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FIRST QUARTERLY PROGRESS REPORT

(Covering the Period October 1, 1977 to December 31, 1977)

on

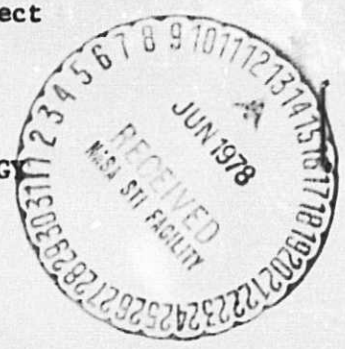
DEVELOPMENT AND EVALUATION OF DIE AND CONTAINER MATERIALS

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

to

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

January 18, 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

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ABSTRACT

This First Quarterly Progress Report on JPL Contract No. 954876 covers the work during the period October 1 to December 31, 1977. Commercial high purity ultrafine Si_3N_4, Al_2O_3 and SiO_2 powders were vacuum dried and stored under nitrogen in sealed containers. Extensive analysis of the chemical, physical and morphological characteristics of these powders has been performed.

The preparation of high purity AlN powder is being investigated by elevated temperature gas phase nucleation reactions involving (1) the reaction of $AlCl_3(g)$ and NH_3 and (2) the reaction between AlCl(g) and NH_3. While optimization of reaction (1) has not been completed, it appears that this process will only give low yields. Preliminary evaluation of reaction (2) has not yet proceeded far enough to permit definitive analysis of results.

The interaction of molten silicon with fused quartz was examined in a Knudsen cell using a mass spectrometer. The solubility of oxygen at the melting point of silicon was calculated to be 1.78×10^{18} atoms/cm^3, and the activity coefficients of oxygen and silicon monoxide, the major vapor species, were calculated to be 4.83×10^{-24} and 7.01×10^{-5}, respectively.

ACKNOWLEDGEMENT

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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 mils 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/cc is an upper limit for general impurities. Exceptions to this are: aluminum, phosphorus, boron, arsenic, and gallium, which may be present one or two orders of magnitude higher, and carbon,

oxygen, and nitrogen, which may be present in amounts dictated by erosion rates (approximately 10^{19} atoms/cc). However, revision of these numbers may occur as knowledge of their specific effects is developed. For example, there are indications that structural imperfections result from carbon levels greater than 1×10^{18} atoms/cc.

(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° 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 die and containers. These materials are based on two solid solutions of general formulae:

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

$Si_{2-x}\ Al_x\ N_{2-x}\ O_{1+x}$ 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) $Si_3N_4 + AlN + Al_2O_3 \rightarrow \beta'$ Sialon

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

In this first three months commercial high purity Si_3N_4, Al_2O_3 and SiO_2 powders have been obtained and analyzed. Ultrafine high purity AlN is being prepared at Battelle's Columbus Laboratories.

TECHNICAL DISCUSSION OF RESULTS THIS QUARTER

Evaluation of Si_3N_4, Al_2O_3, SiO_2 Powders

Handling and Storage

A special procedure was adopted so that the characteristics and reactivity of each powder would remain unchanged t'.roughout the program. High purity ultrafine powders obtained from commercial vendors (see Table 1) were transferred into clean dry glass jars and then vacuum dried at 200 C. After cooling the oven was backfilled with nitrogen and the containers tightly sealed. Powder samples needed for analysis were obtained by opening the sealed containers under a nitrogen atmosphere in a glove bag.

During the vacuum drying of the Si_3N_4 powder a deposit formed on the glass door of the oven. This deposit was chemically analyzed and found to be ammonium chloride.

Chemical Analysis

Spark Source Mass Spectrographic analysis and Optical Emission Spectroscopic analysis were performed in order to identify cation and anion impurities. The major impurities as indicated in Tables 2 and 3 are mainly in the range 10-100 ppmw with the exception of the Cl impurity in Si_3N_4, which is 5000 ppmw. In Si_3N_4 the other major impurities are Na(10) and Mo(12). The main impurities in the SiO_2 are Na(20), Cl(14), Ca(30) and Fe(30), and in the Al_2O_3 powder they are Na(40), Mg(20), Si(50), P(20), Cl(100), Fe(50) and Ca(100).

Oxygen analysis was performed on two samples of the Si_3N_4 powder using the inert gas fusion method. The average value was 2.90 percent.

Thermalgravimetric Analysis

Small weight losses were recorded for all three powders (see Figure 1). These are probably due to evolution of the remaining chloride,

TABLE 1. SUPPLIERS OF COMMERCIAL POWDERS

Powder	Vendor
Al_2O_3 grade RC-HP-DBM	Reynolds Metal Co.
SiO_2 Cabosil EH-5 grade	Cabot Corporation
Si_3N_4 SN 402 grade	GTE Sylvania, Inc.

TABLE 2. EMISSION SPECTROGRAPHIC ANALYSES OF Si_3N_4, Al_2O_3, SiO_2 POWDERS

Powder	Impurities (PPMW)							
	Ca	Si	Mg	Mo	Al	Fe	Ga	Ni
Si_3N_4	nd	Major	<5	10	10	nd	nd	nd
SiO_2	nd	Major	<5	<10	10	nd	nd	nd
Al_2O_3	10	100	5	nd	Major	50	300	<10

nd = not detected.

TABLE 3. MASS SPECTROGRAPHIC ANALYSES OF Si_3N_4, SiO_2, and Al_2O_3 (ppmw)

Element	Sample Designation Si_3N_4 33616-100	SiO_2 33616-200	Al_2O_3 33616-300	Element	Si_3N_4 33616-100	SiO_2 33616-200	Al_2O_3 33616-300
Li	<0.004	<0.006	<0.002	Sn	0.4	≤0.4	≤0.2
Be	<0.004	<0.004	<0.02	Sb	<0.1	≤0.2	≤0.07
B	0.96	0.1	0.06	Te	<0.2	<0.2	<0.06
F	0.1	0.6	0.4	I	<0.06	<0.07	<0.1
Na	10	20	40	Cs	<0.2	<0.4	<0.2
Mg	<10	<20	20	Ba	<0.1	<0.1	<0.1
Al(a)	≤10	≤10	Major	La	<0.04	<0.1	<0.07
Si	Major	Major	50	Ce	<0.1	0.2	<0.04
P	1	≤6	20	Pr	<0.1	<0.07	<0.02
S	≤1	<0.6	4	Nd	<0.2	<0.3	<0.2
Cl	5000	14	100	Sm	<0.2	<0.3	<0.2
K	≤0.2	0.2	0.8	Eu	<0.1	<0.2	<0.1
Ca	≤6	30	6	Gd	<0.1	<0.2	<0.1
Sc	<0.2	<0.7	<0.1	Tb	<0.02	<0.06	<0.03
Ti	<2	<1	<0.3	Dy	<0.2	<0.3	<0.1
V	<0.2	0.2	<1	Ho	<0.04	<0.2	<0.03
Cr	2	<5	2	Er	<0.1	<0.2	<0.1
Mn	<3	0.06	0.4	Tm	<0.2	<0.6	<0.3
Fe	<1	30	50	Yb	<0.2	<0.3	<0.1
Co	<0.3	0.3	0.01	Lu	<0.07	<0.06	<0.04
Ni	<1	≤2	1	Hf	<0.1	<0.3	<0.2
Cu	<4	5	0.2	Ta	<1	<2	<2
Zn	<2	0.4	2	W	0.2	<0.2	<0.1
Ga	<2	<0.4	100	Re	<0.06	<0.2	<0.06
Ge	<1	<0.6	<0.7	Os	<0.1	<0.6	<0.1
As	≤0.2	≤0.04	≤0.04	Ir	<0.4	<0.3	<0.2
Se	≤3	≤3	≤0.2	Pt	<0.2	<0.2	<0.1
Br	4	<0.2	0.1	Au	<0.06	<0.6	<0.03
Rb	<0.2	<0.07	<0.1	Hg	<0.1	<0.3	<0.1
Sr	<1	<1	<0.2	Tl	<0.2	<0.3	<0.1
Y	<0.1	<0.3	<0.04	Pb	0.2	0.1	0.2
Zr	<0.04	<0.6	<0.2	Bi	<0.06	<0.07	<0.03
Nb	<0.1	<1	<0.02	Th	<0.04	<0.07	<0.03
Mo	12	<0.4	≤0.2	U	<0.1	<0.3	<0.2
Ru	<0.2	<0.7	≤0.1				
Rh	≤0.02	<0.2	<0.03				
Pd	<0.7	<0.7	<0.2				
Ag	<0.2	<0.2	<0.1				
Cd	<0.2	<0.7	<0.3				
In	<0.06	<0.1	<0.04				

