Final Report

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

May, 1979

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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ABSTRACT

Specific compositions of high purity silicon aluminum oxynitride (Sialon) and silicon beryllium oxynitride (Sibeon) solid solutions are shown to be promising refractory materials for handling and manipulating solar grade silicon into silicon ribbon.

Well controlled processing schedules were developed for fabricating high purity Sialon and Sibeon materials. Essentially the impurity content of the hot pressed ceramics was due only to impurities from the original starting powders. A ceramic shaping die was successfully formed by diamond machining of a hot pressed blank. Projected manufacturing cost estimate for 10^5 dies per year is $5.4 per die.

Evaluation of the interaction of these materials in contact with molten silicon indicates that solid solutions based upon β-Si_3N_4 are more stable than those based on Si_2N_2O. Sibeon is more resistant to molten silicon attack than Sialon, and both materials should preferably be used in an inert atmosphere rather than under vacuum conditions. This is because removal of oxygen from the silicon melt as SiO enhances the dissolution of aluminum and beryllium. The wetting angles of these materials are low enough (37° for $x = 0.75$ β' Sialon and 49° for $x = 0.35$ Sibeon) for these materials to be considered as both die and container materials.

TECHNICAL CONTENT STATEMENT

This report contains information prepared by Battelle's Columbus Laboratories under the JPL Contract. Its contents are not necessarily endorsed by the Jet Propulsion Laboratory, California Institute of Technology, or by the National Aeronautics and Space Administration.

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HIGHLIGHTS AND ACHIEVEMENTS

(1) A new material, silicon beryllium oxynitride, has been developed. It is an extremely promising die material.

(2) Silicon aluminum oxynitride is an additional promising refractory material for manipulating molten silicon.

(3) Well controlled processes for fabricating high quality dies of these materials have been developed. Essentially no metal impurities were added during handling and processing of the starting powders. Final materials contained only impurities inherent in the initial powders.

(4) A ceramic shaping die has been successfully fabricated from these very hard ceramics.

(5) Extensive thermodynamics data has been generated on the interaction of molten silicon with refractory materials. This data gives a better insight into the processes occuring between molten silicon and potential die and container materials.

TECHNICAL PAPERS

(1) I. Sekercioglu, and R. R. Wills, "Preparation of the Si_2N_2O-Al_2O_3 Silicon Aluminum Oxynitride", J. Amer. Ceram. Soc., to be published.

(2) R. R. Wills, I. Sekercioglu, J. S. Ogden, C. A. Alexander, and D. E. Niesz, "Relative Stabilities of β-Si_3N_4 Solid Solutions in Contact with Molten Silicon", J. Amer. Ceram. Soc., to be published.

(3) R. R. Wills, I. Sekercioglu, and D. E. Niesz, "Interaction of Molten Silicon with Silicon Aluminum Oxynitrides", J. Amer. Ceram. Soc., to be published.

(4) R. R. Wills, I. Sekercioglu, J. S. Ogden, C. A. Alexander, and D. E. Niesz, "Thermodynamic Stabilities of β-Si_3N_4 Solid Solutions in Contact with Molten Silicon", in preparation.

(5) R. R. Wills, I. Sekercioglu, J. S. Ogden, and D. E. Niesz, "Silicon Metal Oxynitride Ceramics for Manipulating Solar Grade Silicon", in preparation.

DEVELOPMENT AND EVALUATION OF DIE AND CONTAINER MATERIALS

by

R. R. Wills and D. E. Niesz

INTRODUCTION

Objectives and Scope

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 was to develop and evaluate refractory die and container materials. The performance targets for the die and container materials were given in the statement of work as:

(a) The material must be mechanically stable to temperature 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 1×10^{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.

Synopsis of Program of Study

(1) Solution thermodynamics of the interaction of molten silicon with selected refractory materials.

(2) Fabrication of high purity single phase silicon aluminum and silicon beryllium oxynitrides.

(3) Assessment of silicon beryllium and silicon aluminum oxynitrides in contact with molten silicon.

(4) Manufacturing process specifications and projected cost estimate for 10^5 units per year for dies and containers.

SOLUTION THERMODYNAMICS

The interaction of molten silicon with SiC, Si_3N_4, BeO, Al_2O_3, SiO_2, and a mullite composition was studied in a Knudsen cell using a mass spectrometer to monitor the vapor species. The objective was to gain a more detailed understanding of the reaction processes, and to identify possible die and container materials.

SiC and Si_3N_4 crucibles and crucible lids (see Table 1) were fabricated by chemical vapor deposition, and the BeO and Al_2O_3 crucible and lids were formed by ultrasonic machining of hot pressed bodies. The fused quartz crucible and crucible lid were fabricated from appropriate tubing and plate. The dimensions of the Knudsen cell crucible and crucible lid are given in Figure 1.

High purity silicon (Texas Instruments, Inc., 118 ohm cm-N type) was used in all the studies. After contact with the crucible material at 1430 C for 3 hours, each silicon sample was appropriately analyzed for contaminants. Metal cation concentrations were determined by mass spectrometric spark source analysis (MSSS). Carbon analysis was carried out in a Leco Carbon analyzer, and oxygen and nitrogen contents were determined by monitoring the nitrogen and SiO released when molten silicon reacted with a tungsten crucible. The impurity levels, which are summarized in Table 2, indicate that SiO_2 is the ceramic most resistant to molten silicon attack; BeO is by far the most stable metal oxide other than SiO_2, and Si_3N_4 is the stabler of the two nonoxide ceramics evaluated. Agreement with literature values for the solubilities of oxygen, nitrogen, and carbon, which were made by activation analysis, is good (see Table 3).

Table 4 lists the main vapor species (vapor pressures greater than 1.013×10^{-4} N/m^2 (1×10^{-9} atm) detected over molten silicon for each of the six ceramics. Evaluation of the data shows that the apparent vapor pressures of silicon are lower for the carbide and nitride crucibles than for the oxide crucibles.

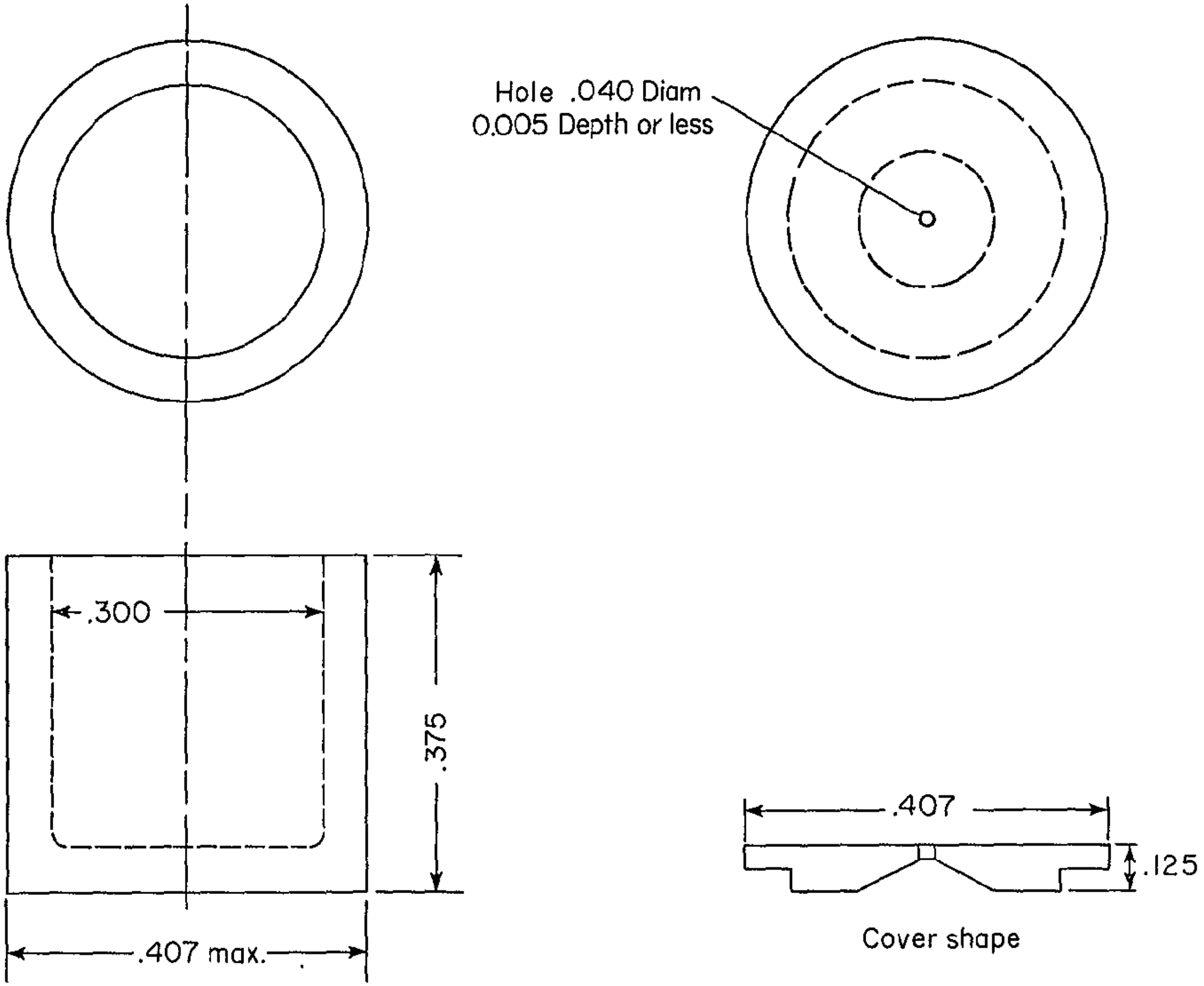
The difference among silicon vapor pressures suggests that either (1) there is interaction between the silicon and the crucible that reduces

TABLE 1. FABRICATION OF KNUDSEN CELL CRUCIBLES AND LIDS

Material	Method of Fabrication	Supplier
Si_3N_4	Chemical Vapor Deposition	Battelle
SiC	Chemical Vapor Deposition	Deposits and Composites, Inc.
Al_2O_3 (a)	Hot Pressing/Ultrasonic Machining	Battelle
BeO (a)	Hot Pressing/Ultrasonic Machining	Battelle
Mullite (b)	Ultrasonic Machining	Coors/Battelle
SiO_2	Machining/Glass Forming	Battelle

(a) Reynolds Metal Co. Al_2O_3 Powder RC-HP-DBM Brush Wellman Co. BeO Powder UOX Grade.

(b) Fabricated by Coors Porcelain Company. Material believed to contain approximately 30 percent glass phase.



Crucible

Crucible cover

FIGURE 1. KNUDSEN CELL CRUCIBLE AND LID

TABLE 2. SOLUBILITIES OF OXYGEN, NITROGEN, CARBON, BERYLLIUM AND ALUMINUM IN MOLTEN SILICON

Impurity Level, ppm	BeO	Al_2O_3	Knudsen Cell Crucible SiO_2	 Si_3N_4	 SiC	Mullite/Glass
O	212	315	196			0.2
N				360		
C					7000	
Al		15 wt. percent				3 wt. percent
Be	5000					

TABLE 3. SOLUBILITIES OF OXYGEN, CARBON AND NITROGEN (atoms/cm^3) IN MOLTEN SILICON AT 1430 C

	Present Study	Literature
Oxygen	1.8×10^{18}	1.8×10^{18} Kaiser & Keck(1) * 2.2×10^{18} Yatsurugi(2)
Nitrogen	3.3×10^{18}	6.0×10^{18} Yatsurugi
Carbon	6.4×10^{19}	4.5×10^{18} Yatsurugi 1.3×10^{19} Voltmer(3)

References are located on Page 45.

TABLE 4. VAPOR PRESSURES OF MAIN SPECIES[(a)] DETECTED IN THE KNUDSEN CELL AT 1430 C[(b)]

Species	Vapor Pressure (N/m^2) Over SiO_2	 BeO	 Al_2O_3	 SiC	 Si_3N_4	 Mullite/Glass
Si	4.35×10^{-2}	2.02×10^{-2}	3.54×10^{-2}	4.65×10^{-4}	1.21×10^{-3}	8.40×10^{-3}
Si_2	1.41×10^{-4}	2.12×10^{-4}	1.41×10^{-6}	1.31×10^{-4}		
SiO	2.32	1.41	2.73		6.08×10^{-4}	1.52×10^{-1}
Be		1.31×10^{-2}				
Al_2O			7.80×10^{-3}			1.82×10^{-3}
AlO			1.01×10^{-3}			
Al			9.72×10^{-3}			3.24×10^{-4}
Si_2C				3.86×10^{-4}		
Si_2N					1.11×10^{-3}	
N_2					7.09×10^{-2}	

(a) Species confined to those detected above 1.013×10^{-4} N/m^2 (1×10^{-9} atm).
(b) Time at temperature, 3 hours.

the activity of the silicon, or (2) the lowest value is really the vapor pressure of silicon and all of the higher values result from fragmentation of silicon from the more volatile silicon monoxide species. The question of fragmentation is difficult to address because of the interdependence of the electron voltage of the ion source and the sensitivity of the mass spectrometer. However, all of the mass spectrometric vapor pressures reported are determined at a 26 electron-volt potential. These operating conditions are not expected to cause significant fragmentation.

The first experimental melt of silicon in a SiC crucible did not leave any silicon in the crucible. Apparently the silicon went into solution in the crucible. The second experiment was more successful as evidenced by observation of residual silicon which had been molten in the SiC crucible at 1420 C. Metallographic examination of the contact area (Figure 2 is a typical region) shows that the molten silicon penetrates into the silicon carbide and also erodes the surface.

