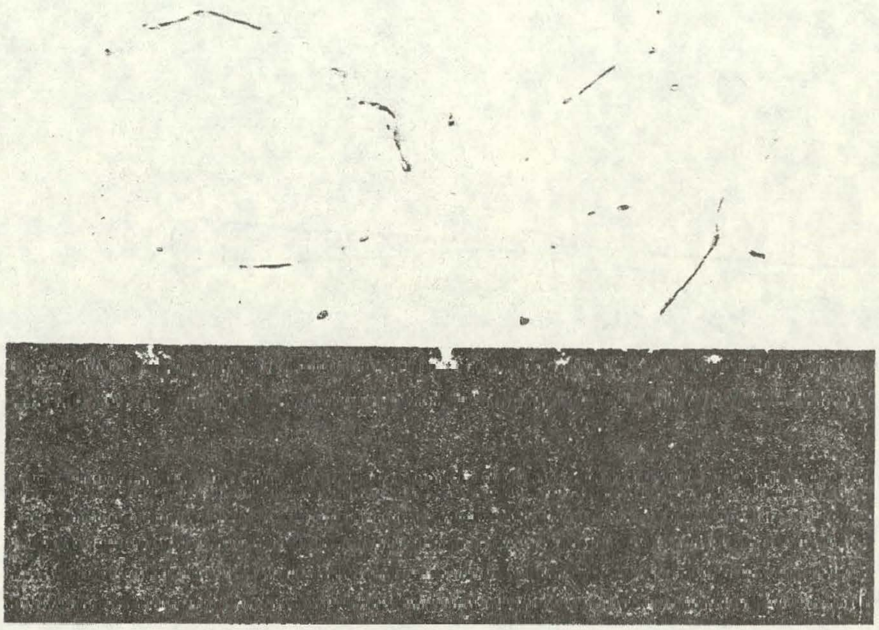
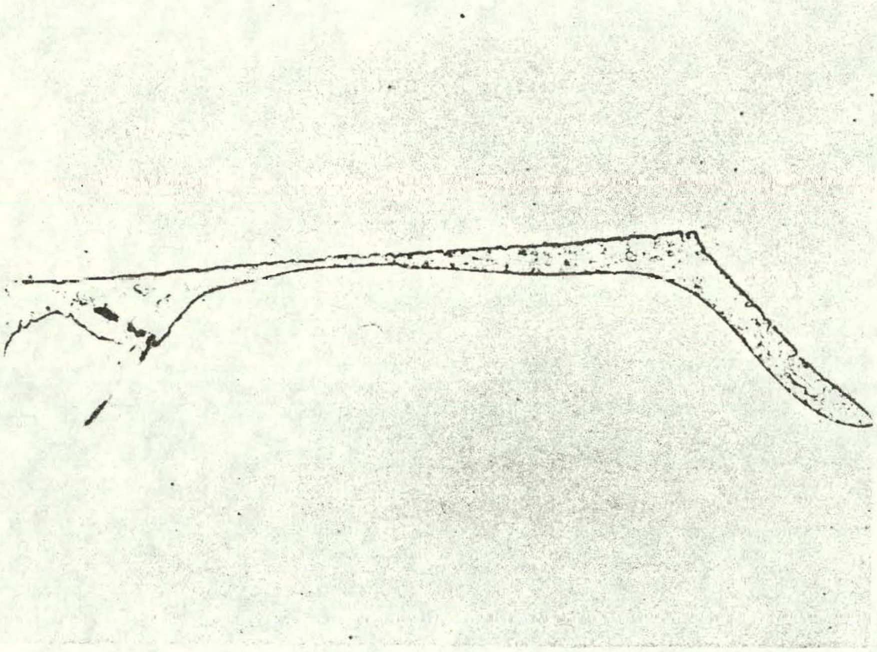


FIGURE 13. WETTING OF $Si_{1.8}Al_{0.2}N_{1.8}O_{1.2}$ SIALON (NO 13) AND $Si_{3.4}Al_{2.6}N_{5.4}O_{2.6}$ SIALON (NO 11) BY MOLTEN SILICON (1 HR AT 1450 C)



4J871
(x100)