(a) Memory from previous sample

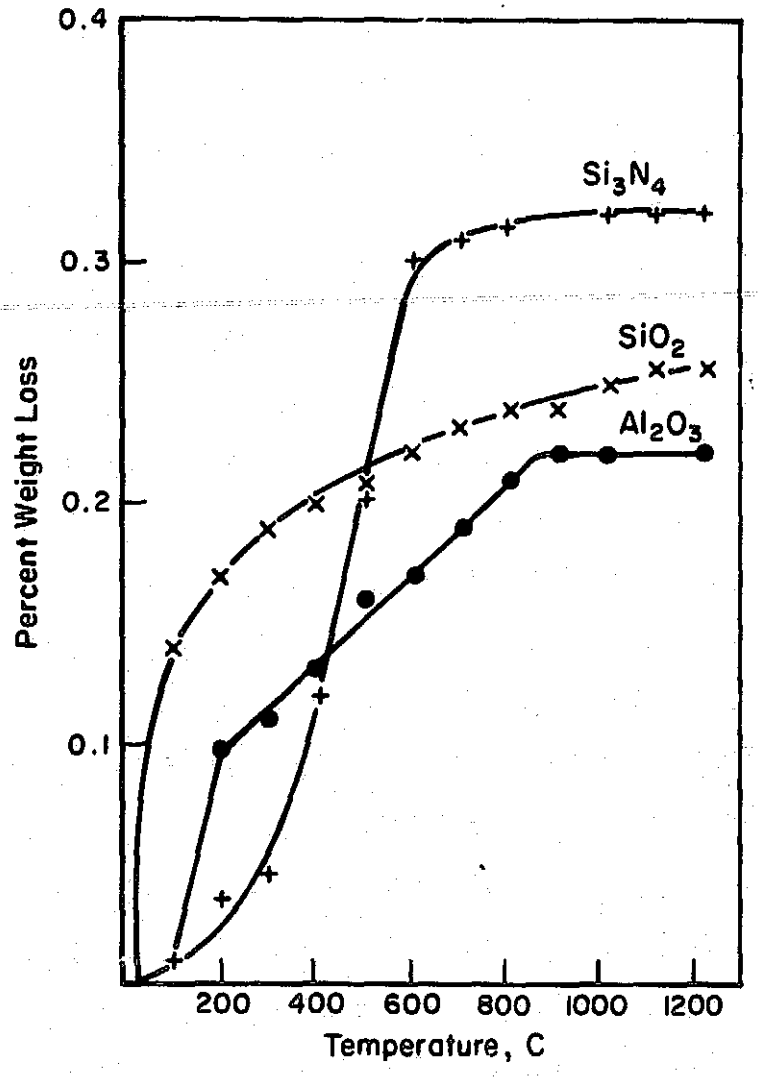

FIGURE 1. THERMOGRAVIMETRIC ANALYSIS OF VACUUM DRIED Si_3N_4, Al_2O_3 AND SiO_2 POWDERS

other absorbed gases and some water vapor picked up in transferring the powders to the thermal gravimetric apparatus. The Si_3N_4 powder is particularly unstable in this respect. Figure 2 shows the results for the vacuum dried powder after it has been exposed to air for a few hours. The weight loss increased to >5 percent. Also in Figure 2 are the data for the as received Si_3N_4 powder. These results support the need for the vacuum drying and storage procedure discussed earlier.

Physical Characteristics

The particle size distribution was determined by a sedimentation technique (Mine Safety Appliances, Inc.) and the surface area measured by nitrogen adsorption using the single point BET method. The surface area data are given in Table 4 and the particle size data in Figure 3. The average powder particle sizes are much higher than suggested by the surface area data probably because the sedimentation technique is measuring the agglomerate size and not ultimate particle size. The presence of agglomerates was confirmed in the compaction behavior of all three powders.

Figure 4 shows the bulk densities, tap densities and change in densities as a function of pressure. The breaks in the straight line graphs (arrowed on the diagram) indicate the presence of weak agglomerates. The low bulk density of the SiO_2 powder (0.0316 g/cm^3, 1.30 percent theoretical) makes it extremely difficult to handle and to disperse in hexane, which is to be used for milling. Consequently, a high purity SiO_2 powder of higher bulk density and particle size is being sought.

Morphology of Si_3N_4, Al_2O_3 and SiO_2 Powders

All powders were examined by transmission electron microscopy. Si_3N_4 and Al_2O_3 powder adhered to the specimen holder, but the SiO_2 powder required dispersing in collodion from which a thin film was made and transferred onto the copper grid.

The SiO_2 powder contained strongly bound aggregates of varying size. Figure 5 shows an aggregate approximately 1.5 μm size and the smaller particles in Figure 6 are 0.05 μm aggregates. Individual particles, calculated to be 0.007 μm in size, are difficult to detect.