The mechanism of attack by the molten silicon appears to involve permeation of silicon into the pores of the silicon carbide, localized dissolution, and subsequent removal of large grains from the bulk of the crucible. Voltmer(3) has shown that at the melting point of silicon the concentration of dissolved carbon is 1.3 x 10^{19} atoms/cm^3. Since the measured carbon content in the above experiment was 6.4 x 10^{19} atoms/cm^3, the molten silicon must contain entrained solid silicon carbide particles. The silicon itself contains enough dissolved carbon to affect the crystalline perfection of a crystal or ribbon formed under these conditions. A similar dissolution mechanism is also operative for Si_3N_4 (see Figure 3). Nitrogen, however, is preferable to carbon as an impurity in solar grade silicon because of its lower electrical activity. Kaiser and Thurmond(4) concluded that the concentration of electrically active impurity states in nitrogen-doped silicon is less than 10^{12} atoms/cm^3, i.e., the number of free electrons amounts to only about 1 percent of the number of nitrogen atoms.

The concentration of a particular impurity in the melt at a given time can be calculated from Henry's Law constant if the vapor pressure of the appropriate species is measured. Henry's Law constants (vapor pressure ÷ impurity concentration) for O, C, N, Be, and Al are given in Table 5 for

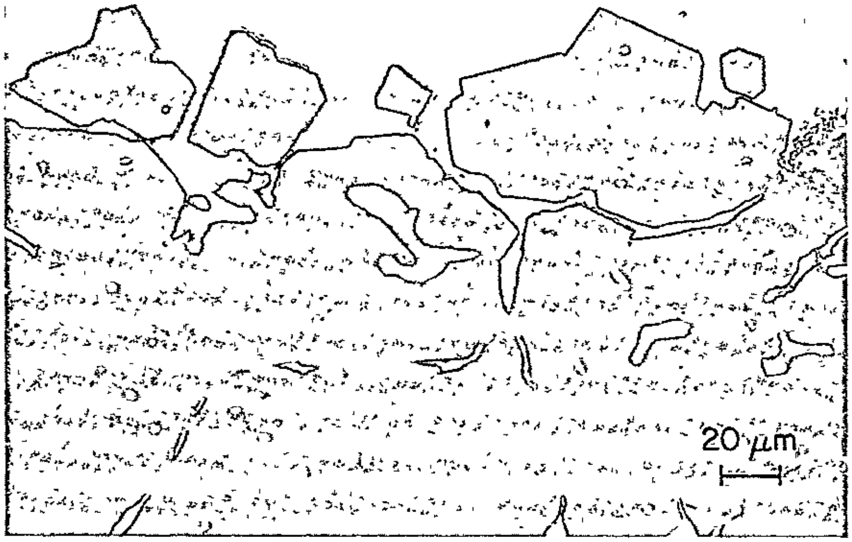


FIGURE 2. Si-SiC INTERFACE AFTER 3 HOURS AT 1700 K, SHOWING PENETRATION OF THE Si INTO THE SiC

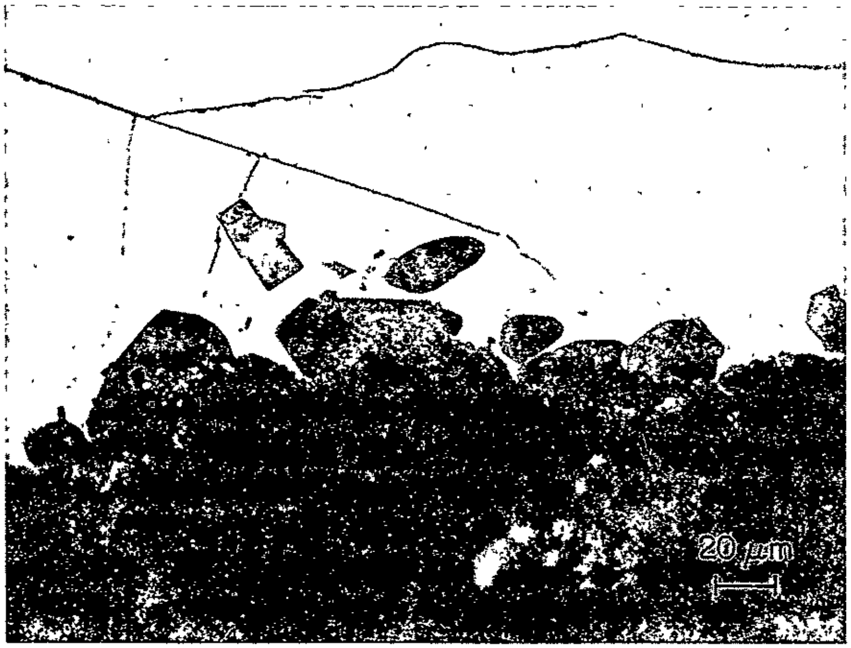


FIGURE 3. Si-Si_3N_4 INTERFACE AFTER 3 HOURS AT 1700 K

concentrations $\leq$ 7000 ppm. A separate experiment was conducted to determine the value for Al since the Al_2O_3 crucible doped the silicon excessively (15 weight percent). Aluminum impurities in the SiO_2 crucible contaminated the silicon to a level of 20 ppm, and by monitoring the vapor pressure of aluminum species above the melt, Henry's Law constant could be determined.

TABLE 5. HENRY'S LAW CONSTANTS

Species	Henry's Law Constant (N/m^2)
O	5.06×10^{-16}
N	1.92×10^{2}
Al	1.31×10^{-1}
Be	2.63
C	2.43×10^{-7}

These values for Henry's Law constants were used to calculate the concentrations of Be, Al, O, and N in silicon for both the silicon-β' Sialon and the silicon-Sibeon systems. As discussed later, this proved to be particularly useful for the oxygen concentration, since it could not be measured experimentally.

PROCESSING AND FABRICATION OF SILICON METAL OXYNITRIDES

The candidate materials are solid solutions, which can be represented by the following 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

$Si_{6-x}Be_xN_{8-2x}O_{2x}$ where $x \leq 0.8$ at 1760 C.

The first material, referred to as β' Sialon, is a solid solution between β-Si_3N_4 and $Al_2O_3 \cdot AlN$. The second material, a solid solution between Si_2N_2O and Al_2O_3, is known as O' Sialon. β' Sibeon, the third material, is a solid solution between β-Si_3N_4 and Be_2SiO_4. Since none of these materials are commercially available, the objective of this task was to prepare high purity single phase materials so that the possible potential of these materials as dies and containers could be evaluated. Particular attention was paid to minimizing and eliminating impurities and second phases in these ceramics, which could be deleterious to their compatibility with molten silicon. These silicon metal oxynitride ceramics were prepared by the following reactions:

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

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

(3) $Si_3N_4 + SiO_2 + BeO \rightarrow \beta'$ Sibeon.

1. Characterization and Preparation of Powders

A special procedure was adopted to ensure that the characteristics and reactivity of each powder remained unchanged during the development of the processing schedules for these materials. Essentially, high purity ultrafine powders obtained from commercial vendors (see Table 6) were vacuum dried at 200 C in clean glassware, and stored under nitrogen in tightly sealed containers. It was recognized that commercial AlN powder was not as high a purity powder as the other powders, and attempts were made to prepare a high purity ultrafine powder by gas phase nucleation processes using $AlCl_3(g)$ and $AlCl(g)$ species as the source of aluminum. Despite considerable process engineering and modifications in reactor design, only small amounts of AlN powder were produced. It is thought that the difficulty in producing AlN powder may be because the reaction path involves the interaction of nitrogen atoms with the aluminum chloride species. The residence time for nitrogen atoms could be very short in view of the stability of nitrogen gas, thus making the recombination of a nitrogen atom much more preferable than their reaction with $AlCl(g)$ or $AlCl_3(g)$. A further factor is the lack of nucleating sites that can stabilize intermediate compounds, and promote reactions within chemisorbed layers. Such mechanisms operate in a chemical vapor deposition coating process but are restricted in the gas phase process.

All the powders were fully characterized in terms of their chemical, structural, and physical properties (see Table 7), so that factors determining their reactivity were known and the silicon metal oxynitride materials could be fabricated reproducibly. Three Si_3N_4 powders were examined because, as discussed below, these powders behave differently and affect the fabrication of the silicon metal oxynitride materials. Cabosil EH-5 grade SiO_2 powder was originally chosen as the SiO_2 powder because of its high purity (see Table 8), but its high surface area (384 m^2/g) makes it difficult to handle, and consequently, its use was restricted to processing of Sibeon materials where only small amounts of SiO_2 were required.

Extensive chemical characterization of the commercial AlN powder was performed, since this powder can be a substantial source of unwanted impurities such as carbon, unreacted aluminum metal, and oxygen. No free aluminum metal was found in the Cerac AlN powder, but the powder contained 1.48 percent oxygen and 0.06 percent carbon. Before batch formulation of appropriate powder mixtures, the AlN powder was milled for 8 hours in a high purity Al_2O_3 ball mill. Milling reduced the average particle size of the powder to 5 μm.

TABLE 6. COMMERCIAL POWDERS USED IN THE PREPARATION OF THE SILICON METAL OXYNITRIDE CERAMICS

Powder	Vendor
Al_2O_3, grade RC-HP-DBM	Reynolds Metal Company
Si_3N_4, grades SN402 and 502	GTE Sylvania, Inc.
Si_3N_4, High-Purity grade	Kawecki-Berylco Industries, Inc.
SiO_2, Cabosil EH-5 grade	Cabot Corporation
SiO_2, -325 mesh grade, 99.9 percent pure	Atomergic Chemetal Company
BeO, UOX grade	Brush Wellman, Inc.
AlN, High Purity grade, -200 mesh	Cerac, Inc.

TABLE 7. CHARACTERIZATION OF POWDERS

Chemical	Structural	Physical
Emission spectroscopy	Transmission Electron microscopy	Particle size distribution
Spark source mass spectrography	Optical microscopy	Surface area
Oxygen Analysis of nonoxide powders	Scanning electron microscopy	Compaction curves for bulk density, agglomerate strength and bulk density as a function of pressure
Thermogravimetric analysis		
Carbon analysis of AlN powder		
Aluminum and nitrogen analysis of AlN powder		

TABLE 8. MASS SPECTROGRAPHIC ANALYSIS OF Si_3N_4, SiO_2, and Al_2O_3 (ppmw)

Element	SN402 Grade Si_3N_4 33616-100†	Cabosil Grade SiO_2 33616-200†	Al_2O_3 33616-300†	KBI High Purity Si_3N_4 Grade 523-87-2†	Cerac AlN	SN502 Grade Si_3N_4	Atomergic SiO_2
Li	<0.004	<0.006	<0.002	0.05	30	0.01	0.2
Be	<0.004	<0.004	<0.2	0.03	<0.4	<0.003	<0.002
B	0.06	0.1	0.06	7	5	0.2	2
F	0.1	0.6	0.4	1	<0.7	<0.1	0.1
Na	10	20	40	5	100	5	100
Mg	<10	<20	20	≤10	100	5	<20
Al(a)	<10	≤10	Major	200	Major	60	100
Si	Major	Major	50	Major	300	Major	Major
P	1	≤6	20	5	10	0.2	3
S	≤10	<0.6	4	6	20	0.6	1
Cl	5000	14	100	10	10	500	20
K	0.2	0.2	0.8	1	15	0.6	20
Ca	≤6	30	6	≤30	15	12	60
Sc	≤0.2	<0.7	<0.1	<0.2	<0.2	<0.3	<0.1
Ti	<2	<1	<0.3	20	12	7	20
V	<0.2	0.2	<1	0.2	0.3	0.2	0.5
Cr	2	<5	2	30	25	10	<1
Mn	<3	0.06	0.4	7	4	0.2	<1
Fe	<1	30	50	400	300	10	30
Co	<0.3	0.3	0.01	<0.2	1	0.4	<1
Ni	<1	≤2	1	20	6	0.2	<2
Cu	<4	5	0.2	7	20	0.7	<2
Zn	<2	0.4	2	≤0.2	20	0.5	<2
Ga	<2	<0.4	100	4	60	0.4	1
Ge	<1	<0.6	<0.7	<0.3	<2	<0.1	<0.3
As	≤0.2	≤0.04	≤0.04	0.05	0.6	0.02	<0.3
Se	<3	<3	≤0.2	<0.1	<1	<2	<0.05
Br	4	<0.2	0.1	<0.03	2	0.2	0.1
Rb	<0.2	<0.07	<0.1	0.1	30	0.2	<0.4
Sr	<1	<1	<0.2	0.2	2	0.3	5
Y	<0.1	<0.3	<0.04	0.1	<0.1	3	2
Zr	<0.04	<0.6	<0.2	0.1	1	60	3
Nb	<0.1	<1	<0.02	0.2	<0.1	<0.2	<0.2
Mo	12	<0.04	≤0.2	1	2	400	2
Ru	<0.2	<0.7	<0.1	<0.1	<0.6	<0.1	<0.1
Rh	<0.02	<0.2	<0.03	<0.1	<0.5	<0.7	<0.06
Pd	<0.7	<0.7	<0.2	<0.3	<0.2	<0.4	<3
Ag	<0.2	<0.2	<0.1	<0.1	<0.5	<0.03	<0.1
Cd	<0.2	<0.7	<0.3	<0.1	<0.5	<0.06	<0.1
In	<0.06	<0.1	<0.04	<0.02	<0.3	<0.04	<0.1

(a) Memory from previous sample.

†Lot No.