FIGURE 14. INTERFACE BETWEEN MULTIPHASE $Si_{3.6}Al_{2.4}N_{5.6}O_{2.4}$ SIALON AND SILICON SHOWING PRECIPITATES IN SILICON PHASE



4J874
(x500)

FIGURE 15. ENLARGED VIEW OF ALUMINUM RICH PRECIPITATE

The reaction of $Si_{1.8}Al_{0.2}N_{1.8}O_{1.2}$ Sialon with molten silicon appears to be complex, in that a loosely bonded reaction zone (see Figures 16 and 17) formed close to the ceramic material. Aluminum could not be detected in the outer silicon layer by electron probe analysis, which indicates its concentration is <1000 ppm, the detection limit of the apparatus. The concentrations of aluminum and silicon are 0.15 percent Al and 90.7 percent Si in the white layer and 0.16 percent Al, 63.6 percent Si in the dark reaction zone. Further work is needed to identify these two zones.

Particulate formation in the silicon-rich white layer suggests that the reaction mechanism was one of solution and reprecipitation in which the molten silicon first attacked the ceramic, probably at the grain boundaries, dissolving oxygen and nitrogen with the aluminum. Further work is required before this reaction is fully understood, but the above results suggest that the Sialon reaction zone phase might be a potential die and container material.

Preparation of Silicon Nitride Crucibles and Lids

The activity coefficients of O, N, Be, Al, and C in molten silicon are being determined (1) to aid in the selection of potential candiate die and container materials and (2) to determine the optimum compositions of silicon metal oxynitride solid solutions. Materials in the form of a small crucible are evaluated in a Knudsen cell. The dimensions of the crucible and the lid (which has a small hole in it to generate Knudsen flow conditions) were given in the first quarterly report.

During this second quarter, the work on preparation of silicon nitride crucibles and lids was initiated.* The chemical reactions investigated for forming Si_3N_4 crucibles on graphite mandrels were:

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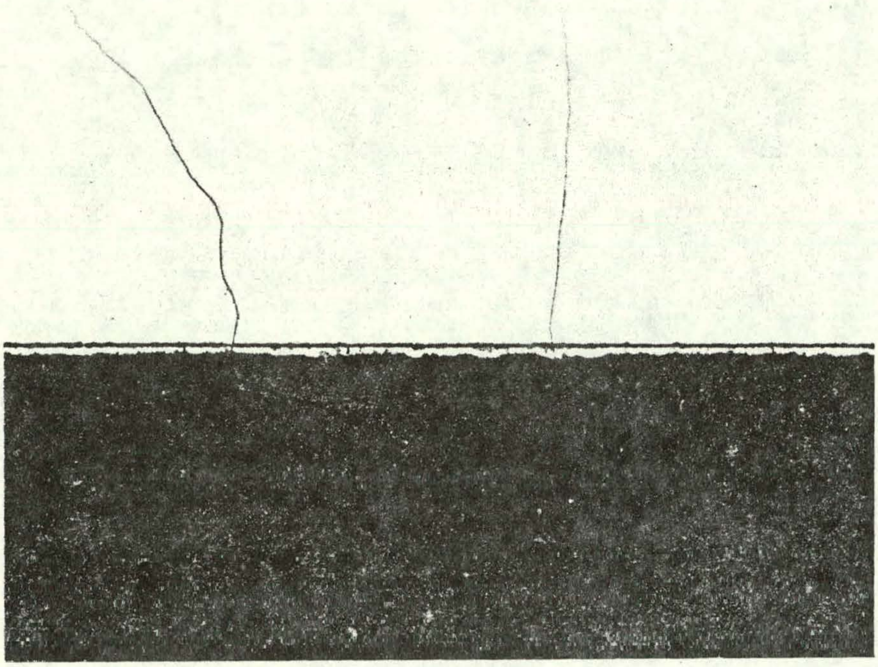
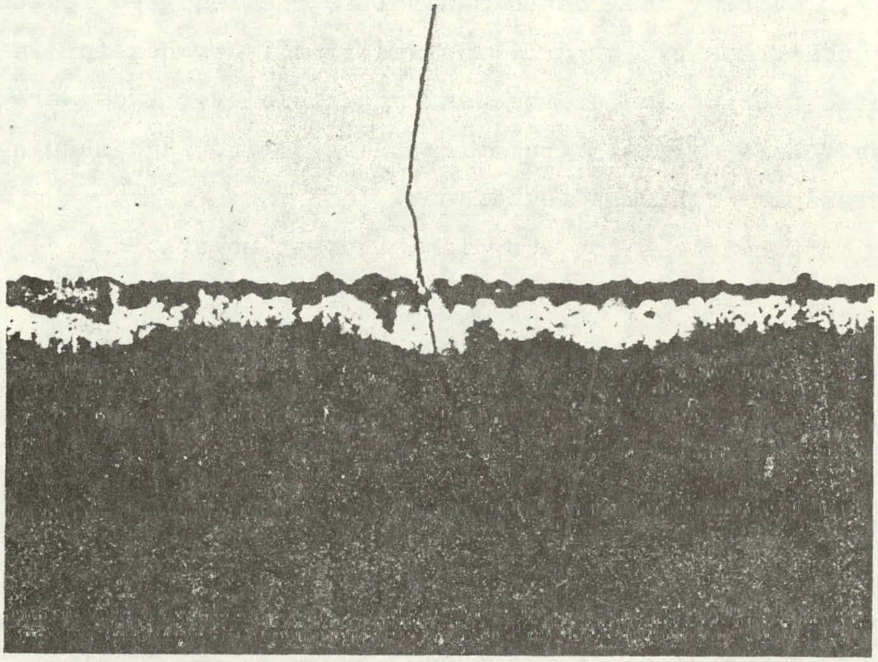
* These crucibles will be used in the determination of the activity of nitrogen in molten silicon.