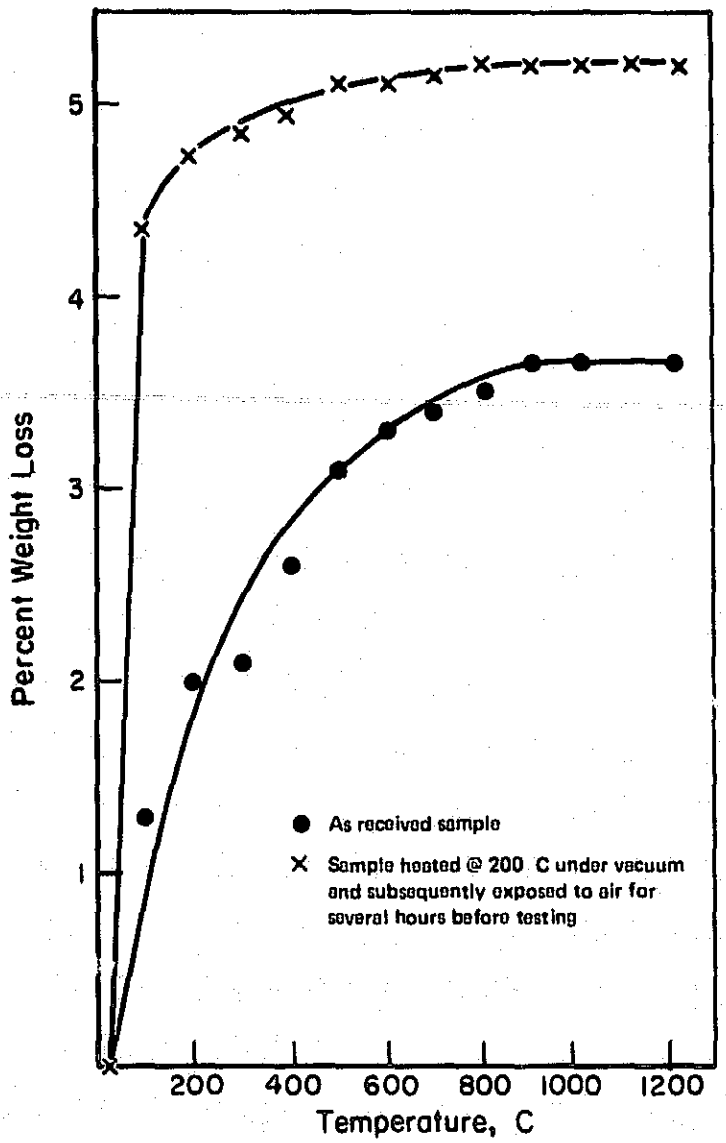

FIGURE 2. THERMOGRAVIMETRIC ANALYSIS OF AS RECEIVED Si_3N_4 AND VACUUM DRIED Si_3N_4 POWDER EXPOSED TO AIR FOR SEVERAL HOURS