TABLE 8. (Continued)

	SN402 Grade	Cabosil Grade		KBI High Purity			
	Si_3N_4	SiO_2	Al_2O_3	Grade	Cerac	SN502 Grade	Atomergic
Element	33616-100	33616-200	33616-300	523-87-2	AlN	Si_3N_4	SiO_2
Sn	0.4	≤0.4	≤0.2	0.7	3	<0.2	0.2
Sb	<0.1	<0.2	<0.07	<0.02	<0.3	<0.05	<0.1
Te	<0.2	<0.2	<0.06	<0.1	<0.2	<0.2	<0.3
I	<0.06	<0.07	<0.1	<0.1	30	<0.1	<0.2
Cs	<0.2	<0.4	<0.2	<0.05	0.3	<0.2	<0.1
Ba	<0.1	<0.1	<0.1	2	20	<0.03	4
La	<0.04	<0.1	<0.07	<0.03	<0.1	<0.01	1
Ce	<0.1	0.2	<0.04	<0.2	<0.3	<0.2	<1
Pr	<0.1	<0.07	<0.02	<0.02	<0.2	<0.03	<0.2
Nd	<0.2	<0.3	<0.2	<0.1	<0.4	<0.1	<0.4
Sm	<0.2	<0.3	<0.2	<0.1	<0.3	<0.1	<0.2
Eu	<0.1	<0.2	<0.1	<0.04	<0.01	<0.1	<0.1
Gd	<0.1	<0.2	<0.1	<0.05	<0.3	<0.1	<0.3
Tb	<0.02	<0.06	<0.03	<0.01	<0.1	<0.01	<0.06
Dy	<0.2	<0.3	<0.1	<0.1	<0.3	<0.05	<0.6
Ho	<0.04	<0.2	<0.03	<0.02	<0.1	<0.02	<0.2
Er	<0.1	<0.2	<0.1	<0.07	<0.2	<0.04	<0.4
Tm	<0.2	<0.6	<0.3	<0.1	<0.4	<0.1	<0.06
Yb	<0.2	<0.3	<0.1	<0.2	<9.3	<0.1	<0.1
Lu	<0.06	<0.06	<0.04	<0.03	<0.1	<0.1	<0.06
Hf	<0.1	<0.3	<0.2	<0.1	<0.1	<0.1	<0.5
Ta	<1	<2	<2	<0.1	<1	<0.1	<3
W	0.2	<0.2	<0.1	<0.1	7	<0.1	<0.1
Re	<0.06	<0.2	<0.06	<0.1	<0.3	<0.03	<0.06
Os	<0.1	<0.6	<0.1	<0.1	<0.4	<0.05	<0.07
Ir	<0.4	<0.3	<0.2	<0.1	<0.3	<0.1	<0.1
Pt	<0.2	<9.2	<0.1	<0.1	<0.3	<0.04	<0.1
Au	<0.06	<0.6	<0.03	<0.04	<0.1	<0.01	<0.03
Hg	<0.1	<0.3	<0.1	<0.1	<0.3	<0.05	<0.1
Tl	<0.2	<0.3	<0.1	<0.2	<0.1	<0.04	<0.04
Pb	0.2	0.1	0.2	<0.03	2	<0.06	2
Bi	<0.06	<0.07	<0.03	<0.02	5	<0.03	<0.04
Th	<0.06	<0.07	<0.03	<0.02	<0.1	<0.03	<0.1
U	<0.1	<0.3	<0.2	<0.02	<0.1	<0.03	<0.1

2. Batch Formulation and Mixing

An important prerequisite for obtaining a single phase high purity ceramic is that all stages of the fabrication process be tightly controlled and monitored. In formulating the mixtures required to fabricate the desired silicon metal oxynitride compositions allowance was made for two factors: the oxygen contents of the Si_3N_4 and AlN powders and the weight losses of all the powders according to the thermogravimetric analysis data.

All milling operations used in the preparation of O' Sialon and β' Sialon samples were performed in new high purity 1 gallon Al_2O_3 ball mills using high density high purity Al_2O_3 balls from Coors Porcelain Company. Details of the cleaning procedure used to prepare these ball mills for mixing Sialon powder mixtures are given in the process specification. Impurity pickup during milling was checked by milling a 150 g Si_3N_4-Al_2O_3-SiO_2 powder batch for 24 hours in 1000 cm^3 of n-hexane* using 3000 g of Al_2O_3 balls. Samples were drawn after 4, 8, and 24 hours, and analyzed for Si, Al, O, N, and Metallic impurities. No significant change in impurity content was observed, but the nitrogen content of the mixture decreased slightly with increasing milling time. Mainly for this reason, 4 hours was chosen as the optimum milling time.

Mixing of Si_3N_4, BeO, and SiO_2 powders was initially done in polyethylene jars with alumina balls in n-hexane. Although mixing was performed only for 4 hours, aluminum was picked up during this process. Batch No. HP50 (see Table 9) used KBI, Inc. High Purity Grade Si_3N_4 powder that contains 200 ppm aluminum; consequently, aluminum contamination during milling amounted to 250 ppm. Batch No. HP49 consisted of GTE Sylvania, Inc. SN502 Grade Si_3N_4, BeO, and Cabosil Grade SiO_2. The higher aluminum concentration (1300 ppm) of this powder mixture is due to a larger charge of Al_2O_3 balls in the mill (HP49 was milled with 300 g Al_2O_3; HP50 with 100 g Al_2O_3).

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

TABLE 9. MASS SPECTROGRAPHIC ANALYSES OF Si_3N_4-SiO_2-BeO POWDER MIXTURES PREPARED USING Al_2O_3 MILLING MEDIA, ppm

	Sample Designation(a)	
Element	HP49 x = 0.301 Sibeon	HP50 x = 0.138 Sibeon
Li	1	12
Be	~2-5%	~2-5%
B	400	400
F	<0.3	<0.3
Na	35	58
Mg	40	10
Al	1300	450
Si	Major	Major
P	2	16
S	7	7
Cl	12	25
K	1	10
Ca	20	60
Sc	<0.7	<2
Ti	1	10
V	0.03	0.3
Cr	0.04	90
Mn	3	10
Fe	140	1000
Co	0.3	1
Ni	1	8
Cu	2	15
Zn	0.1	0.4
Ga	<1	<1
Ge	<0.3	<0.3
As	<0.06	<0.06
Se	<7	<7
Br	<0.8	<0.8
Rb	-.2	10
Sr	2	45
Y	2	15
Zr	6	15
Nb	2	0.5
Mo	65	12
Ru	0.4	0.7
Rh	0.1	0.1
Pd	0.4	0.4

(a) Batch No. HP49 was prepared using SN502 grade Si_3N_4 powder, and HP50 prepared using KBI Inc. High Purity Grade Si_3N_4 powder.

TABLE 9. (Continued)

	Sample Designation[(a)]	
Element	HP49 x = 0.301 Sibeon	HP50 x = 0.138 Sibeon
Ag	0.1	<0.7
Cd	<0.4	<0.7
In	<0.06	<0.06
Sn	0.2	0.8
Sb	<0.1	<0.1
Te	<0.2	<0.2
I	<0.1	<0.1
Cs	0.2	20
Ba	7	65
La	0.2	7
Ce	0.7	7
Pr	0.07	3
Nd	1	50
Sm	<0.5	<0.5
Eu	<0.2	<0.2
Gd	0.3	20
Tb	<0.08	<0.08
Dy	<0.3	<0.3
Ho	<0.1	<0.1
Er	<0.2	<0.2
Tm	<0.1	<0.1
Yb	<0.3	<0.3
Lu	<0.1	<0.1
Hf	<0.3	<0.3
Ta	<0.3	<0.6
W	<0.3	<0.3
Re	<0.2	<0.2
Os	<0.3	<0.3
Ir	<0.3	<0.3
Pt	<0.3	<0.3
Au	<0.1	<0.1
Hg	<0.3	<0.3
Tl	<0.1	<0.1
Pb	<0.2	<0.2
Bi	<0.1	<0.1
Th	<0.1	<0.1
U	<0.1	<0.1

(a) Batch No. HP49 was prepared using SN502 grade Si_3N_4 powder, and HP50 prepared using KBI Inc. High Purity Grade Si_3N_4 powder.

Substantial reduction in the aluminum impurity level was achieved by using the higher purity grade SN502 grade Si_3N_4 (see Table 8) powder and Teflon^R milling media. However, it was found that this Si_3N_4 powder contained a small percentage of inclusions and agglomerates that could not be broken down using the light-weight Teflon^R cylinders. In samples hot pressed using this powder mixing method, complete conversion to Sibeon did not occur. These large particles were consequently removed by wet sieving through -400 mesh, prior to batch preparation.

Optimum processing was also facilitated by using the ultrafine Cabosil SiO_2 powder in the starting mixture. This high surface area powder resulted in better mixing and aided densification during hot pressing.

3. Fabrication of O' Sialons

O' Sialon, which is a solid solution between Si_2N_2O and Al_2O_3, can be represented by the formula $Si_{2-x}Al_xN_{2-x}O_{1+x}$, where $x \leq 0.4$ at 1760 C. Samples of $x = 0.1$, $x = 0.2$, and $x = 0.35$ O' Sialon were fabricated by hot pressing appropriate powder mixtures of Si_3N_4, SiO_2, and Al_2O_3 at 1750 C. All samples were 98 to 100 percent theoretically dense using a value of 2.80 g/cm^3 as the density of O' Sialon. Fabrication of single phase O' Sialons was found to be strongly dependent upon the nature of the Si_3N_4 powder and the hot pressing cycle. This is discussed further in a technical paper entitled "Preparation of the Si_2N_2O-Al_2O_3 Silicon Aluminum Oxynitride" (see Appendix B).

The total impurity content in a typical hot pressed $x = 0.1$ O' Sialon was approximately 160 ppm (see Table 10), ignoring the iron that was picked up during sample preparation for chemical analysis.

4. Fabrication of β Sialons

β' Sialon, which is a solid solution between β-Si_3N_4 and Al_3O_3N, can be represented by the formula $Si_{6-x}Al_xN_{8-x}O_x$, where $x \leq 4.2$ at 1760 C. As in the case of O' Sialon, samples of different compositions were prepared in order to assess the resistance to molten silicon attack of the β' Sialon

TABLE 10. IMPURITIES IN TYPICAL HOT PRESSED O'SIALON (ppm)

Element	Concentration	Element	Concentration
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(a)	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

(a) Picked up during sample preparation.

solid solution as a function of aluminum content. Samples of x = 0.75, x = 1.0, and x = 2.4 single phase β' Sialons were prepared by hot pressing the desired powder mixtures of Si_3N_4, Al_2O_3, and AlN at 1750 C. All samples were 95 to 100 percent theoretically dense.*

Both SN502 and SN402 grades of Si_3N_4 powder were used in the preparation of β' Sialons, but most of the samples were made using the SN402 grade powder because this Si_3N_4 powder is a more "active" ceramic powder and enables higher density β' Sialons to be achieved. The hot pressing cycle was identical to that used for fabricating O' Sialon (see Appendix B). Details of the fabrication processes are tabulated in the process specification.

5. Fabrication of β' Sibeons

β' Sibeon, which is a solid solution between β Si_3N_4 and Be_2SiO_4, can be represented by the formula $Si_{6-x}Be_xN_{8-2x}O_{2x}$ where $x \leq 0.8$ at 1760 C. Several Sibeon samples were fabricated by hot pressing appropriate Si_3N_4-SiO_2-BeO mixtures at 1750 C and 7000 psi for 1 hour (see Table 11). All three grades of Si_3N_4 powder were used, but the SN502 grade powder was ultimately selected as the optimum powder for two reasons. Firstly, fabrication of single phase Sibeon was not achieved with the SN402 grade powder because chlorine in the Si_3N_4 powder reacted with the BeO to form the volatile compound $BeCl_2$. The second phase in these Sibeon samples had an x-ray diffraction pattern similar to that of Si_2N_2O, but it could also correspond to a silicon oxynitride solid solution. The second reason for the choice of the SN502 Si_3N_4 powder was its higher purity than that of the KBI, Inc. High Purity Grade powder.

As discussed earlier, the addition of a small amount of the high surface area Cabosil grade SiO_2 powder not only aided the mixing process but also enhanced the densification during hot pressing. This is probably

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* The density of β' Sialon decreases with increasing Al_3O_3N content. Densities of samples were compared with those of Si_3N_4 itself (3.18 g/cm^3).

TABLE 11. COMPOSITIONS, DENSITIES, AND PHASE ANALYSIS OF INITIAL HOT PRESSED SILICON BERYLLIUM OXYNITRIDE SAMPLES

Starting Mixture	Composition	Density (g/cm^3)	Phase Analysis
KBI Si_3N_4 + BeO	x = 0.138	3.0	β'
SN502 Si_3N_4 + BeO	x = 0.234	3.02	β'
SN502 Si_3N_4 + BeO + SiO_2	x = 0.301	3.17	β'
SN402 Si_3N_4 - BeO	x = 0.478	3.11	β' + O'

Note: Assuming the density of β' Sibeon is 3.18 g/cm^3, all the above samples have densities >94 percent theoretical.

because the volume of liquid responsible for transient liquid phase sintering was increased. The exact nature of this liquid is not known, but the studies of Huseby and Petzow(5) indicate that it is probably a SiO_2-rich Be-Si-O-N liquid.

Table 12 shows the impurity content of a typical x = 0.35 β' Sibeon sample. Essentially the impurities originated entirely from the original powders. Molybdenum and zirconium, which are major contaminants in the original SN502 Si_3N_4 powder, are present at greatly reduced concentrations because these elements were present mainly in the large inclusions and agglomerates. As discussed earlier, these inclusions and agglomerates were removed prior to batching. While evaluation of all Sibeon samples in contact with molten silicon was conducted, detailed studies were restricted to experiments using this high purity x = 0.35 β' Sibeon.