4J875
(x100)

FIGURE 16. INTERFACE BETWEEN $Si_{1.8}Al_{0.2}N_{1.8}O_{1.2}$ SIALON AND SILICON SHOWING CRACKING IN THE TWO REGIONS AND SEPARATION OF PART OF THE CERAMIC



4J876
(x500)

FIGURE 17. ENLARGED VIEW OF $Si_{1.8}Al_{0.2}N_{1.8}O_{1.2}$ SILICON INTERFACE SHOWING MICROCRACKING AND SEPARATION OF THIN CERAMIC LAYER

$$(1)\quad 4NH_3(g) + 3SiCl_4(g) \xrightarrow{\sim 950\ C} Si_3N_4(s) + 12HCl(g)$$

$$(2)\quad 4NH_3(g) + 3SiHCl_3(g) \xrightarrow{\sim 950\ C} Si_3N_4(s) + 9HCl(g) + 3H_2(g).$$

Cutting the coated mandrel to the required length and removing the graphite, by drilling and finally by heating in air, completed fabrication of the desired crucibles. Lids were made by coating square mandrels, removing the graphite, and shaping the lids by ultrasonic machining techniques.

Conditions for a typical deposition are:

Temperature of mandrel (optical)	950 C
Time	2 hours
Reactant flow	1560 mils/minute
Reactant composition	
Hydrogen	28.8 volume percent
Ammonia	64.1 volume percent
Silicon tetrachloride	7.1 volume percent
Rate of deposition	18 mils/hour.

Typical deposites are shown in Figure 18 in the three stages of graphite removal from crucibles, and a view of a coated flat intended for shaping into lids is presented in Figure 19.

The deposited Si_3N_4 was a translucent white with a nodular outer surface probably resulting from a columnar growth structure. Dimensionally suitable crucibles were prepared in the early experiments, but they typically contained cracks in the thicker sections (>40 mils), exhibited a crazed pattern in the thinner deposits, and were essentially crack free at <1 mil in thickness. Most of the experimental work performed in this report period has been devoted to minimizing this cracking problem.