TABLE 4. SURFACE AREAS OF Si_3N_4, Al_2O_3, SiO_2 POWDERS

Powder	Surface Area (m^2/grm)
Si_3N_4	28.3
SiO_2	384.0
Al_2O_3	3.78

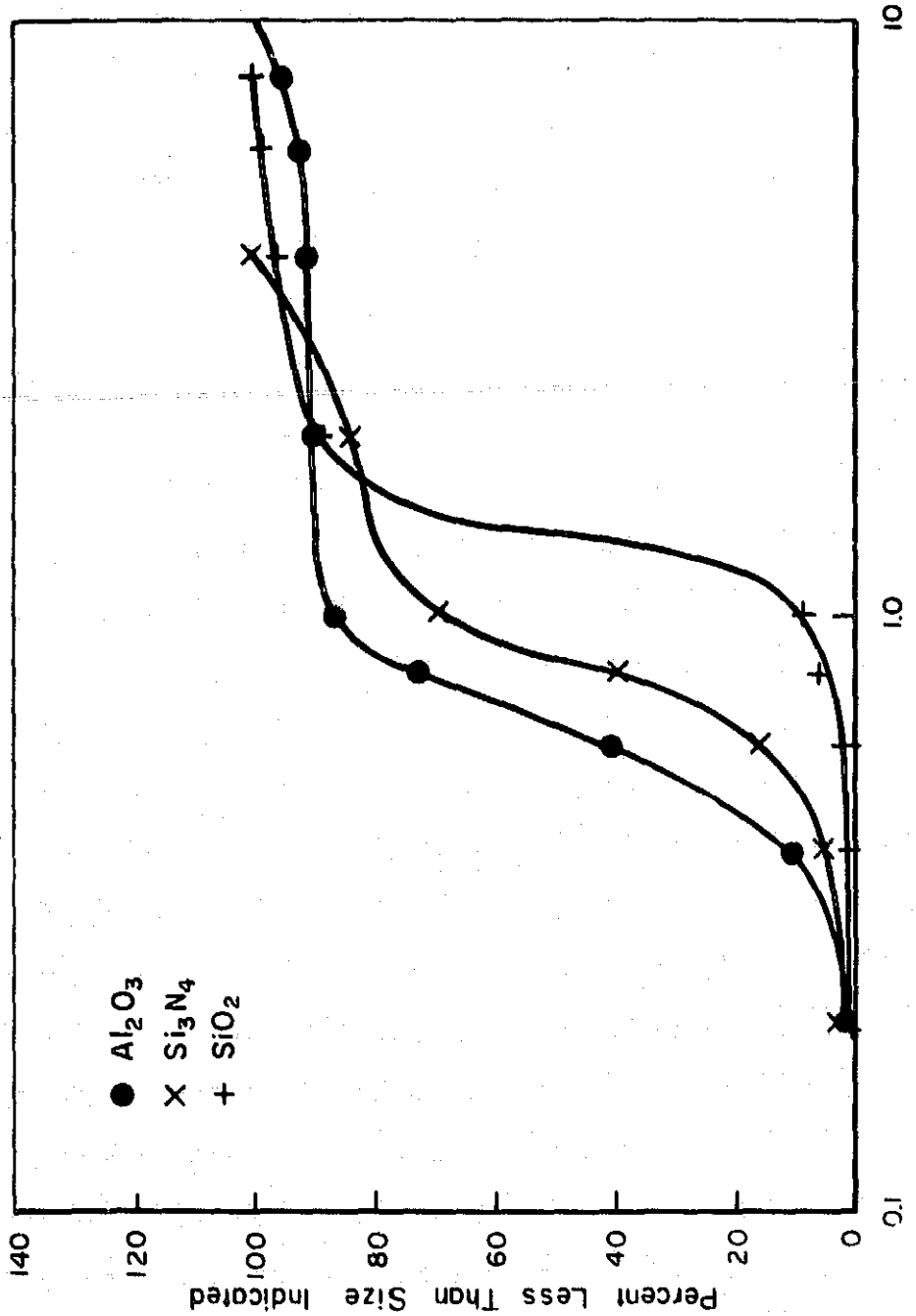

FIGURE 3. PARTICLE SIZE DISTRIBUTION OF Si_3N_4, Al_2O_3 AND SiO_2 POWDERS

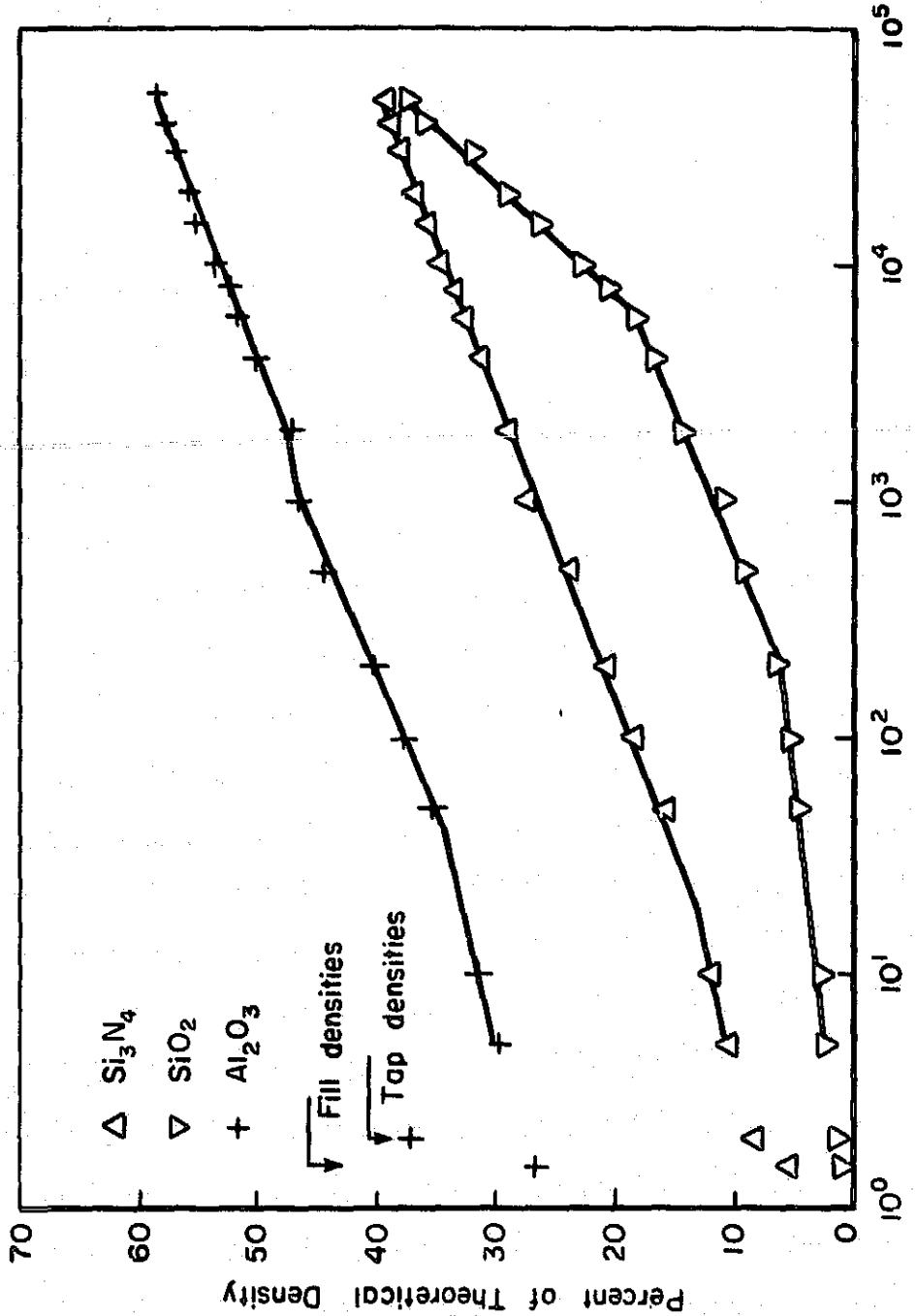

FIGURE 4. COMPACTION CURVES FOR Si_3N_4, Al_2O_3 AND SiO_2 POWDERS

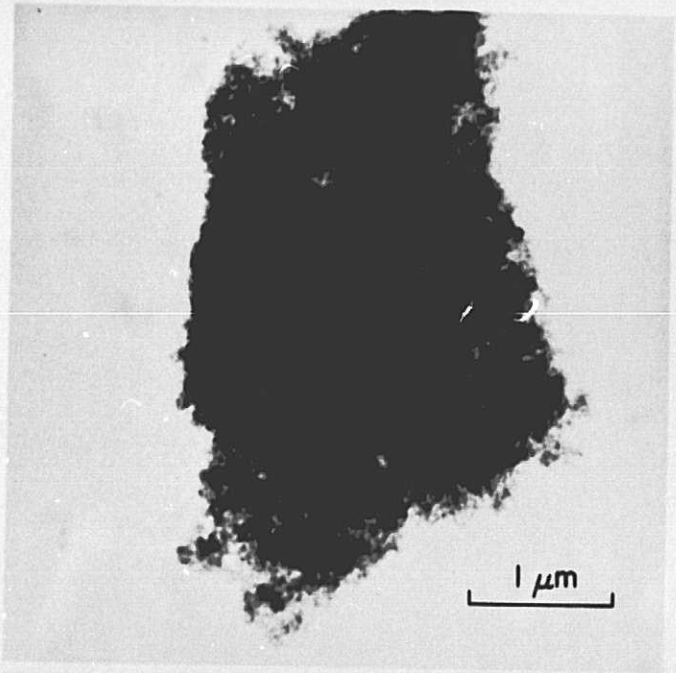

FIGURE 5. LARGE AGGREGATE IN SiO_2 POWDER.

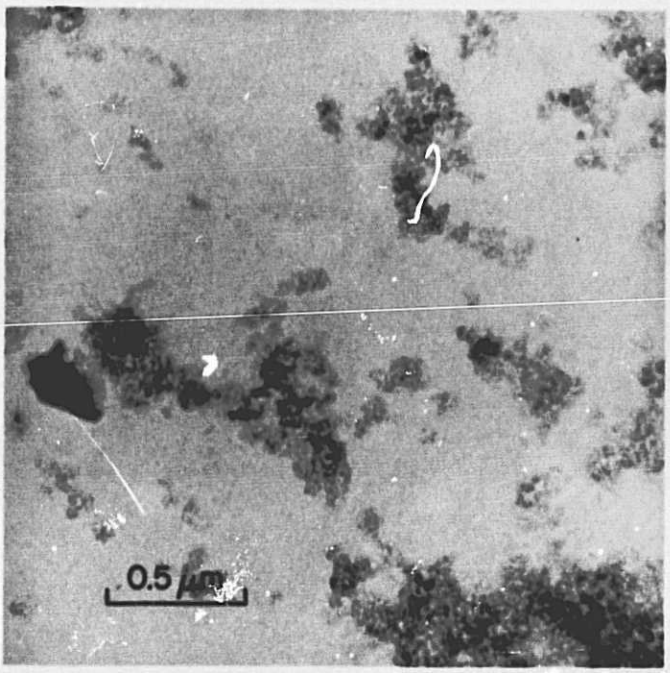

FIGURE 6. DIFFERENT SIZE AGGREGATES IN SiO_2 POWDER.

In Figures 7 and 8 the spherical shape of the Si_3N_4 powder is shown. There is some evidence of bonding between particles, but this does not appear to be particularly strong according to the compaction curve. The particle size range is 0.1-0.75 μm.

The Al_2O_3 powder (Figures 9 and 10) consists of irregular shaped particles usually weakly bound together. The ultimate particle size is in the range 0.2-0.75 μm.

Preparation of High Purity Aluminum Nitride

A review of literature and BCL experience suggests that the most promising candidate systems for preparing a high-purity AlN submicron sized 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) $AlCl(g) + 1/2N_2(g)^* + 3/2H_2(g) \xrightarrow{1200\ C} AlN(s) + HCl(g) + H_2(g)$ $\Delta G = -24.02$ kcal/mole.

Thermodynamically, the most favored reaction of the above is No. (3). However, because of the higher reaction temperature and the inherent complications of the system, it was decided to investigate initially one of the first two systems. In view of the thermodynamic advantage, the chloride system [No. (1)] was chosen.