EVALUATION OF SILICON METAL OXYNITRIDES IN CONTACT WITH MOLTEN SILICON

Assessment of the three silicon metal oxynitrides as potential die and container materials was performed using three tests:

(1) Sessile drop
(2) Capillary rise of molten silicon
(3) Knudsen cell examination of the vapor species above molten silicon in contact with the silicon metal oxynitrides.

After the sessile drop and Knudsen cell tests, the silicon-ceramic interface was examined metallographically and the silicon analyzed by MSSS.

1. O' Sialons

Samples of x = 0.1, x = 0.2, and x = 0.35 O' Sialon were held in contact with molten silicon for 1 hour and 6 hours. After 1 hour a two-layer reaction zone (see Figure 4) formed at the interface. Aluminum could not be

TABLE 12. IMPURITY CONTENT OF X = 0.35 β' SIBEON (ppm)

Element	Concentration	Element	Concentration
Li	< 0.005	Ag	< 0.2
Be	High	Cd	< 0.3
B	0.2	In	< 0.1
F	0.5	Sn	< 0.3
Na	3	Sb	< 0.1
Mg	10	Te	< 0.3
Al	100	I	< 0.1
Si	Major	Cs	< 0.2
P	0.5	Ba	< 0.2
S	1	La	< 0.1
Cl	7	Ce	< 0.1
K	1	Pr	< 0.1
Ca	3	Nd	< 0.2
Sc	< 0.2	Sm	< 0.3
Ti	1	Eu	< 0.2
V	< 0.3	Gd	< 0.3
Cr	1	Tb	< 0.1
Mr	0.1	Dy	< 0.3
Fe	5	Ho	< 0.1
Co	0.3	Er	< 0.2
Ni	1	Tm	< 0.1
Cu	5	Yb	< 0.3
Zn	< 0.1	Lu	< 0.1
Ga	< 0.5	Hf	< 0.3
Ge	< 0.3	Ta	< 0.2
As	< 0.03	W	< 0.2
Se	< 0.5	Re	< 0.3
Br	< 0.1	Os	< 0.3
Rb	< 0.3	In	< 0.3
Sr	< 0.1	Pt	< 0.3
Y	1	Au	< 0.1
Zr	10	Hg	< 0.3
Nb	< 0.05	Tl	< 0.1
Mo	30	Pb	< 0.2
Ru	< 0.3	Bi	< 0.1
Rh	< 0.1	Th	< 0.1
Pd	< 0.3	U	< 0.1

detected in the outer silicon by electron probe analysis, which indicates its concentration is <1000 ppm, the detection limit of the apparatus. The concentrations of aluminum and silicon were determined to be 0.15 percent Al and 90.7 percent Si in the white layer (Region 1), and 0.16 percent Al and 63.6 percent Si in the dark layer (Region 2). The remaining elements in Region 1 would be either oxygen or nitrogen. Region 1 thus has the composition 90.7 percent Si, 0.16 percent Al, and 9.14 percent (oxygen + nitrogen). There is no known crystalline material of this composition and consequently Region 1 is probably a metastable amorphous material.

Particle formation in the silicon-rich Region 1 suggests that the reaction mechanism was one of solution and precipitation in which the molten silicon first attacked the ceramic, probably at the grain boundaries, dissolving oxygen and nitrogen with the aluminum. Region 2 is probably a Sialon material consisting mainly of Si_3N_4 since the silicon content of this phase (63.6 percent) is close to that of Si_3N_4 (60 percent), and also nitrogen was detected in the material. This conclusion is also supported by the observations of Duffy, et al(6) that CVD "silicon oxynitride" forms Si_3N_4 when in contact with molten silicon. However, it should be pointed out that CVD "silicon oxynitride" is not the compound Si_2N_2O, but an amorphous material of general composition SiO_xN_y. O'Donnell(7), et al, examined the compatibility of commercial Si_2N_2O with molten silicon. A reaction zone was observed at the interface, but the identity of this reaction zone was not established.

After 6 hours in contact with molten silicon, O' Sialon samples gave rise to the formation of string-like precipitates (see Figure 5) in the silicon. The concentration of these precipitates increased with increasing Al_2O_3 content of the O' Sialon solid solution. Aluminum and silicon concentrations were determined in these precipitates to be approximately 66 percent and 28 percent, respectively. It is likely that these precipitates also contain oxygen and nitrogen, in which case they are new Sialon materials.

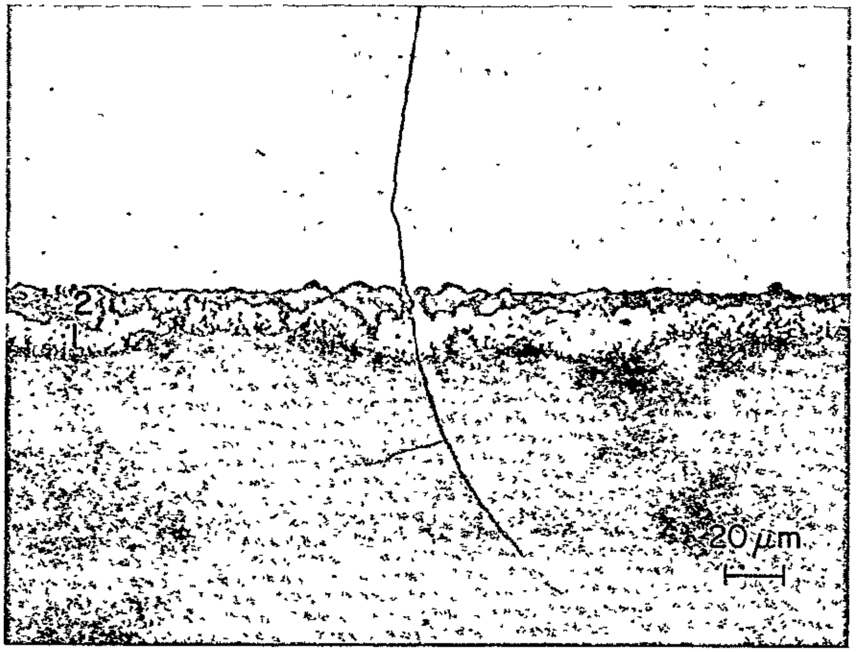

FIGURE 4. X = 0.1 O' SIALON-SILICON INTERFACE

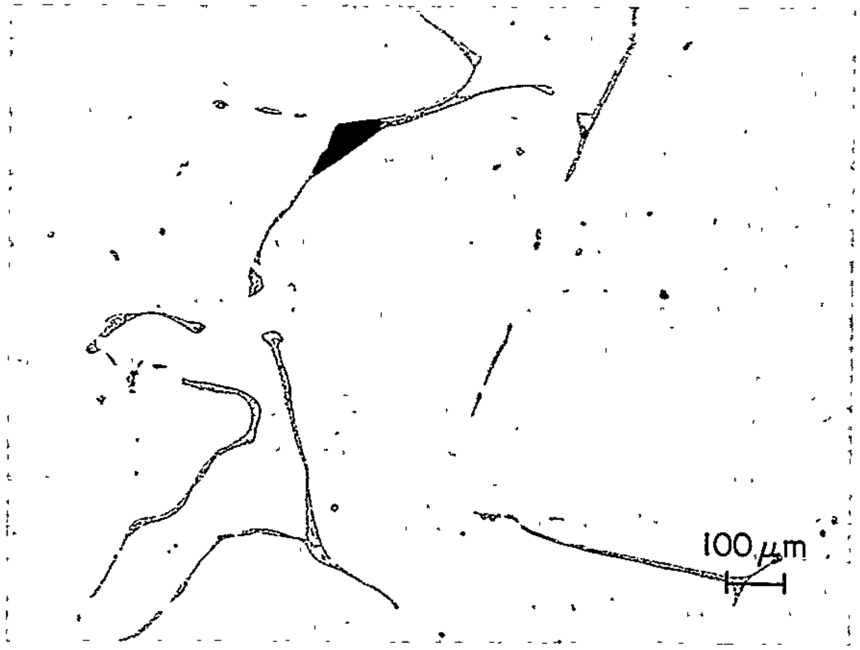

FIGURE 5. PRECIPITATES FORMED IN SILICON AFTER CONTACT WITH X = 0.35 O' SIALON FOR 6 HOURS

The evaluation of O' Sialon employed samples of different aluminum contents, samples containing small amounts of unidentified phases and also samples containing β' Sialon, but in all cases the general behavior was similar. Consequently, there can be no doubt that the O' Sialon solid solution is unstable in contact with molten silicon.

2. β' Sialons

X = 1.0 and X = 2.4 β' Sialons were initially held in contact with molten silicon at 1450 C for 1 hour under an argon atmosphere. Figures 6 and 7, which show the silicon ceramic interface for these two samples, indicate that the concentration of aluminum in the β' Sialon is important. Little reaction is exhibited by x = 1.0 β' Sialon (see Figure 6), but x = 2.4 β' Sialon appears to have suffered considerable erosion. Furthermore, aluminum-rich precipitates were found in the silicon, which had been in contact with x = 2.4 β' Sialon. These precipitates (see Figure 8) appear to be similar to those observed in the reaction of O' Sialons with molten silicon.

In view of the importance of the aluminum content of the β' Sialon solid solution, additional assessment of this silicon metal oxynitride was confined to a composition containing a minimum of aluminum. X = 0.75 β' Sialon is considered to be the lower composition limit for practical fabrication purposes due to difficulties in obtaining high density single phase material with decreasing Al_2O_3 content and also compensating for the SiO_2 content of the Si_3N_4 powder in the powder mixture. Figure 9 shows the x = 0.75 β' Sialon-silicon interface after contact for 1 hour at 1450 C under argon atmosphere. A very small amount of attack, much less than for x = 1.0 and x = 2.4 β' Sialons, appears to have occurred.

The wetting of molten silicon on a polished surface (1 μm) of x = 0.75 β' Sialon in 8.5×10^4 N/m^2 (0.85 atm) argon was observed for approximately 1-1/2 hours. Wetting angle values were taken from photographs of the silicon-Sialon interface over this time interval. The data in Table 13 show that, except for a very small drop at the beginning, which may be due to dissolution of a very thin surface oxide layer, the wetting angle remained essentially constant at 37 degrees.