The weakness inherent in a columnar structure undoubtedly contributed to the cracking problem. This is confirmed in that cracking is observed to follow along the intersection of growth cones. An "as-deposited" stress or a thermal expansion mismatch between the coating

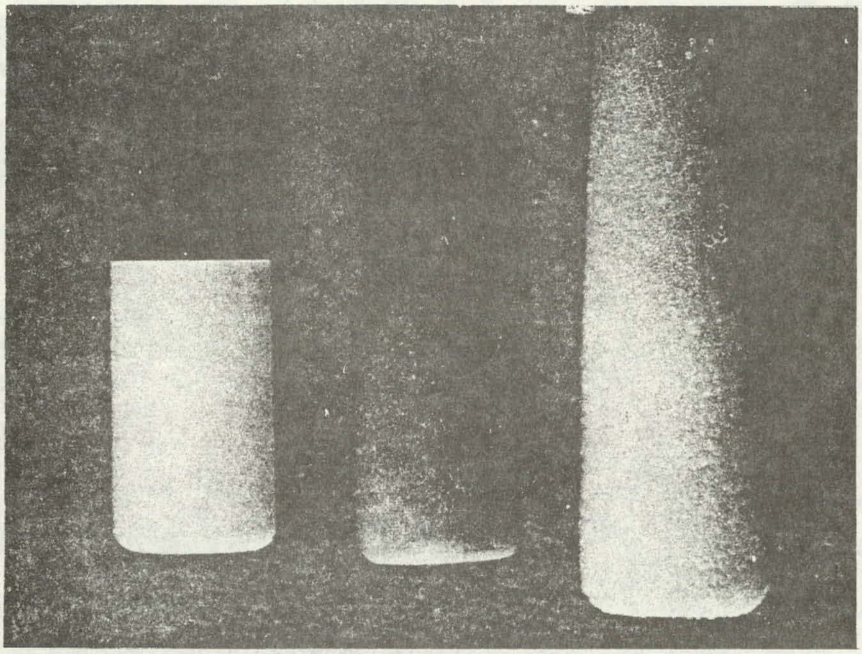


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FIGURE 18. TYPICAL DEPOSITS IN THE THREE STAGES OF GRAPHITE REMOVAL FROM CRUCIBLES

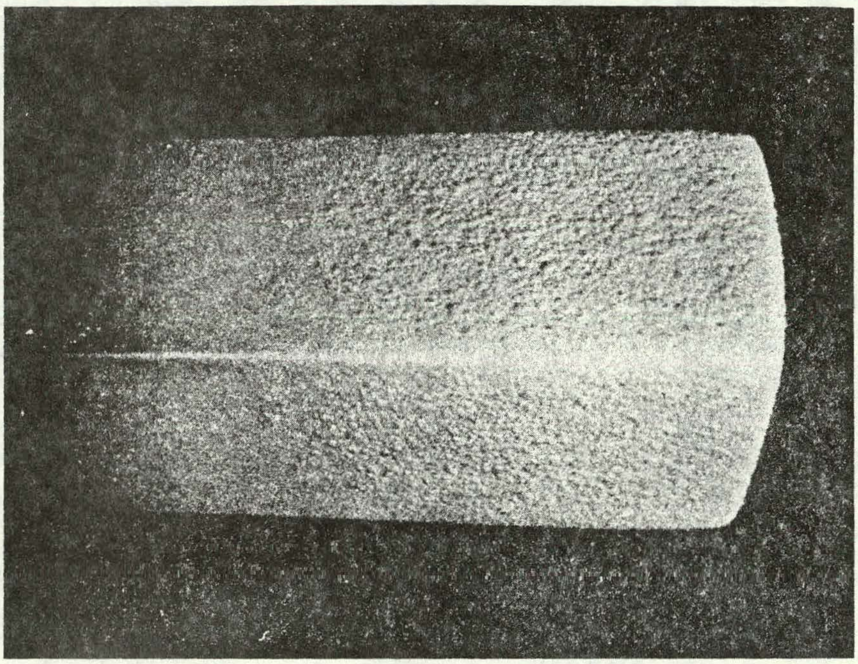

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FIGURE 19. VIEW OF COATED FLAT INTENDED FOR SHAPING INTO LIDS

and the graphite mandrel were considered the most likely candidates for causing the weakened coating to fracture. The latter factor is considered the most probable cause because the extent of cracking was a function of coating thickness and no evidence of coating over a crack was observed. Furthermore, the deposited Si_3N_4 was found to be well bonded to the graphite substrate, which could readily account for the crazing and cracking phenomena in view of their relative thermal expansions (typically 2.7×10^{-6}/C for Si_3N_4 and 3.7×10^{-6}/C for commercial graphite). Accordingly, experiments were designed to (1) develop a less columnar structure by altering the deposition parameters, and (2) minimize stress in the coating by use of various graphites and substrate surface treatments to reduce the coating-to-substrate adherence.