Preparation of AlN by Reaction of Ammonia With Aluminum Trichloride

Since thermodynamically the $AlCl_3$ reaction [No. (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 11). Two separate gas streams were introduced into a

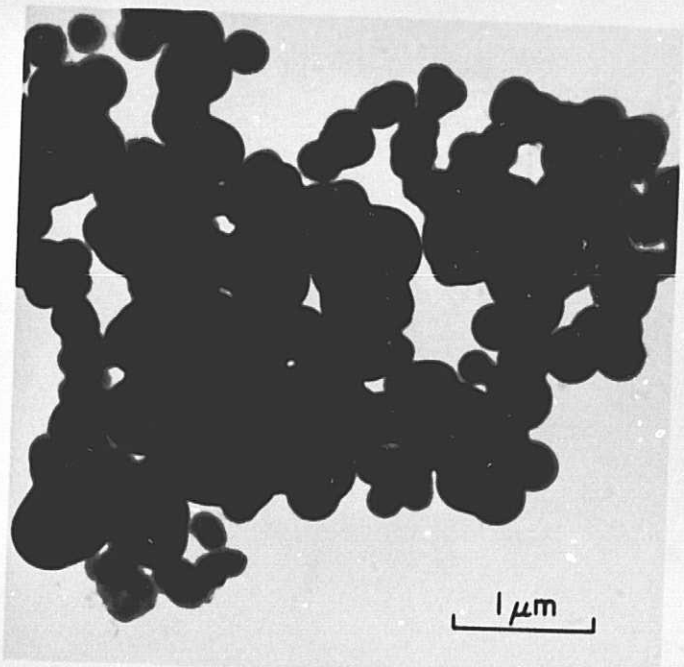

FIGURE 7. SPHERICAL Si_3N_4 PARTICLES.

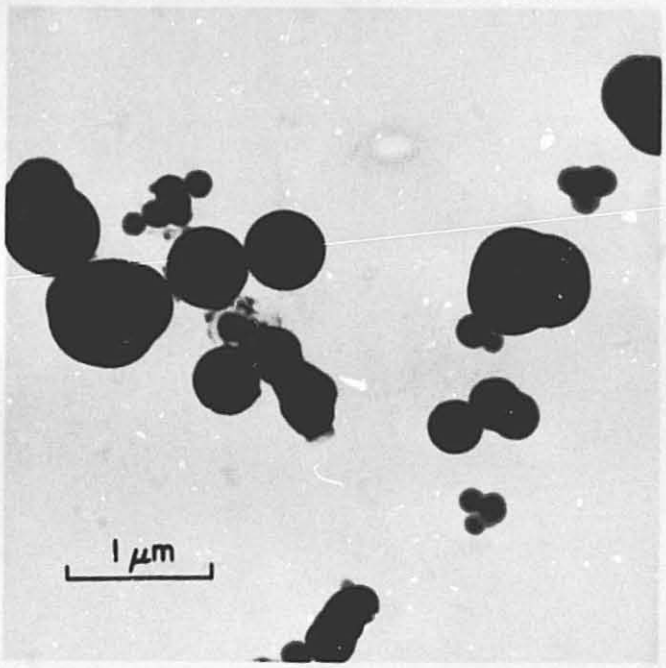

FIGURE 8. 0.1-0.7μm SPHERICAL Si_3N_4 PARTICLES.

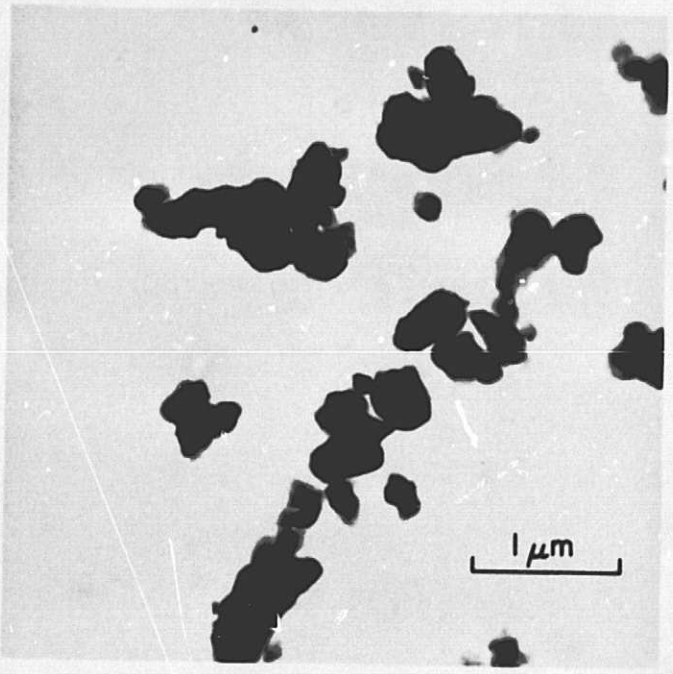

FIGURE 9. IRREGULAR SHAPED Al_2O_3 PARTICLES.

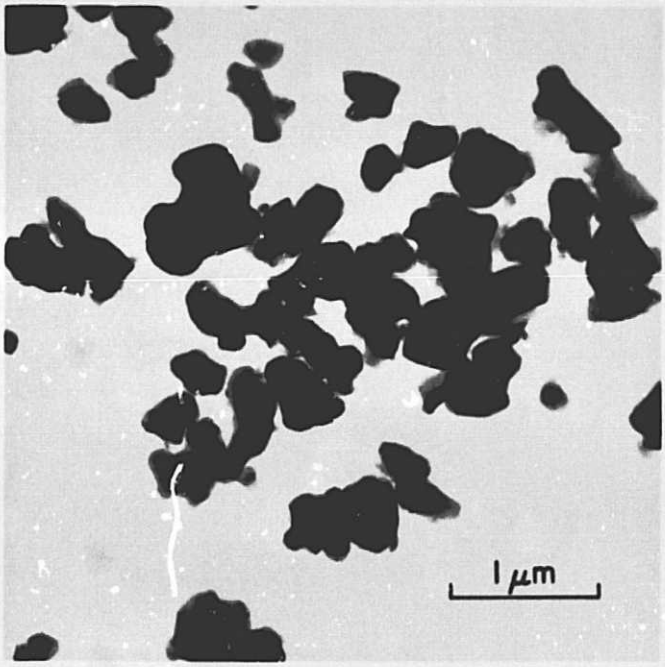

FIGURE 10. IRREGULAR SHAPED Al_2O_3 PARTICLES 0.2-0.75μm.