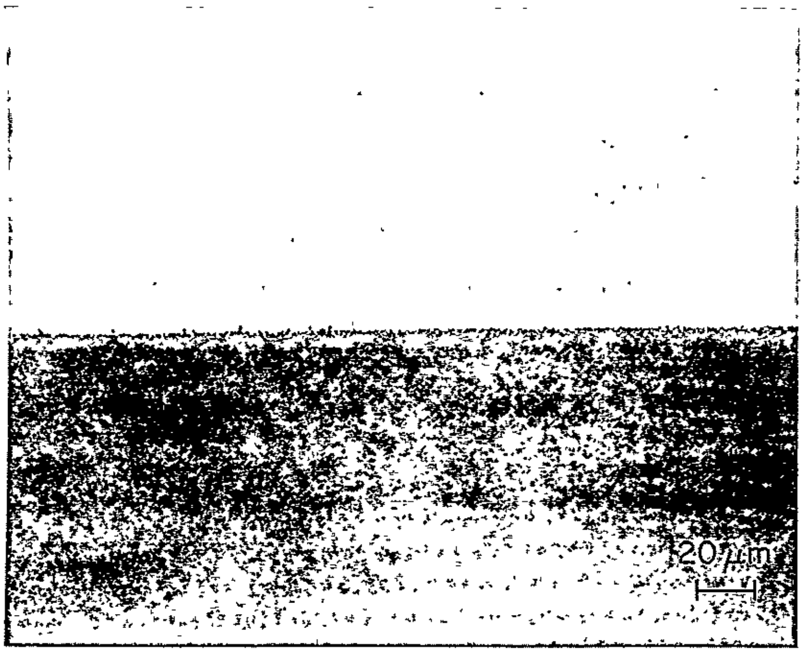

FIGURE 6. INTERFACE BETWEEN X = 1 β' SIALON AND SILICON

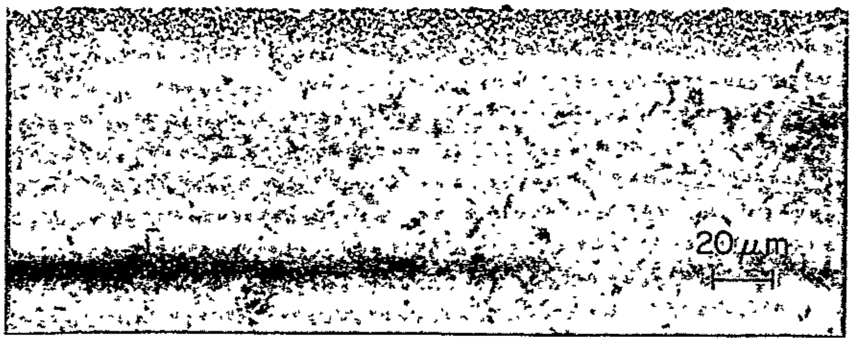

FIGURE 7. INTERFACE BETWEEN X = 2.4 β' SIALON AND SILICON

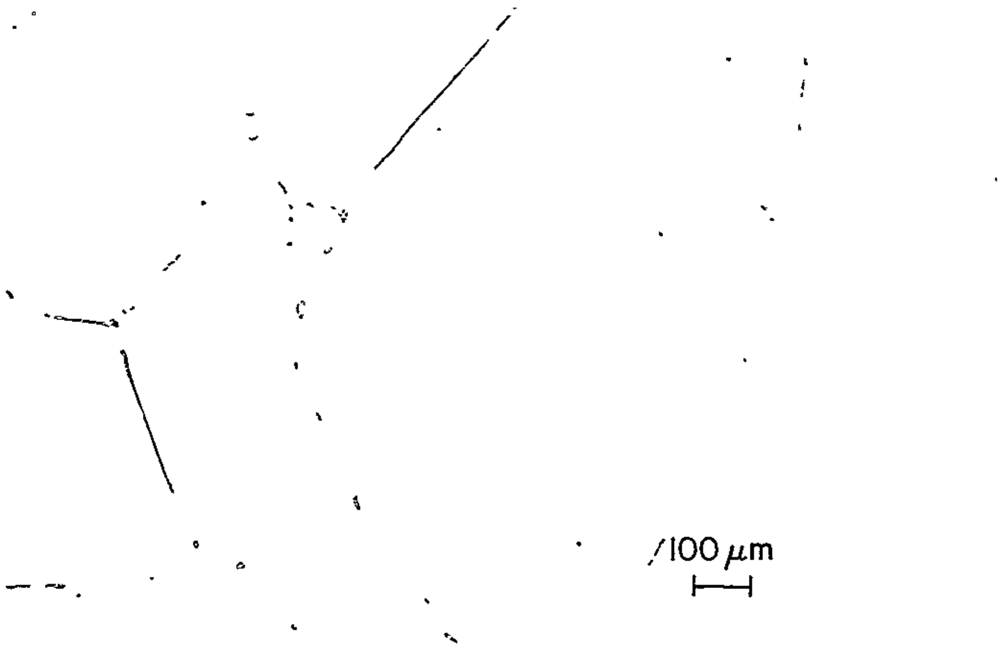

FIGURE 8. ALUMINUM RICH PRECIPITATES IN SILICON AFTER CONTACT WITH X = 2.4 SIALON AT 1450 C FOR 1 HR

FIGURE 9. INTERFACE BETWEEN X = 0.75 β' SIALON AND SILICON AFTER 1 HOUR AT 1450 C UNDER ARGON ATMOSPHERE

For a 37-degree wetting angle the height (H) of the capillary rise in a 0.01-cm thick slot would be 50.2 cm according to the following equation:

$$H = \frac{2\delta}{pg} \times \frac{\cos\theta}{t}$$

δ = 702 dynes/cm

p = 2.33 g/cm^3

g = 981 cm/sec^2

$\cos\theta$ = 0.7986

t = 0.01 cm

This calculated value for the capillary rise is substantially higher than the minimum requirements (2.5 cm) for a candidate shaping die.

These data are very different from those obtained with β' Sialon materials prepared and tested at JPL.(7) JPL prepared materials initially exhibited high wetting angles (80 to 110), but after 15 to 30 minutes, the wetting angle decreased to approximately 50 degrees. The exact reason for the difference in behavior of x = 0.75 β' Sialon and the JPL prepared materials is not known, but is likely to be connected to compositional differences between the materials.

Initial attempts to attain capillary rise of molten silicon in 0.116 cm and 0.041 cm slots cut in x = 0.75 β' Sialon were unsuccessful. The experiment was repeated in the sessile drop apparatus so that the movement of liquid silicon could be observed. After holding the temperature at 1440 C for 50 minutes, no rise occurred. The argon was then pumped out of the chamber, and as the vacuum approached about 100 microns, pressure bubbles were released from the molten silicon. At a pressure of about 2 to 3 microns, the bubbling stopped, and the silicon began to rise in the capillary. The temperature was then raised to approximately 1450 C and the furnace backfilled with argon. The molten silicon remained in the slot.

The likely explanation for this behavior is that the silicon was saturated with oxygen with respect to SiO_2 by the silica crucible. Thus, the thin SiO_2 passivation layer on the die was not dissolved. Since silicon has a wetting angle of 80 degrees on silica, no capillary rise was observed in argon. Assuming the oxygen concentration of the melt is 200 ppm, the partial pressure of SiO would be 2.026 N/m^2 (2×10^{-5} atm). At a vacuum level of 1 micron (1×10^{-3} torr) SiO would be removed and the molten silicon would begin to dissolve SiO_2 to maintain chemical equilibriums with the SiO_2. This would result in solution of the SiO_2 passivation layer on the die, followed by capillary rise.

Table 14 gives the data obtained from examination of the silicon $x = 0.75$ β' Sialon reaction in the Knudsen cell at 1430 C. The system was held at temperature for 3 hours. The oxygen concentration in the silicon (0.1 ppm) is below the detection limit of the mass spectrometer, and the value shown in Table 14 was calculated from Henry's Law Constant for oxygen in the $O-Si-Al_2O_3$ system. The nitrogen and aluminum impurity levels calculated from their respective Henry's Law Constants are in good agreement with the measured values. It is likely, therefore, that the calculated value for the oxygen content is an accurate one. Compared with the silicon-Si_3N_4 system, the partial pressures of N_2 and Si are almost identical, but the partial pressure of SiO is two orders of magnitude higher. The data in Table 14 imply that aluminum is homogeneously distributed throughout the silicon, but this is not the case. Figure 10 shows the x-ray image of aluminum in silicon after it contacts with $x = 0.75$ β' Sialon in the Knudsen cell. Four particles or clusters of precipitates are evident.

The vapor pressure data suggest that the loss of SiO vapor from the molten silicon allows the reaction between the crucible and the molten silicon to continue, thereby causing the aluminum concentration to build up in the silicon. It was consequently thought that aluminum dissolution would be reduced under inert atmosphere conditions, and that the oxygen content of molten silicon may control this dissolution process. The data in Table 15 confirm this hypothesis, the aluminum concentration having decreased from 5000 ppm to 50 ppm for similar contact times. Apparently, the reaction stops once the melt is saturated with oxygen.

TABLE 13. WETTING ANGLE FOR MOLTEN SILICON IN CONTACT WITH X = 0.75 β' SIALON AT 1450 C IN 0.83 atm ARGON

Time, minutes	Wetting Angle, C
3	44.3
7	39.5
12	36.0
27	37.5
37	36.5
49	37.0
58	37.0
69	39.0
72	38.5
87	38.5

TABLE 14. INTERACTION OF MOLTEN SILICON WITH X = 0.75 β' SIALON IN THE KNUDSEN CELL

Main Vapor Species[(a)]	Partial Pressure (N/m^2)	Impurity Concentration (ppm)
SiO	7.09×10^{-2}	[O] 0.1 (calc)
N_2	3.44×10^{-2}	[N] 312 [N] 360 (calc)
Al	3.74×10^{-4}	[Al] 5000 [Al] 2800 (calc)
Si_2N	4.35×10^{-3}	
Si	5.57×10^{-3}	

(a) Species with vapor pressures below 1.01×10^{-4} N/m^2 (1×10^{-9} atm) not given in table.

TABLE 15. EFFECT OF ATMOSPHERIC CONDITIONS ON THE DISSOLUTION OF ALUMINUM AND OXYGEN IN MOLTEN SILICON

	Vacuum	Argon
Aluminum (ppm)	5000	50
Oxygen (ppm)	0.1	180

3. β' Sibeons

All β' Sibeon samples were exposed to molten silicon at 1450 C for 1 hour in an argon atmosphere. None of the samples showed any sign of attack (see Figure 11), regardless of sample density or the presence of the additional "silicon oxynitride" phase.

The wetting of molten silicon on a polished surface of $x = 0.35$ β'-Sibeon in 0.83 atmosphere of argon pressure was observed for 1 hour. Wetting angle values were being taken from photographs of the silicon-Sibeon interface over this time interval. The data in Table 16 show that except for a small drop in the beginning, the wetting angle remained essentially constant at 49°. As in the case of $x = 0.75$ β' Sialon, this small initial drop in wetting angle could be due to dissolution of a thin surface oxide layer.

The characteristics of the capillary rise test with Sibeon were similar to those observed with β' Sialon; the molten silicon did not rise up the 31.3 mil (0.0736 cm) wide slot without first removing some oxygen as SiO by volatilization. After capillary rise the argon pressure was raised to 8.40×10^{-4} N/m^2 (0.83 atmospheres), and the molten silicon remained stable for the remaining 1 hour duration of the test. For a 49° wetting angle, the height of capillary rise in a 0.01 cm wide slot would be about 40.2 cm, substantially higher than the minimum requirements (2.5 cm) for a candidate shaping die.

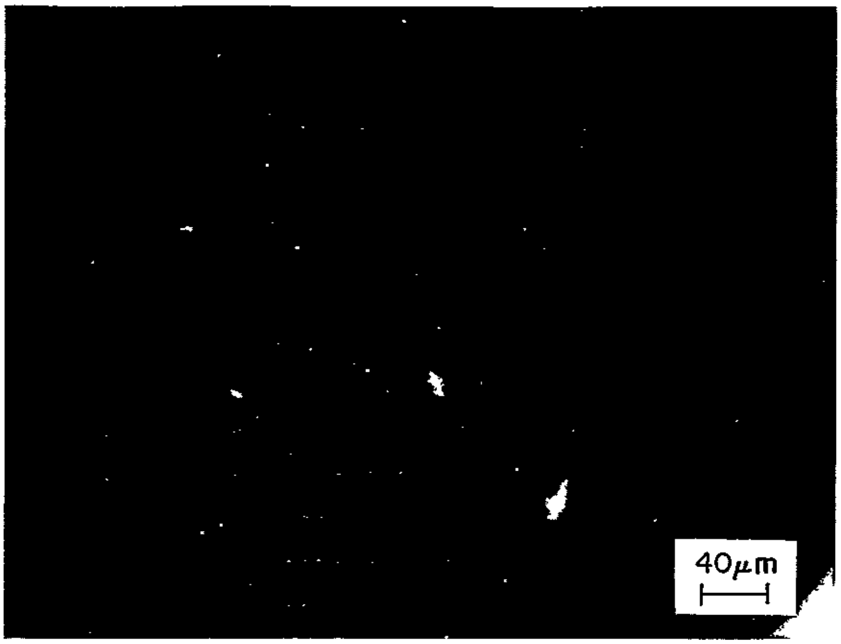

FIGURE 10. X-RAY IMAGE OF ALUMINUM IN SILICON. SILICON HELD IN CONTACT WITH X = 0.75 β' SIALON IN KNUDSEN CELL. LIGHT SPECKLES DUE TO BACKGROUND.

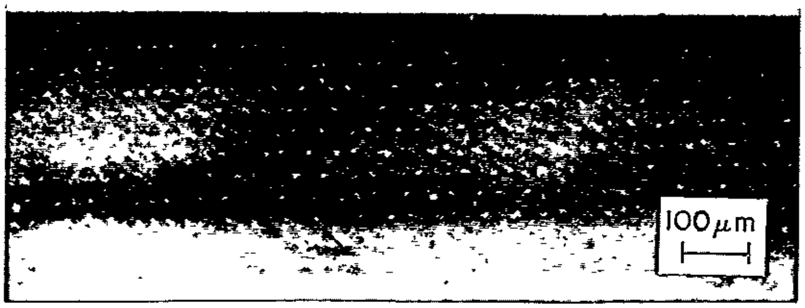

FIGURE 11. TYPICAL INTERFACE BETWEEN β' SIBEON SAMPLE AND SILICON AFTER 1 HR AT 1450 C IN ARGON ATMOSPHERE

In Table 17 the Knudsen cell data for the silicon - $x = 0.35$ β' Sibeon reaction at 1430 C are given. The vapor pressures of the main species, SiO, Si, Si_2N, are very similar to those found for the silicon - β' Sialon system, but the vapor pressures of the beryllium species (Be, BeO) are well below that of Al(g) 3.74×10^{-4} N/m^2 (3.7×10^{-9} atm). As indicated in the footnote to Table 17, the vapor pressures of Be and BeO were initially $<10^{-5}$ N/m^2 and fell to $<10^{-7}$ N/m^2 after 3 hours. The vapor pressure data thus indicate that Sibeon is more stable in contact with molten silicon than Sialon. This conclusion is also supported by the relative beryllium and aluminum concentrations present in the silicon samples (Be, 10 ppm, Al 5000 ppm) after the Knudsen cell experiments.

The above results are consistent with the data obtained for BeO and Al_2O_3, since BeO was found to be more resistant to attack than Al_2O_3; consequently, Sibeon would be expected to be more stable than Sialon.

In the studies with β' Sialon, it was postulated and proven that Sialon was more stable under inert atmosphere conditions than under vacuum conditions, because loss of oxygen as SiO from the melt enhanced aluminum dissolution. Sibeon behaves similarly, i.e., Sibeon is more resistant to attack under inert atmosphere conditions. The beryllium impurity concentration in one sample of silicon held in contact with $x = 0.35$ Sibeon at 1435 C for 1 hour under 0.83 atmosphere argon was <1 ppm. In another sample the beryllium concentration was <3 ppm. The oxygen contents of these samples were not determined.

The above data for O' Sialon, β' Sialon, and Sibeon indicate that the β-Si_3N_4 solid solutions (β' Sialon and Sibeon) are distinctly more resistant to molten silicon attack than the Si_2N_2O solid solution (O' Sialon). Furthermore, Sibeon is more stable than β' Sialon, and both materials should preferably be used in an inert atmosphere rather than under vacuum conditions. The effect of composition on the stability of the β-Si_3N_4 solid solution was only studied for β Sialon, but it is clear that the dissolution of metal cations in molten silicon will be increased by increasing the metal cation concentration of the solid solution. Additional fundamental studies are needed to determine the kinetics of the dissolution process as a function of time, temperature, and composition of the solid solutions.