Under Item (1) above, (a) $SiHCl_3$ was substituted for $SiCl_4$, (b) temperatures were varied from 870 to 1125 C, (c) $SiCl_4$ ($SiHCl_3$) content of reactant stream was varied from 3.3 to 12.1 volume percent, and (d) N-to-Si ratio in the reactant stream was varied from 3.3 to 13.6. Under Item (2) above, three types of graphite were used, i.e., CS, ATJ, and POCO. Also the latter two were coated with pyrolytic carbon to promote release from the deposit upon cooling.

Although improvements were made, none of these steps were completely successful in yielding noncolumnar, uncracked deposits which are visualized to result in the strongest crucibles and lid blanks. Nevertheless, three crucibles have been submitted for possible use and material has been made available for the shaping of three lids.

Solution Thermodynamics

Mass spectrometric studies of Al_2O_3 and BeO crucibles in contact with molten silicon have been performed this quarter. For completeness, the data previously obtained for SiO_2 are also discussed.

The data for all three materials are summarized in Table 9. Oxygen concentrations were determined from the SiO or CO species

TABLE 9. SUMMARY OF THERMODYNAMICS DATA

	Crucible Material		
	BeO	Al_2O_3	SiO_2
P SiO	1.4×10^{-5} atm	2.7×10^{-5} atm	2.9×10^{-5} atm
P Si	2×10^{-7} atm	3.5×10^{-7} atm	4.3×10^{-7} atm
P O_2	2×10^{-25} atm	8×10^{-25} atm	1×10^{-24} atm
[O] in Si	212 ppm	315 ppm	196 ppm
[Be] in Si	5000 ppm		
a*[Be]	4.3×10^{-4}		
[Al] in Si		15%, 20 ppm†	
a [Al]		2.8×10^{-5}, 2.0×10^{-7}†	
a [BeO]	3×10^{-3}		
γ**[BeO***]	0.6		
a [Al_2O_3]		6×10^{-4}	
γ [Al_2O_3]		4×10^{-3}	

* a = activity.

** γ = activity coefficient.

*** Based upon metal concentration.

† Using silicon contaminated by Aluminum from SiO_2 crucible.

liberated by reaction of the contaminated silicon with either tungsten or carbon. In all cases the oxygen concentration increased substantially from its initial 4 ppm level in the as-received silicon. The oxygen concentration, however, shows only a modest variation for each material: BeO ([0] in Si 212 ppm), Al_2O_3 ([0] in Si 315 ppm) and SiO_2 ([0] in Si 196 ppm).

The activities computed from the experiments indicate that oxygen tends to be associated with the Be and Al in the molten silicon, Be, Al, Al_2O, and AlO being the metal vapor species observed in the Knudsen cell (see Tables 10 and 11). The thermodynamic activity (a) of the oxide crucibles in the melt can be computed by utilizing standard thermodynamic equations and by making use of the relationship among activities:

$$a\ (\text{crucible}) = a\ (\text{metal}) + a\ (\text{oxygen}).$$

For the case of BeO the activity is 3×10^{-3}, and using the value of 5000 ppm for the crucible the activity coefficient (γ) is computed to be 0.6. This indicates that there is only a slight attraction between silicon and BeO, and that BeO offers potential as a crucible material. Al_2O_3 has an activity of 6×10^{-4} and an actively coefficient of 4×10^{-3} using 15 weight percent for the crucible. Further studies to determine the activity of aluminum were performed at concentrations substantially less than 15 weight percent dissolved aluminum in order to obtain data at impurity levels likely to be representative of those during actual solar silicon processing. After contact with SiO_2, the silicon melt contained 20 ppm aluminum (see Table 12), and at this concentration the activity of aluminum is reduced by a factor of 100 to 2.0×10^{-7}.