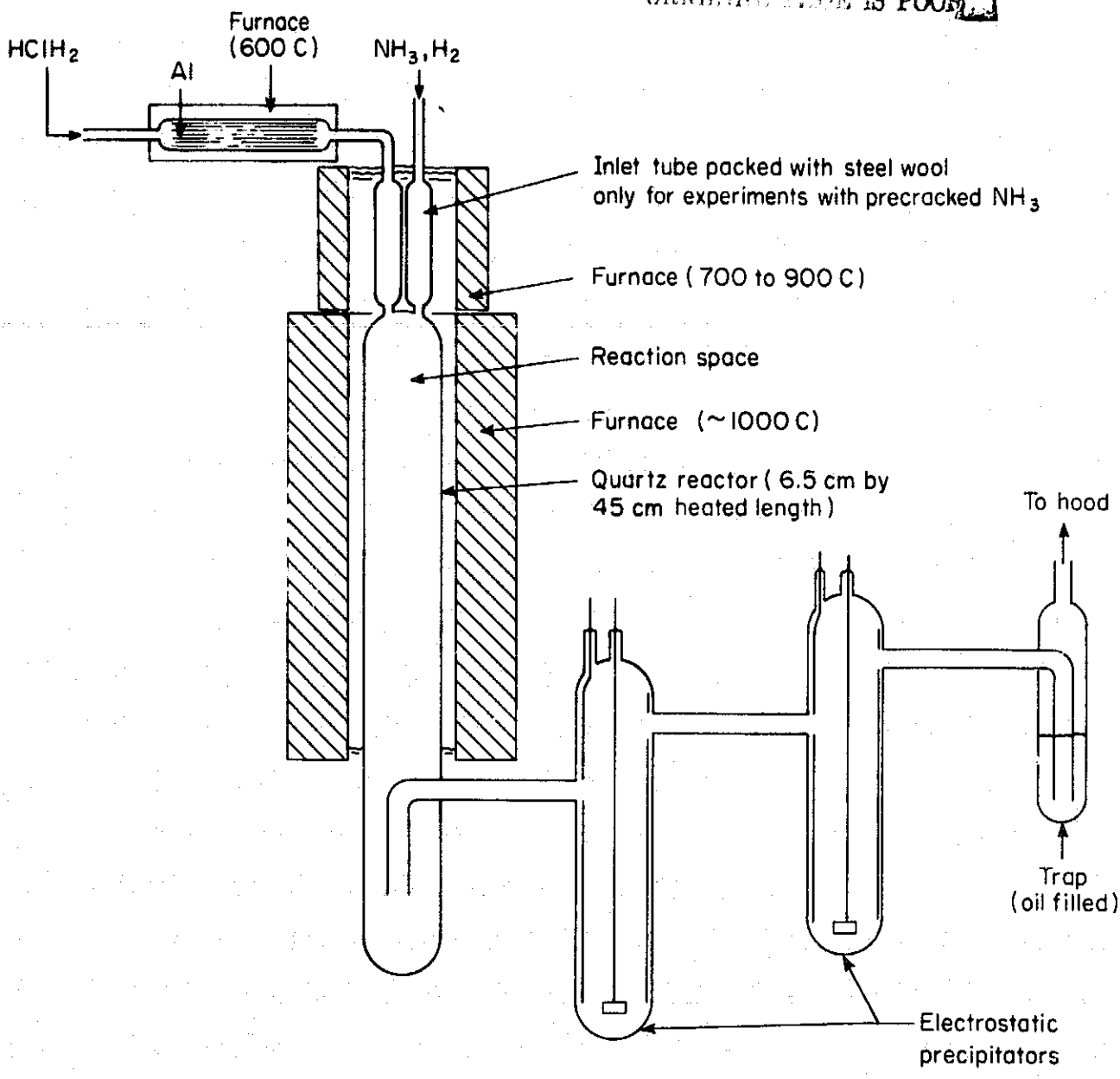

FIGURE 11. APPARATUS FOR INVESTIGATING $AlCl_3 + NH_3$ REACTION FOR PREPARATION OF AlN

6.5-cm-diameter by 45-cm-long chamber. One of these streams was an unprecracked* mixture of NH_3 and N_2 and the other was the reaction product ($AlCl_3$) from an adjacent 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 electrostatic 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_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 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 at a gas flow of 290 cm^3/minute (NH_3/Ar of ∿5) in a quartz cracker (10-cm diameter by 28 cm) filled with steel wool and maintained at a temperature of 800 C. NH_3 was completely (>99 percent) dissociated.

---

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

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 as 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 indicating 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.

The ratio of reactants for the run in which the above product was ($NH_3/AlCl_3$) 18. This value was varied from 18 down to four without significant change in results. A product from the second variation of the aluminum trichloride reaction (i.e., with precracked ammonia) at a ratio ($NH_3/AlCl_3$) of three 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 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.

Preparation of AlN by Reaction of
Ammonia with Aluminum Monochloride

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.

$HCl(g) + Al(\ell)$ 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

$$(2)\quad 1/2N_2^{*} + 3/2\ H_2 + AlCl(g) \xrightarrow{1000\ C} AlN(s) + HCl(g) + H_2(g)\quad \Delta G = -24.02\ kcal/mole\ .$$

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 the higher temperatures and the handling of molten aluminum make for more complicated apparatus and slower experimental turn around time.

The AlN powder forming system (Figure 12) 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.

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* 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.