TABLE 16. WETTING ANGLE FOR MOLTEN SILICON IN CONTACT WITH X = 0.35 β'-SIBEON AT 1470 C IN 8.40 x 10^{-4} N/m^2 (0.83 atm) ARGON

Time (minutes)	Wetting Angle (degrees)
0	55.0
3	49.5
7	50.0
8	50.5
13	51.0
18	51.0
23	49.0
28	48.5
33	50.0
38	49.5
43	49.0
48	48.0
53	47.0
68	48.0
Average	49±2

TABLE 17. INTERACTION OF MOLTEN SILICON WITH X = 0.35 β' SIBEON AT 1430 C IN THE KNUDSEN CELL

Main Vapor Species[(a)]	Partial Pressure (N/m^2)	Impurity Concentration (ppm)
SiO	6.58 x 10^{-2}	[O] <1 (calc)
Si_2N	5.87 x 10^{-3}	[N] 288 [N] 240 (calc)
N_2	2.43 x 10^{-2}	[Be] 10
Si	1.31 x 10^{-2}	[Be] 0.4 (calc)

(a) Species with vapor pressures below 1.01 x 10^{-4} N/m^2 not given in the table. Be, BeO detected below 10^{-5}, and below 10^{-7} N/m^2 (10^{-12} atm) level after 3 hours.

ASSESSMENT OF SIBEON AND SIALON AS DIE AND CONTAINER MATERIALS

In the previous section, it was shown that β' Sibeon and β' Sialon are very resistant to molten silicon attack, particularly if they are used in an inert atmosphere environment. In this section these materials are discussed in terms of the performance targets as specified in the introduction.

1. Mechanical Stability

Sibeon and Sialon are both fabricated at 1750 C, and are consequently expected to be stable at temperatures close to the melting point of silicon. These materials do not show phase changes below this temperature.

2. Dimensional Stability

For dies dimensional stability to 0.127 mm (0.5 mil) over a 24-hour period is required. The present study has not indicated any significant erosion of material but enhanced erosion may occur using flowing silicon. Silicon ribbon must be pulled using these materials to determine quantitaively their dimensional stability.

3. Chemical Stability in Molten Silicon

In sessile drop tests the beryllium and aluminum contents of 100-200 mg silicon samples have been lower than found for any other metal-cation-containing ceramic. While the results are very encouraging, evaluation of silicon ribbon formed using these materials must be performed before a complete assessment can be made.

4. Fabrication of Dies and Containers

The Sibeon and Sialon materials have been developed primarily for the die application as this is the more difficult of the two components. It has also been demonstrated that a die can be made from these materials.

Containers could also be made from these materials, but additional consideration and effort need to be given to the sinterability of the powder mixtures if high density crucibles are to be made.

5. Capillary Rise

The wetting angles of Sibeon and Sialon are low enough (49° and 37°) to enable a capillary column of silicon 1 to 3 cm wide x 0.01 cm thick to be supported a minimum height of 2.5 cm. In fact the low wetting angles will support much higher columns, as calculated earlier.

DIE FABRICATION AND PROJECTED COST ESTIMATES

Several billets of Sialon of dimensions 2-5/8 inches diameter and 0.5 inch thick were fabricated, as described previously, by hot pressing silicon nitride-alumina-aluminum nitride mixtures at 1750 C. Two initial attempts to fabricate dies according to the dimensions given in Figure 12 were unsuccessful due to excessive "chipping" of the Sialon. This was thought to be due to point loading of the die in clamping, causing excessive stresses. This problem was overcome by casting the blank in Epon* resin so that it could be clamped better during machining. Figure 13 shows the final machined ceramic shaping die. In this die the dimensions of the original one-piece die design (see Figure 12) supplied by JPL were modified slightly to give the die more strength during machining and handling. Essentially the modification involves a thicker die wall and shoulder (see Figure 14).

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* Epon Resin 815, Ceilcote Company, Inc., Berea, Ohio 44017.

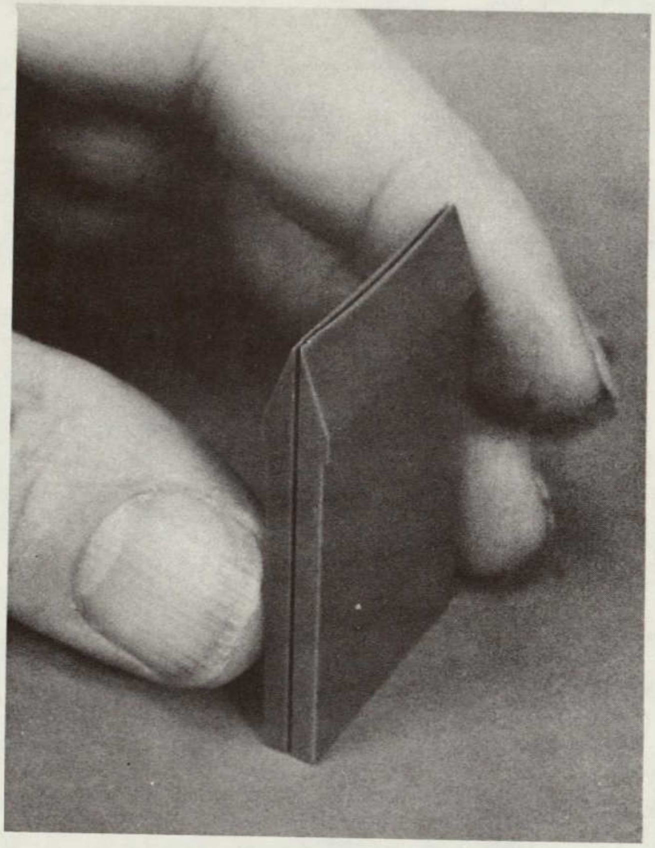


FIGURE 13. X = 0.75 β' SIALON CERAMIC SHAPING DIE

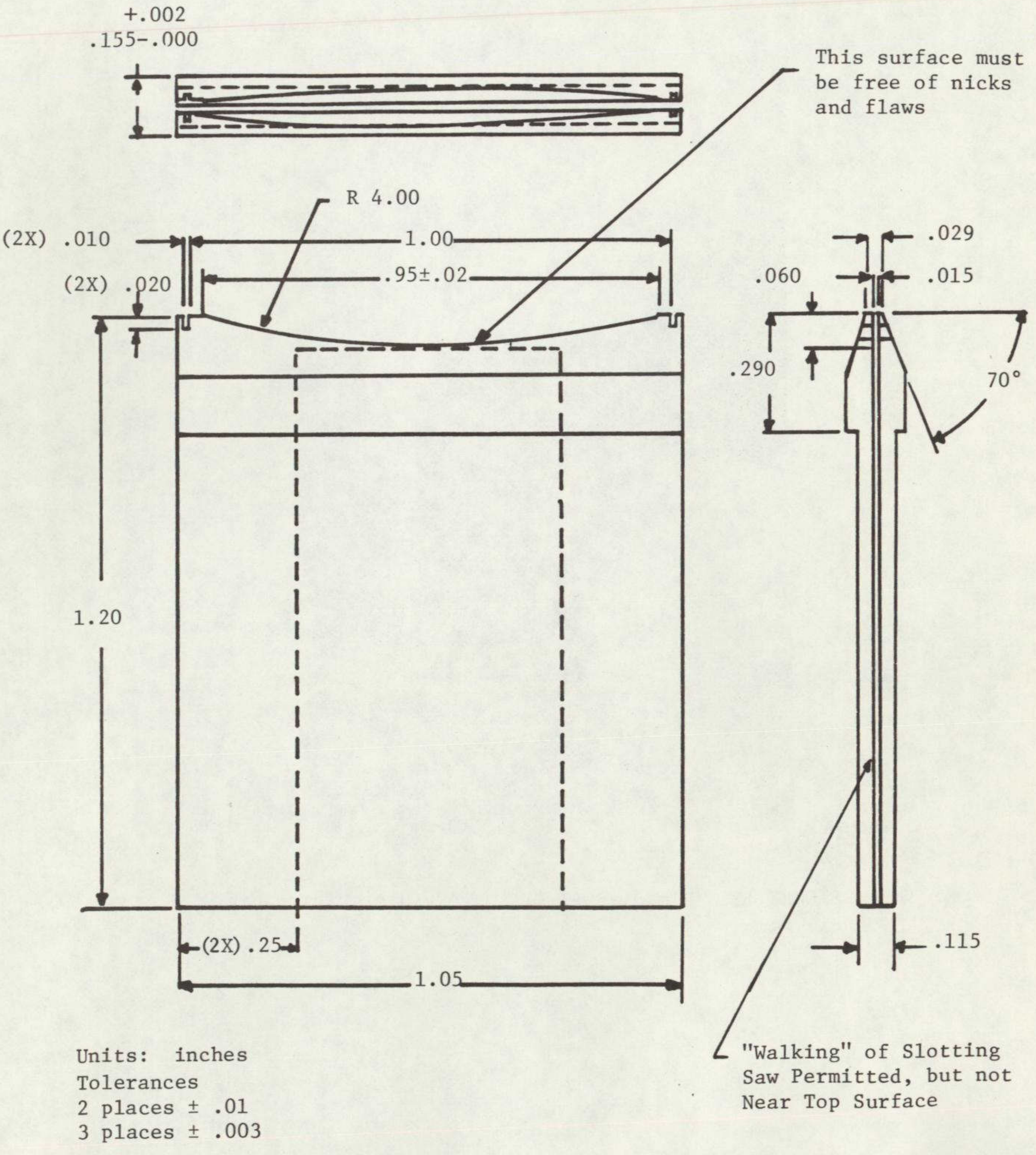
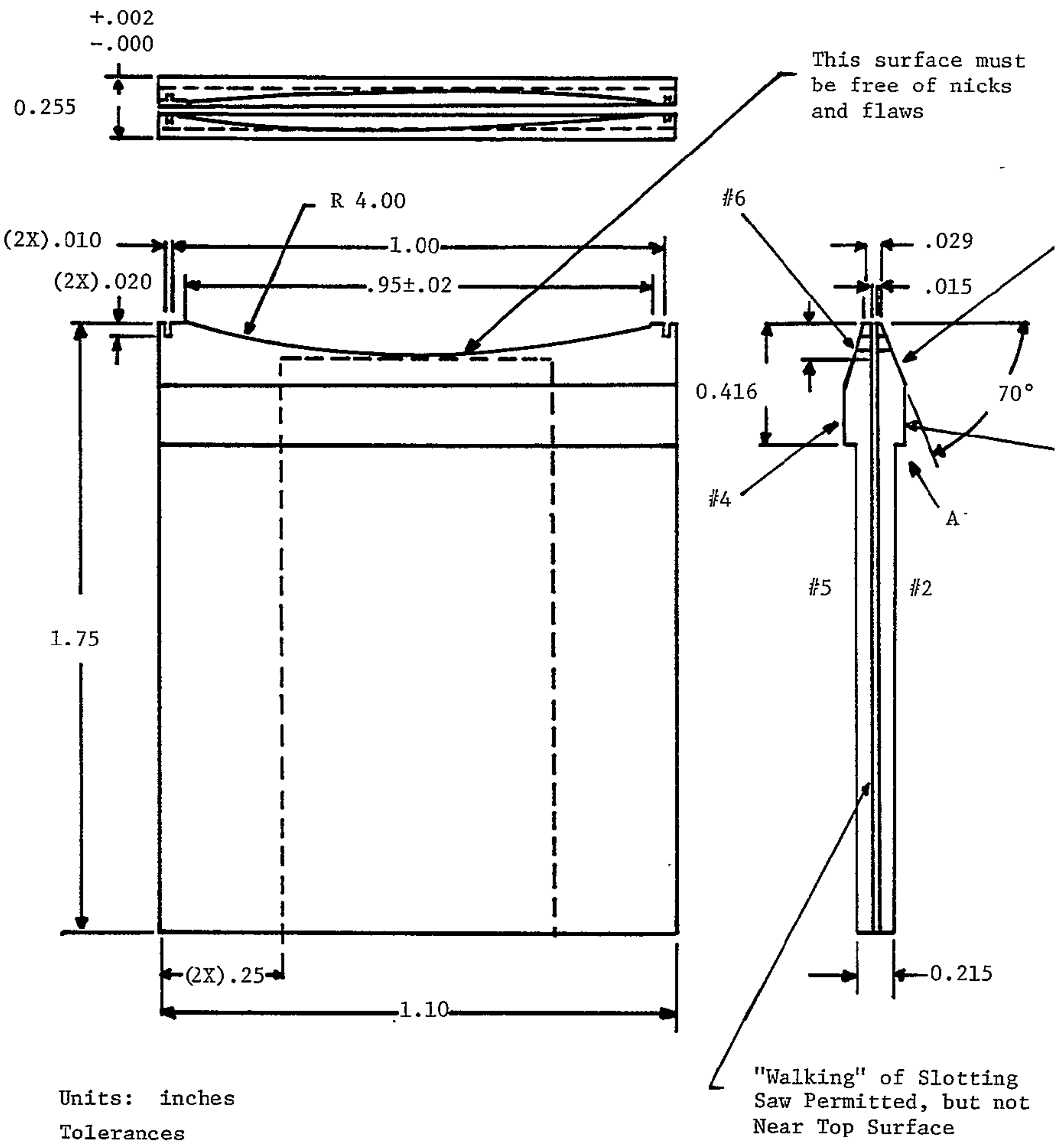


FIGURE 12. ORIGINAL ONE-PIECE DIE DESIGN SUPPLIED BY JPL



Units: inches

Tolerances
2 places ± .01
3 places ± .003

FIGURE 14. MODIFIED ONE-PIECE DIE DESIGN (SURFACE NUMBERS ARE REFERRED TO IN THE PROCESS SPECIFICATION)

From a rectangular block the shoulder configuration was first formed. The radius of curvature on the top of the die was formed next, with the capillary slots and the 0.060 inch slot at the top of the die machined last. The capillary slot came out as 0.020 inch instead of 0.015 inch because the diamond wheel had one or two high spots. Details of all the machining and handling steps are given in the process specification.