The exact mechanism of the dissolution of Al_2O_3 in the melt is not fully understood at this time. In Figure 20 the vapor pressures of the volatile aluminum and Al_2O species first increase with increasing temperature, as would be expected, but above 1170 C a slight decrease in vapor pressure is observed.

TABLE 10. VAPOR SPECIES ABOVE SILICON IN A BeO CRUCIBLE AT 1695 K

Species	Pressure, atm
SiO	1.41×10^{-5}
Si	1.61×10^{-7}
Si_2	2.1×10^{-9}
Si_3	5×10^{-10}
Si_4	1.7×10^{-10}
Si_5	9×10^{-12}
Si_6	8×10^{-12}
Be	1.3×10^{-7}

TABLE 11. VAPOR SPECIES ABOVE SILICON IN CONTACT WITH Al_2O_3 AT 1690 K

Species	Pressure, atm
SiO	2.75×10^{-5}
Si	3.48×10^{-7}
Al	9.62×10^{-8}
Al_2O	7.7×10^{-8}
AlO	1×10^{-8}
Na*	5.1×10^{-11}
Al_2	2×10^{-9}
Si_2	1.4×10^{-9}
Si_3	5×10^{-10}
Si_2O_2	2×10^{-10}
Si_4	2×10^{-10}
Si_5	6×10^{-12}
Si_6	6×10^{-12}

* Impurity in Al_2O_3 crucible.

TABLE 12. MASS SPECTROGRAPHIC ANALYSES OF AS-RECEIVED SILICON AND SILICON HELD IN CONTACT WITH SiO_2 CRUCIBLE AT 1690 K (ppm)

Elements	Silicon as Received	Silicon Melted in SiO_2
Be	-	-
Na	1	25
Mg	-	10
Al	-	20
Si	Major	Major
P	1	3
S	2	5
Cl	7	16
K	-	3
Ca	-	3
Ti	-	10
Cr	-	3
Mn	-	1
Fe	3	5
Co	2	3
Ni	-	10
Cu	-	3
Zr	-	-
Nb	-	-
Mo	-	-
Ta	-	-
W	-	-
Pb	-	1

- < 1 ppm.