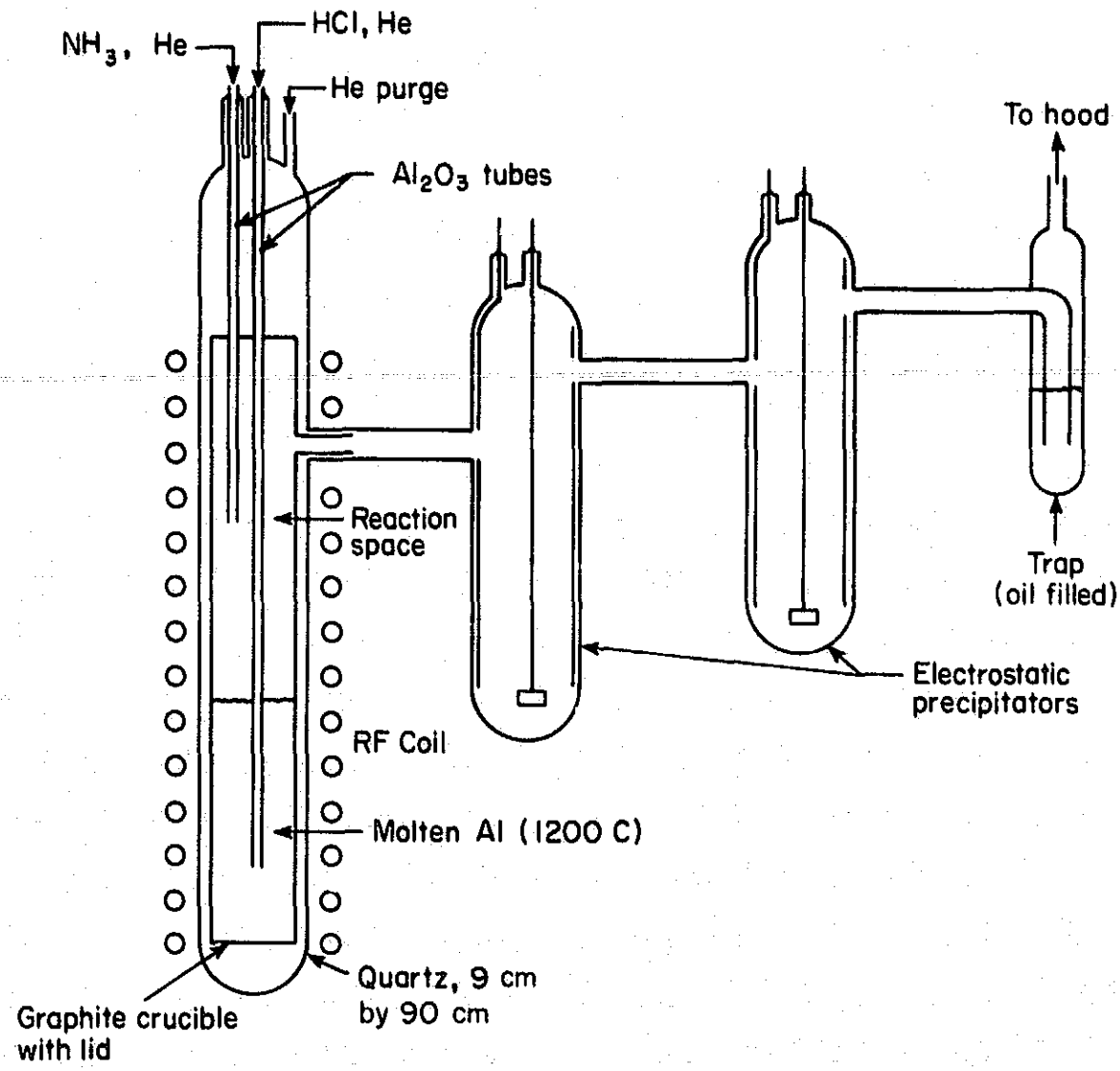

FIGURE 12. APPARATUS FOR INVESTIGATING AlCl + NH_3 REACTION FOR PREPARATION OF AlN

The AlCl system has been shown to be operable but the investigation has not yet proceeded far enough to permit definitive analysis of results. Light gray powder has been obtained but is as yet undetermined in yield and composition.

Solution Thermodynamics

A fused quartz crucible and crucible lid were fabricated from tubing and plate quartz to the dimensions given in (Figure 13). Although the dimensions of the crucible are not critical, the narrow channel in the lid required to generate Knudsen flow conditions must be accurately machined. This was done by diamond drilling.

Initially a silver calibration was conducted by placing 4.5mg of silver in the SiO_2 cell and then completely vaporizing the silver while monitoring the silver signal from the Nuclide mass spectrometer. This calibration serves as a reference for any other material being vaporized from this cell, provided the relative ionization cross sections of the species are known. The mass spectrometric investigation of the reaction between silicon and silicon dioxide was subsequently carried out using high purity silicon (Texas Instruments, Inc. 118 ohmcm-N type). The results are given in Tables 5 and 6. The observed pressures for the main silicon species are in good agreement with those of Hultgrew, et al.[1] (see Figure 14). From these data the calculated pressure of oxygen for the system at 1700 K is 10^{-24} atm.

The oxygen concentration of the silicon after melting in fused quartz is 112PPM by weight, (196PPM atomic). This determination was performed by placing a single grain from the silicon melt in a tungsten crucible. The grain of Si was carefully selected from the center of the melt so that it had no direct contact with the fused quartz. This operation was performed in the room atmosphere, so there may be some surface oxygen contributing to this 196PPM. The tungsten Knudsen cell is placed in the mass spectrometer and the SiO signal is monitored continuously as the sample is heated up to 1410 C. (The phase diagram indicates that about 5 percent Si will dissolve in tungsten. This solution probably reduces

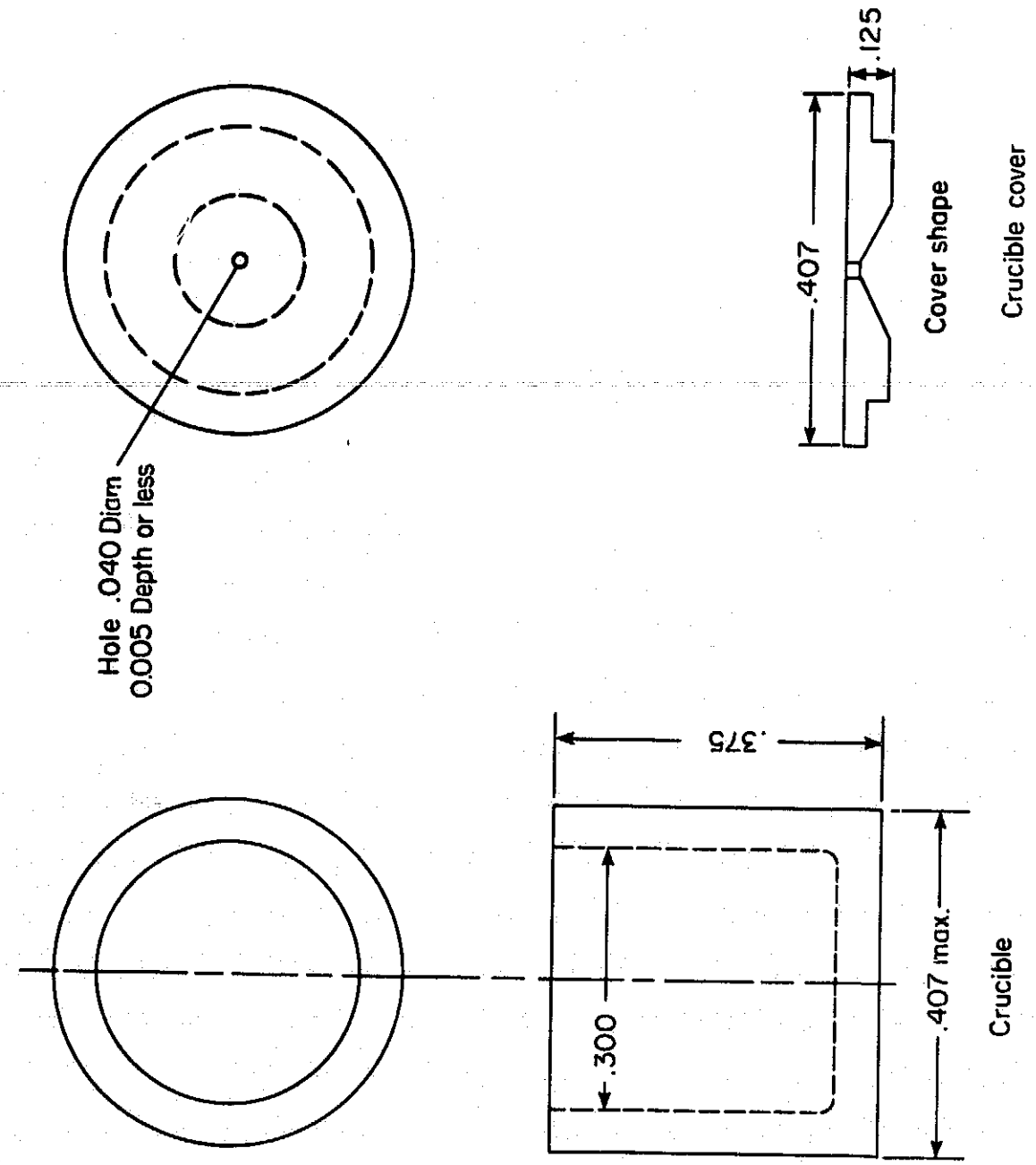

FIGURE 13. KNUDSEN CELL CRUCIBLE AND LID

TABLE 5. VAPOR SPECIES OBSERVED FROM 0.0580g Si IN 0.7825g SiO_2 AT 1700 K

Species	Pressure
Si	4.18×10^{-7} atm
SiO	2.32×10^{-5}
Si_2	1.37×10^{-9}
SiO_2	2.04×10^{-10}
Si_2O_2	1.1×10^{-10}
Si_3	4.7×10^{-10}
Si_4	1.5×10^{-10}
Si_5	1×10^{-11}
Si_6	6×10^{-12}