If the density of the ceramic is slightly reduced, the increased porosity will improve the ceramic's fracture toughness. This could be beneficial in the machining operation, and may allow the machining to be done without casting the ceramic in Epon resin. Future work needs to concentrate on optimizing the machining process.

Projected Cost Estimates

The above described method of fabricating dies is suitable for producing a limited number of dies, but would not be used to manufacture 10^5 dies per annum at a competitive price. Throughput i.e., number of dies per hot pressing cycle, and diamond grinding are major cost elements in the unit due cost. Consequently, the cost projections given below are based on a process that accounts for these cost drivers.

In essence, the process consists of powder mixing, green forming of rectangular blocks, green machining of the shoulders of the one piece die, stack pressing using graphite tooling, and finish machining of the die surface together with diamond cutting of the slots at the sides and top of the die. Cost projections are also given below for the Hot Isostatic Pressing (HIP) process. In this process, the green machined one-piece die is glass encapsulated and pressed at temperature using an inert gas. The glass "can" is removed prior to final diamond machining.

Cost projections for the manufacture of 10^5 dies per annum were made using the JPL interim price estimation guidelines$^{(8)}$, which are expressed in the following equation:

$$\text{Price} = \frac{0.49\text{EQPT} + 97\text{SQFT}\ 2.1\text{DLAB} + 1.3\text{MATS} + 1.3\text{UTIL}}{\text{QUAN}} \qquad (1)$$

EQPT is the cost of purchasing enough equipment to manufacture the product at an annual quantity of QUAN.

SQFT, the total area, in square feet, required by the equipment and the operators of the equipment required to produce QUAN units per year.

DLAB, is the annual cost of direct labor, not including fringe benefits or overhead, required to manufacture an annual quantity of QUAN.

MATS, is the annual cost of direct materials and supplied used in manufacturing QUAN units of the product per year.

UTIL, is the annual direct utility expenses of operating the manufacturing facility at a production rate of QUAN units per year.

For the uniaxial hot pressing process it is assumed that a 2 man-year effort will be required to prepare powder mixtures, green press die shapes, hot press, and also set up and supervise the final diamond grinding. A breakdown of the equipment needed to fabricate the dies is shown in Table 18. The equipment is assumed to be fully utilized in a 8-hour working day. Utilities are assumed to be $10,000 per annum, and labor costs $24,000.

TABLE 18. EQUIPMENT NEEDED TO PRODUCE 10^5 DIES/ YEAR BY UNIAXIAL HOT PRESSING

Item	Cost
One Mill 20 lb. capacity	$ 5,000
Die Press	$ 30,000
Dry Grinder	$ 50,000
Hot Press	$ 25,000
Generator	$ 95,000
Vacuum Equipment	$ 30,000
8 Diamond Grinders	$160,000
Hoods, Sinks, etc.	$ 5,000
Total	$400,000

The cost of materials is largely the cost of Si_3N_4 powder (\$200,000) and graphite (\$125,000). Approximately 20 g of Si_3N_4 powder is needed to produce one die. Assuming this facility can be operated within 1800 square foot, the overall price per die is:

$$\frac{0.49.400,000 + 1800.97 + 2.1.24000 + 1.3.325,000 + 1.3.10,000}{10^5}$$

$$= \underline{\$8.6}$$

This price includes the cost of Si_3N_4 powder at \$40 per lb. At \$2 per lb. the unit die cost would be reduced to <u>\$5.9</u>. In view of the intense activity related to Si_3N_4, it is likely that the cost of powder will come down to the \$.50 to \$2 per the range.

Hot isostatic pressing is another possible manufacturing technology that could be used to fabricate dies. If a manufacturing facility were constructed solely for die fabrication unit die costs, using \$40 per lb. Si_3N_4 powder, would be <u>\$8.8</u>. Savings in graphite costs are offset by increased capital costs. In practice the HIP unit would be idle 50 to 75 percent of the time because of the high number of dies that could be pressed in one cycle. Assuming the HIP unit is fully utilized by processing an additional product line and allowance is made in the purchase price of the equipment die costs are reduced to <u>\$8.1 each</u>. The lowest projected cost assuming \$2 per lb. Si_3N_4 is <u>\$5.4</u> per die.

Further cost savings could be achieved with the HIP process if substantially larger number of dies were required. This is because added cost for a larger zone furnace in the autoclave would be less than the cost of additional hot pressing equipment and graphite materials. These cost savings would depend upon the exact number of dies required.

CONCLUSIONS

(1) Specific compositions of silicon beryllium oxynitride and silicon aluminum oxynitride solid solutions with a β-Si_3N_4 structure show good resistance to molten silicon attack. The silicon beryllium oxynitride is the more resistant material. Both these materials are good candidate materials for manipulating molten silicon into silicon ribbon.

(2) Silicon beryllium oxynitride and silicon aluminum oxynitride solid solutions with a β-Si_3N_4 crystal structure are more stable than the silicon aluminum oxynitride with a Si_2N_2O crystal structure. The latter ceramic is unsuitable for this application.

(3) The stability of these materials is greater under inert atmosphere conditions than under vacuum conditions. Loss of oxygen from the molten silicon under vacuum conditions enhances the dissolution of aluminum and beryllium from these oxynitride ceramics.

(4) High purity ceramic shaping dies can be fabricated by careful powder processing, uniaxial hot pressing, and diamond machining.

RECOMMENDATIONS FOR FURTHER WORK

(1) The effects of temperature, time, and composition on the reaction of molten silicon with the two candidate die materials ($x = 0.75$ β' Sialon, and $x = 0.35$ β' Sibeon) need to be determined to assess the stability of these materials over extended time periods.

(2) The stability of the Sibeon solid solution as a function of composition should be evaluated since a higher Be_2SiO_4 content will enhance the sinterability of Si_3N_4-BeO-SiO_2 powder mixtures. Efforts to improve the sinterability of Si_3N_4-SiO_2-Al_2O_3-AlN mixtures should also be pursued.

(3) Evaluation of silicon ribbon formed using Sialon and Sibeon dies.

(4) Optimization of die machining processes.

(5) A detailed breakdown of cost elements in the manufacturing of dies.

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APPENDIX A

MATERIALS AND PROCESS SPECIFICATIONS

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MATERIALS AND PROCESS SPECIFICATIONS

Raw Material Specifications

1.0 Aluminum Oxide (Al_2O_3)

1.1 Chemical Properties

1.1.1 Impurity analysis by SSMS* in PPM**, maximum allowed.

Li	50	Ca	70
Be	3	Ti	10
B	4	Cr	5
Na	75	Mn	5
Mg	15	Fe	50
Si	80	Ga	75
P	5	Mo	10
S	10		

All other impurities less than 1 ppm each

1.2 Physical Properties

1.2.1 Density

1.2.1.1 True density - 3.97 g/cc

1.2.1.2 Bulk density - 26 percent of theoretical

1.2.1.3 Tap density - 37 percent of theoretical

1.2.2 Crystal structure - only α-Al_2O_3 (corundum) by x-ray diffraction analysis

1.2.3 Surface area - greater than 3.5 m^2/gram by BET nitrogen absorption

1.2.4 Particle size

1.2.4.1 Sieve analysis - 100 percent through 400 mesh screen by wet sieving

1.2.4.2 Centrifugal sedimentation (MSA)

Particle size in microns	Cumulative Weight percent maximum
+10	0.5
+5	2
+3	3
+2	5
+1	12
+0.5	60
+0.4	89
+0.3	95
+0.2	97
+0.1	100

Average size less than 0.5 micron

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* Spark source mass spectroscopy

** Parts per million

1.2.5 Thermogravimetric weight loss analysis - weight loss should be less than 0.25 percent from room temperature to 1200 C in argon atmosphere, after drying at 180 C in vacuum for 4 hours.

1.3 Packaging and Shipping - Al_2O_3 should be packed in polyethylene bags and shipped in cardboard drums. The net weight of the drums should be about 20 to 25 lb.

1.4 Storage and Handling - Aluminum oxide should be kept in its original containers until use. For accurate batching, however, it should be dried at 110 C for 4 hours prior to weighing.

1.5 Recommended source - RC-HP-DBM high purity grade alumina, Reynolds Metal Company.

2.0 Aluminum Nitride (AlN)

2.1 Chemical Properties

2.1.1 Impurity analysis - The metallic purity of AlN should be better than 99.8 percent.

Carbon	0.06	percent maximum
Oxygen	1.5	percent maximum
Nitrogen	32.4	percent minimum
Aluminum	65.2	percent minimum

The carbon, oxygen, and nitrogen should be determined by inert gas fusion analysis. The total aluminum analysis should be determined by wet chemistry.

2.1.2 All other total impurities as determined by spark source mass spectroscopic analysis should not exceed 0.12 percent.

2.1.3 All chemical analysis should be made after processing (milling) and drying at 180 C in vacuum for 4 hours.

2.2 Physical Properties

2.2.1 Density - 3.26 gram/cm^3 (theoretical)

2.2.2 Crystal structure - analysis should show only well developed hexagonal AlN and no other crystalline phase

2.2.3 Particle size - average particle size should be less than 5 micron as determined by MSA centrifugal method.

2.2.3.1 Sieve analysis - sieve analysis should be made on coarse AlN material. For a -200 mesh material:

Mesh opening	Weight percent
+140	7.2 maximum
+200	20.0 maximum
+270	32.0 maximum
+325	40.0 maximum
-325	60.0 minimum

AlN having such a coarse particle size distribution sould be either milled or rejected.

2.2.3.2 MSA centrifugal particle size - AlN material for formulating sialon x = 0.75 should have finer particle size distribution than indicated below.

Particle size in microns	Cumulative weight percent maximum
+20	0
+15	4
+10	8
+8	15
+6	40
+4	65
+2	82
+1	95
+0.5	98

The average particle size should be less than 5 micron.

2.2.4 Thermogravimetric analysis - The total weight loss from room temperature to 1200 C should be less than 0.40 percent in argon atmosphere. The TGA should be made after milling the powder in hexane and drying in vacuum (20 inches Hg) at 180 C for 4 hours.

2.2.5 Weight loss - For accurate formulation of the batch a TGA (thermogravimetric analysis) should be made from room temperature to 1200 C in argon after heating the sample at 180 C in vacuum for 4 hours. The maximum weight loss should be less than 0.40 percent.

2.2.6 Metallographic examination - No significant amount of metallic impurities should be present (maximum 0.1 present). A metallographic examination should be made by casting various sieve fractions in a resin (Epon^{R}) then grinding and polishing the cast powder fractions with kerosene.

If any significant amount of metallic impurities is detected inside the larger particles, either the lot should be rejected or the size fractions containing metallic impurities should be discarded, then milled to reduce the particle size.

If no significant amount of metallic impurites can be detected, then the lot should be milled to reduce the particle size.

2.3 Packaging and Shipping - AlN should be packed in double wall polyethylene bags under dry nitrogen and shipped in cardboard drums. Net weight of the drums should be about 20 to 25 lb.

2.4 Storage and Handling - AlN should be stored in its original containers until use. Weighing and handling should be in low humidity (less than 50 percent RH) and low temperature (68-75 F) environment, or in dry boxes under dry nitrogen atmosphere. The bags temporarily opened to air should be resealed under nitrogen.

AlN is very reactive with moist air. As a result of the reaction, it forms oxide layer and liberates ammonia. This reaction increases the oxygen content and decreases the nitrogen content of the product.

2.5 Recommended source - 99.8 percent pure, -200 mesh CERAC AlN powder.

3.0 Beryllium Oxide (BeO)

3.1 Chemical properties - Maximum acceptable impurity levels in ppm.

Li	3	Cr	10
B	3	Mn	5
Na	50	Fe	50
Mg	50	Co	3
Al	80	Ni	7
K	30	Cu	5
Ca	50	Mo	5

All others should be less than 1 ppm each.

3.2 Physical Properties

3.2.1 Density

3.2.1.1 True density - 3.025 gram/cc

3.2.1.2 Bulk density - 0.2 gram/cc

3.2.1.3 Tap density - 0.4 gram/cc

3.2.2 Crystal structure powder diffraction - should show only well crystallized BeO and no other phases

3.2.3 Particle size - centrifugal sedimentation (MSA) particle size distribution

Particle Size in microns	Cumulative weight percent maximum
+20	1
+14	2
+8	10
+4	35
+1	75

Average particle size 2 to 3 microns.

3.2.4 Weight loss

3.2.4.1 Drying loss - 0.3 weight percent (1 percent maximum) at 110 C in vacuum oven (29 inches Hg vacuum) for 1 hour.

3.2.4.2 Ignition loss after drying - 0.5 weight percent (1 percent maximum) after heating 3 hours at 1000 C.

3.3 Packing and Shipping - BeO should be packed in polyethylene bags and shipped in metal containers. The net weight of the containers should be 20 to 25 lb. A label should be attacked indicating net weight, lot number, and nature of product. The label should include the word "danger" and warn against inhaling dust or fumes in accordance with relevant Government regulations. Shipping of BeO should be in accordance with (DOT) regulations.