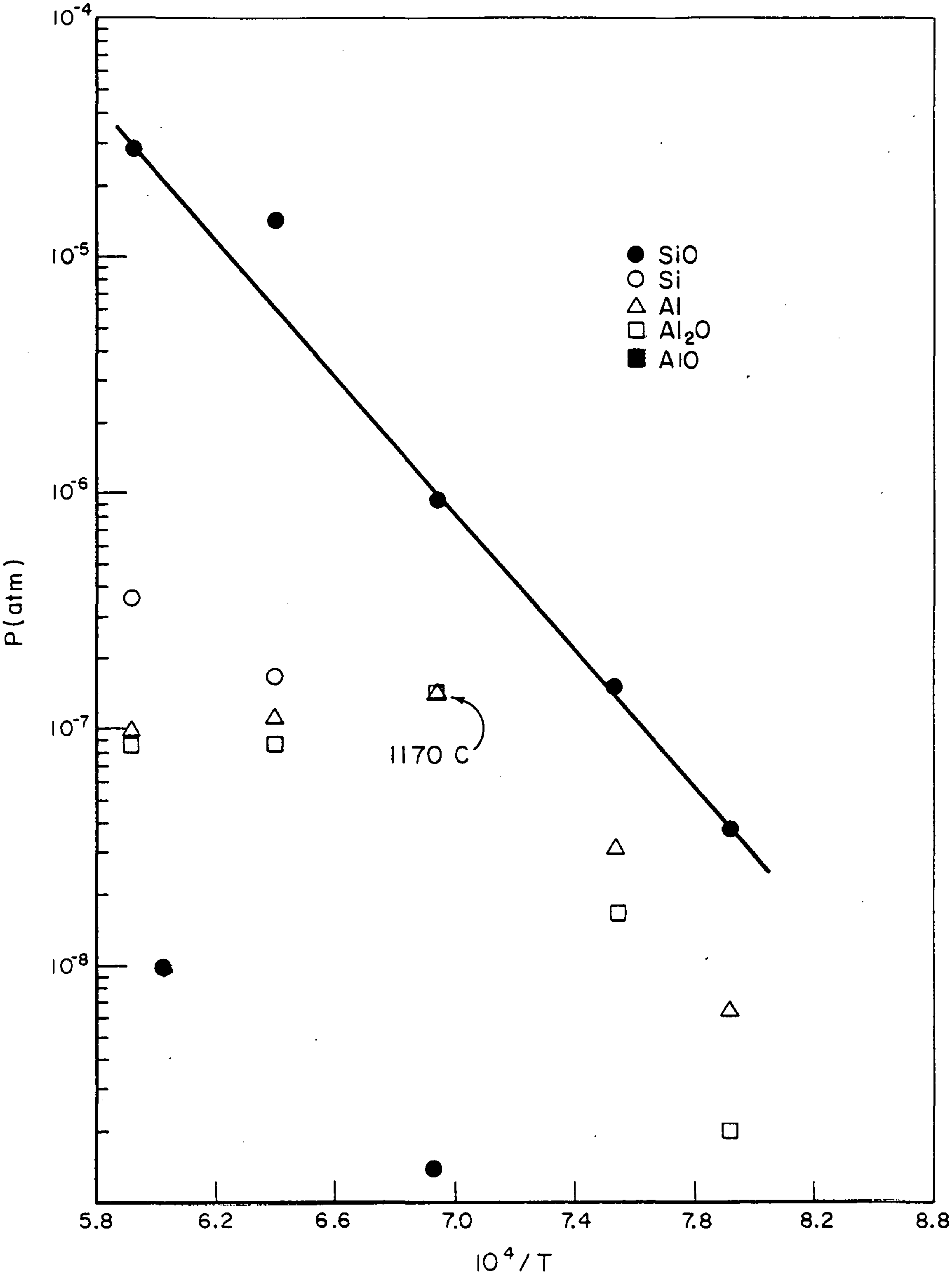

FIGURE 20. VARIATION WITH TEMPERATURE OF VOLATILE SPECIES ABOVE THE SYSTEM $Si\text{-}Al_2O_3$

Figure 21 shows the SiO pressure above silicon in each crucible; the shape of each line represents the steady-state reaction kinetics for that particular crucible density and grain size. The SiO(g) pressure is a measure of the oxygen in solution in the melt at any given time. From the Henry's Law constants (K = partial pressure/oxygen concentration), it is possible to calculate the oxygen concentration in the melt at a given time by measuring the SiO(g) pressure. The Henry's Law constants for oxygen are given in Table 13 for these three materials together with the values for beryllium and aluminum. These data will be used later to determine the concentrations of oxygen and aluminum (and possibly beryllium) in molten silicon when experiments with the Sialon materials (and possibly silicon beryllium oxynitrides) are performed.

Although the initial primary emphasis of this program is the development and assessment of the two Sialon solid solutions, the above data showing the greater resistance of BeO to attack by molten silicon suggest that a silicon beryllium oxynitride may possibly be a better die and crucible material than any of the Sialon materials.

PLANS FOR WORK NEXT QUARTER

(1) Determine the solution thermodynamics of carbon and nitrogen using SiC and Si_3N_4 crucibles in contact with molten silicon. Initiate studies of the Sialons.

(2) Fabricate $S_{1.9}Al_{0.1}N_{1.9}O_{1.1}$, $Si_{1.8}Al_{0.2}N_{1.8}O_{1.2}$, and $Si_{3.6}Al_{2.4}N_{5.6}O_{2.4}$ Sialons using new Si_3N_4 and AlN powders. Establish the lower solid solution limit of β' Sialon that can be hot pressed to ≥ 90 percent theoretical density.

(3) Perform sintering trials on all four Sialons.