TABLE 6. VAPOR PRESSURE OF SiO AS A FUNCTION OF TEMPERATURE .0580g Si IN 0.7825g SiO_2

Temp	Species	Pressure
1490 K	SiO	1.43×10^{-7} atm
1556	SiO	6.64×10^{-7}
1615	SiO	2.27×10^{-6}
1664	SiO	5.32×10^{-6}
1648	SiO	4.0×10^{-6}
1690	SiO	7.63×10^{-6}
1704	SiO	8.88×10^{-6}

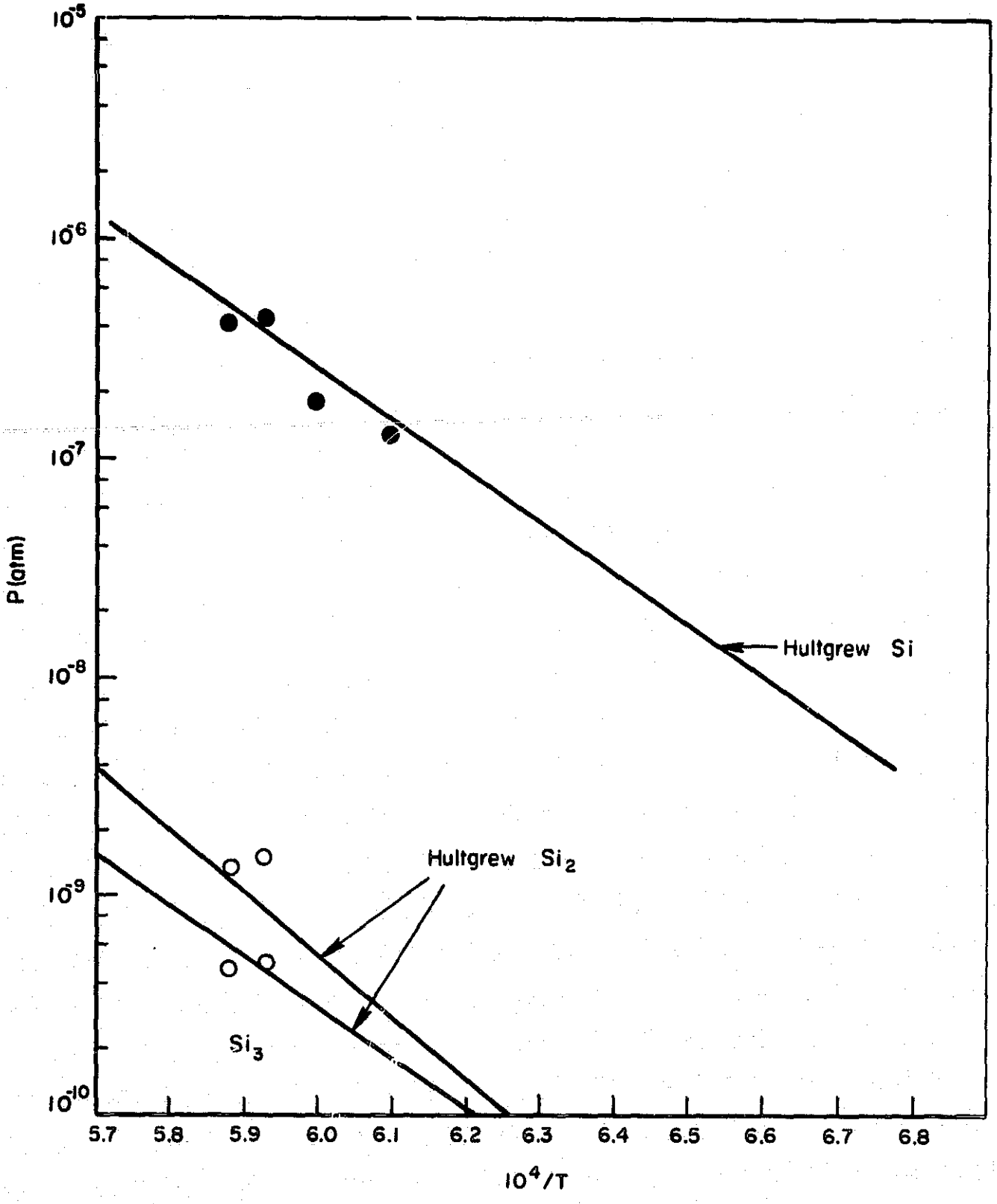

FIGURE 14. VAPOUR PRESSURES OF Si, Si_2 AND Si_3

the SiO from the Si.) The total SiO signal was compared to the SiO calibration (where the total signal is measured from a known amount of SiO) to determine the oxygen content.

Summary of Data at 1700 K

$P_{SiO} = 2.9 \times 10^{-5}$ atm

$P_{Si} = 4.3 \times 10^{-7}$ atm

$P_{O_2} \approx 10^{-24}$ atm

[O] in Si = 196PPMA

The measured pressure of SiO is a function of the oxygen available to the silicon, and as such is an indicator of the oxygen in solution in the melt at any time. It is a function of the area contact with the crucible, the crucible material, and the grain structure of the crucible. As such it can then become a most valuable figure of merit in evaluative crucible-molten silicon interactions.

The concentration of oxygen (196PPMA) is equivalent to 1.78×10^{18} atoms/cm^3. This is in good agreement with the value of $\sim 1.8 \times 10$ found by Kaiser & Keck[2] who related the absorption at 9 μm in the infrared to the oxygen concentration as determined by vacuum fusion analysis.

The activity coefficient (f) is calculated from the following relation:

$$f = \frac{\text{concentration in the vapor phase}}{\text{concentration in the molten silicon}}$$

Using the value of 196PPMA as the concentration of oxygen [O] or silicon monoxide in silicon at 1700 K the activity coefficients of silicon monoxide and oxygen monoxide were calculated to be 7.01×10^{-5} and 4.83×10^{-24}, respectively.

These data together with similar data for Al, Be, N and C, which will be generated in the next quarter, will be used to aid the selection of die and container materials and also the selection of optimum compositions of the β' and O' Sialon solid solutions.

PLANS FOR WORK NEXT QUARTER

(1) Fabricate initial Sialon compositions by hot pressing.

(2) Perform initial evaluation of hot pressed Sialon materials.

(3) Determine the solution thermodynamics of Al, C, Be, N using Al_2O_3, BeO, SiC and Si_3N_4 crucibles in contact with molten silicon.

NEW TECHNOLOGY

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

REFERENCES

1. Hultgrew, Orr, Anderson and Kelly, "Selected Values of Thermodynamic Properties of Metal". Wiley & Sons Publishers.

2. W. Kaiser and P. M. Keck, Journal of Applied Physics, 28, 1957, p 822.