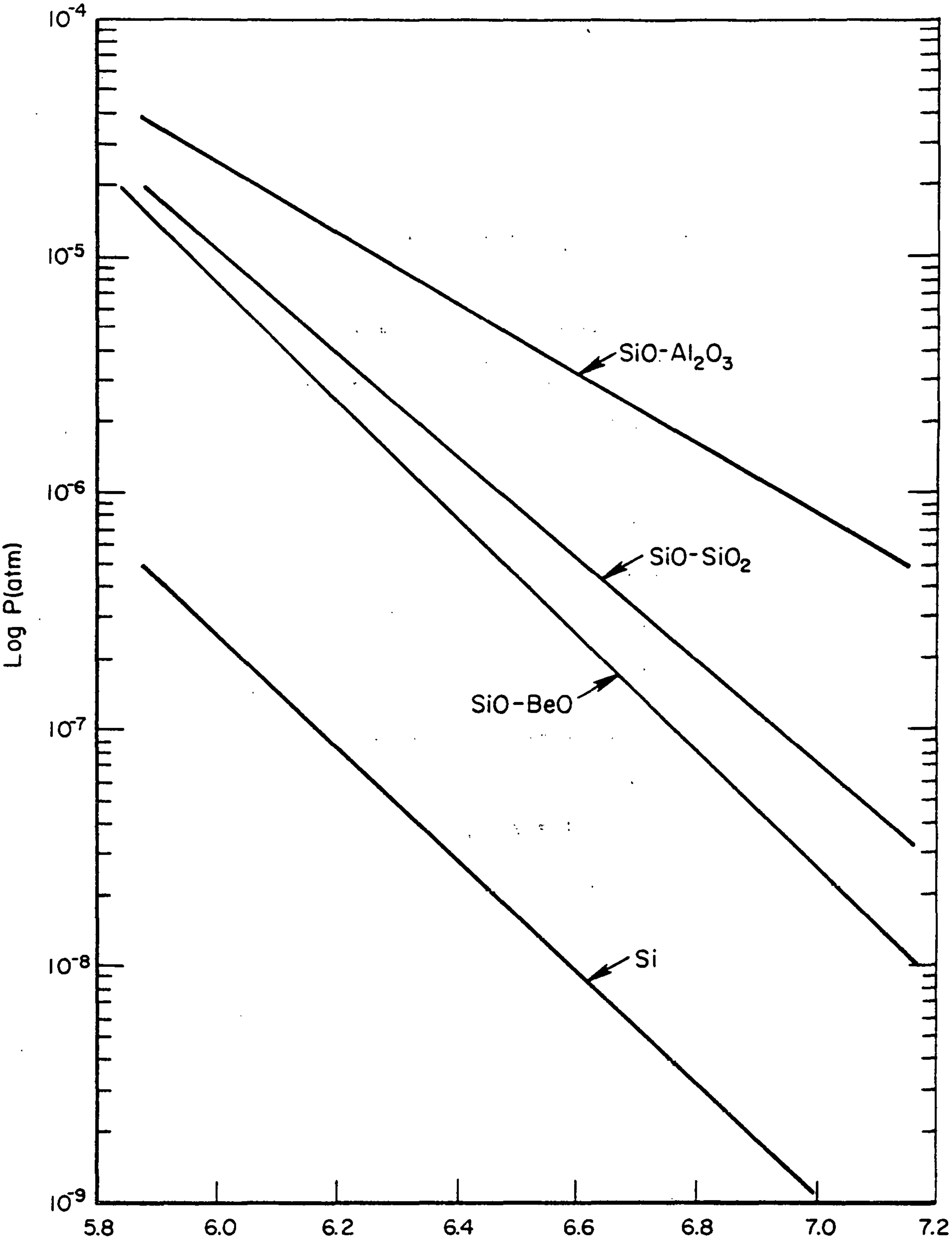

FIGURE 21. VARIATION OF SiO(g) PRESSURE ABOVE SILICON IN CONTACT WITH Al_2O_3, SiO_2 AND BeO CRUCIBLES

TABLE 13. HENRY'S LAW CONSTANTS

System	Value of Constant, atm
O-Si-SiO_2	5×10^{-21}
O-Si-Al_2O_3	2.5×10^{-21}
O-Si-BeO	$9.4 \times 10^{-}$
Al-Si-Al_2O_3	6.4×10^{-7}*
Al-Si-Al_2O_3	1.3×10^{-6}†
Be-Si-BeO	2.6×10^{-5}

* For [Al] = 15 weight percent.

† For [Al] = 20 ppm.

NEW TECHNOLOGY

No items of new technology have been specifically reported so far.

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