3.4 Storage and Handling - Inhalation of concentrations of beryllium in excess of occupational standards described below can cause serious lung disorders. The occupational Safety and Health Administration (OSHA) of the U.S. Department of Labor has established mandatory standards for occupational exposures as set forth in 29CFR,* Section 1910.3, Table G-2. In summary, this regulation provides that:

(a) The daily weighted average exposure over an 8-hour day may not exceed 2.0 micrograms of beryllium per cubic meter of air.

(b) Short-term exposure above 5.0 micrograms per cubic meter but not greater than 25 micrograms per cubic meter are permissible for a total of no more than 30 minutes during an 8-hour working period.

In storing and handling the beryllium products, the facility should be equipped to monitor the exposure levels and the contamination should be disposed in accordance with the regulations of OSHA.

3.5 Recommended source and producer UOX grade BeO, Brush Wellman, Inc.

4.0 Amorphous Silicon Nitride (Si_3N_4)

4.1 Chemical Properties - All chemical analysis shall be made after baking the powder at 180 C in vacuum oven (29 inches Hg) at least for 4 hours.

4.1.1 Oxygen content - maximum 2.9 percent as determined by inert gas fusion analysis

4.1.2 Nitrogen content - minimum 36.9 percent as determined by inert gas fusion analysis

4.1.3 Chlorine maximum 0.50 percent.

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* National Council Data Sheet 562 Revision A (Extensive).

4.1.4 Other impurities in ppm by SSMS

Na	15	Fe	10
Mg	15	Cu	5
Al	15	Zn	3
Ca	10	Mo	25
Ti	15		

All other impurities should be less than 1 ppm each.

4.2 Physical Properties

4.2.1 Density

4.2.1.1 True density - 3.18 gram/cc

4.2.1.2 Bulk density - 5 percent of theoretical

4.2.1.3 Tap density - 8 percent of theoretical

4.2.2 Crystal structure - mainly amorphous, 5-10 percent α-Si_3N_4 by x-ray diffraction analysis

4.2.3 Surface area - greater than 10 meter square/gram

4.2.4 Particle size

4.2.4.1 Sieve analysis - 100 percent through 325 mesh screen

4.2.4.2 Centrifugal sedimentation (MSA) particle size

Particle size microns	Cumulative Weight percent, maximum
+5	0
+3	10
+2	15
+1.5	20
+1.0	30
+0.9	40
+0.85	50
+0.8	60
+0.7	75
+0.6	85
+0.4	95
+0.2	98

Average particle size 0.7-0.8 micron range.

4.2.5 Weight loss, by TGA - should be less than 0.35 percent from room temperature to 1200 C in argon atmosphere, after baking at 180 C in vacuum for 8 hours.

4.3 Packaging and shipping - The material should be packed in double wall polyethylene bags under dry nitrogen and shipped in cardboard drums. The net weight of the drums should be about 20-25 lb. The containers should be property labeled indicating net weight, lot number, grade, and nature of the material.

4.4 Storage and Handling - Amorphous silicon nitride produced from $SiCl_4$ by CVD process contains considerable amount of ammonium chloride. Due to the ammonium chloride content and extremely fine particle size of CVD Si_3N_4, it absorbs considerable amount of moisture from air. It should be stored in tight containers under dry nitrogen. Handling and weighing should be performed under low humidity conditions or in dry boxes. If containers opened to atmosphere they should be resealed under dry nitrogen after heating at 180 C under vacuum for 4 hours. For accurate batch formulation the powder should be previously baked at 180 C under vacuum for 4 hours.

4.5 Source - GTE Sylvania, Inc., SN402 type amorphous silicon nitride.

5.0 Crystalline Silicon Nitride (Si_3N_4)

5.1 Chemical Properties - All chemical analysis shall be made after baking the powder at 180 C in vacuum (29 inches Hg) at least for 4 hours.

5.1.1 Oxygen content - should be less than 1.40 percent maximum, determined by inert gas fusion analysis.

5.1.2 Nitrogen content - should be 38.7 percent minimum, determined by inert gas fusion analysis.

5.1.3 Maximum permissible impurities in ppm

Na	10	Cr	10
Mg	15	Fe	20
Al	75	Y	3
Ca	15	Zr	60
Ti	15	Mo	100

5.1.4 Chlorine content - should be less than 0.05 percent

5.1.5 Other impurities - all other impurities should be less than 1 ppm each by spark source mass spectroscopy.

5.2 Physical Properties

5.2.1 Density

5.2.1.1 True density - 3.18 gram/cc

5.2.1.2 Bulk density - 3.5 percent of theoretical

5.2.1.3 Tap density - 5.5 percent of theoretical

5.2.2 Crystal structure by x-ray powder diffraction - 60 percent crystalline (95 percent α, 5 percent β) 40 percent amorphous.

5.2.3 Surface area - greater than 3.5 meter square per gram, as determined by nitrogen BET analysis.

5.2.4 Particle size - Sieve analysis, in propanol

Sieve size	Cumulative weight percent, maximum
+60 mesh	0.4
+100	0.7
+325	3.5
+400	7.5
-400	92.5 minimum

The +400 mesh fraction of the material contains hard sintered agglomerates; they should be discarded. Average particle size of -400 mesh fraction should be less than 0.6 micron.

5.2.5 Thermogravimetric analysis - Weight loss, by TGA, should be less than 0.20 percent from room temperature to 1200 C in argon atmosphere, after baking at 180 C in vacuum for 4 hours.

5.3 Packaging and Shipping - The material should be packed in polyethylene bags under dry nitrogen and shipped in cardboard drums. The net weight of drums should be about 20-25 lb. The containers should be properly labeled indicating net weight, lot number, grade and nature of the material.

5.4 Storage and Handling - The material should be stored in dry nitrogen. Handling and weighing should be performed under low humidity conditions or in dry boxes. If containers opened to atmosphere, they should be resealed under dry nitrogen. For accurate batch formulation the powder should be previously baked at 180 C in vacuum (29 inches Hg) for 4 hours.

5.5 Source - GTE Sylvania, Inc., SN502 type calcined silicon nitride.

6.0 Amorphous Fumed Silica (SiO_2)

6.1 Chemical Properties

6.1.1 Nominal purity - 99.8 percent purity

6.1.2 Maximum permissible impurities, by Spark Source Mass Spectroscopy

Be	2	Ca	20	Ni	2
B	10	Ti	2	Zn	30
Na	40	V	2	Zr	5
Mg	40	Cr	2	Nb	10
Al	10	Mn	3	Mo	2
P	300	Fe	10	Sn	3
Cl	50	Co	20	Ba	20

6.1.3 All other impurities should be less than 1 ppm each.

6.2 Physical Properties

- 6.2.1 Density
  - 6.2.1.1 True density - 2.2 gram/cc
  - 6.2.1.2 Bulk density - 0.03 gram/cc
  - 6.2.1.3 Tap density - 0.04 gram/cc
- 6.2.2 Crystal structure by x-ray powder diffraction - amorphous
- 6.2.3 Surface area - by BET nitrogen absorption 375 square meter/gram
- 6.2.4 Nominal particle size - particle size is about 80 Å (it may be calculated from surface area assuming spherical particles).
  - 6.2.4.1 Sieve analysis - maximum 0.02 weight percent on 325 mesh screen.
  - 6.2.4.2 Centrifugal sedimentation (MSA) particle size - Due to its nature of extremely small particle size and tendency to agglomerate, the centrifugal MSA does not give accurate particle size distribution. However, the average weak agglomerate size may be ascertained.
- 6.2.5 Thermogravimetric analysis
  - 6.2.5.1 Weight loss, TGA - Maximum weight loss should be 0.4 percent from room temperature to 1200 C in argon after baking at 180 C in vacuum (29 inches Hg) for at least 4 hours.
  - 6.2.5.2 Ignition loss to 1000 C of as received moisture free material should be less than 2 weight percent.

6.3 Packaging and Shipping - The material should be packed in polyethylene lined (impervious to moisture) heavy walled paper bags. The bags should be properly labeled indicating net weight, lot number, grade, and nature of the material.

6.4 Storage and Handling - The material should be stored and handled under very low humidity conditions or in dry boxes. It should be always dried or baked in vacuum at 180 C for 4 hours before batching. Breathing of fumed silica should be avoided by wearing a properly designed mask or should be handled in dry boxes or exhausted hoods.

6.5 Source - Cabot Corporation - Cabosil EH-5 grade or Cabosil M-5 grade (with higher bulk density for easier handling, average size 140 Å).

Process Specifications

Processing Aluminum Nitride (AlN)

Purpose: To reduce the particle size distribution of -200 mesh 99.8 percent pure AlN by milling in hexane.

(1) Ball Mill - Either 99.5 percent pure alumina ball mills or the mills should have a polyethylene or polyurethane linings. In this work gallon size 99.5 percent purity Coors alumina ball mills were used.

(2) Milling Balls - 3/4 to 1 inch diameter 99.5 percent pure alumina balls.

(3) Ball Charge - The milling balls should occupy about 50 percent of the mill volume (4000 grams of milling balls for a gallon size mill).

(4) Milling Balls to AlN Ratio - The milling balls to AlN charge ratio should be 4.44 (900 grams AlN for 4000 grams of balls).

(5) Milling Liquid - The milling liquid is n-hexane, 1.06 cc per gram of AlN charge (or 475 cc per pound).

(6) Milling Speed - 74 rpm, 71 percent of critical speed for 6.5 inch diameter mill. For a larger size mill the speed should be about 60-65 percent of the critical speed.

(7) Milling Time - The milling time is 8 hours. For a larger size mill, the milling time may be longer to produce the desired particle size.

(8) Hexane Removal - The hexane should be evaporated at a low temperature (25-30 C) under a vacuum aspirator.

(9) Ball Separation - The milling balls can be separated from the powder batch by sieving through a 40 mesh screen. The balls and powder may pick up iron contamination during the sieving operation. The iron contamination from the balls should be eliminated before reusing them. This can be achieved by milling the balls with 60 mesh tabular alumina in deionized water, then rinsing and drying the balls. Preferably screens should have a plastic mesh (nylon) or a plastic coated wire mesh.

(10) Drying the AlN Batch - The batch should be dried at 150 C in vacuum and stored under dry nitrogen until use.

(11) For an accurate formulation of the sialon batch, the processed AlN should be analyzed for its aluminum, oxygen, and nitrogen content as well as its weight loss to 1200 C.

Processing Calcined Si_3N_4

Purpose: To break up weak agglomerates and eliminate large strong agglomerates of GTE SN502 Si_3N_4 powder by milling and sieving.

(1) Mill - Polyethylene or polyurethane lined milled (in this study gallon size polyethylene jars were used)

(2) Milling Balls - 1/2 to 3/4 inch diameter Tefton® balls or cylinders.

(3) Ball Charge - 1500 grams Teflon® balls for a gallon mill volume.

(4) Milling Balls to Si_3N_4 Ratio - The milling balls to charge ratio, in terms of weight, 5 to 1 (300 grams Si_3N_4 powder for a gallon size mill).

(5) Milling Liquid - The milling liquid is isopropanol, 6.5 cc isopropanol per gram Si_3N_4 powder (or 2950 cc per pound of Si_3N_4).

(6) Milling Speed - 74 rpm, 75 percent of critical speed for 6 inch diameter polyethylene jar mills. For larger size mills the speed may be 65-70 percent of critical speed.

(7) Milling Time - Milling time 6 to 8 hours.

(8) Separating the Balls - Separate the Teflon® balls by dumping the slurry through a sieve with about 1/4 inch openings.

(9) Eliminating the large Agglomerates - Eliminate the large agglomerates by screening the slurry successively through 60, 100, 200, 270, 325, and 400 mesh screens.

(10) Filtering the Isopropanol - Filter out the isopropanol from -400 mesh fraction through an appropriate filter under a vacuum aspirator. (In this study an ashless filter paper was used.)

(11) Drying the Cakes - Dry the cakes at 150-160 C under vacuum overnight.

(12) Storage - Store the dried cakes under dry nitrogen until use.

Processing X = 0.75 Sialon

1.0 Formulation and Batching

1.1 Raw Materials

- GTE SN402 Si_3N_4
- 99.8 pure processed Cerac AlN
- RC-HP-DBM grade Reynolds Al_2O_3

1.2 Target Composition

The β'-sialons have the general formula of $Si_{6-x}Al_xO_xN_{8-x}$
For practical reasons the composition x = 0.75 is chosen:

$Si_{5.25}Al_{0.75}O_{0.75}N_{7.25}$

The target composition in weight percentages:

Si	Al	O	N		Si_3N_4	Al_2O_3	AlN
52.426	7.20	4.266	36.11	or	87.29	9.065	3.645

1.3 Formulation of the Batch

Formulation of the 0.75 sialon batch should be calculated to yield the target composition using the determined compositions of the raw materials and taking into account their weight losses, total impurity contents and any Al_2O_3 pick-up during milling.

For the specific lots of raw materials used in this project the weight percent of the raw materials for x = 0.75 sialon batch is

- GET SN402 Si_3N_4 88.42 percent
- Processed Cerac AlN 8.33 percent
- RC-HP-DBM Reynolds Al_2O_3 3.24 percent

1.4 Weighing the Raw Materials

Weigh the raw materials in low humidity conditions or in dry boxes. Accuracy of weighings should be at least for

- GTE SN402 Si_3N_4 to ± 0.1 percent
- Processed Cerac AlN to ± 0.05 percent
- RC-HP-DBM Reynolds Al_2O_3 ± 0.05 percent

2.0 Milling 0.75 Sialon Batch

2.1 Wet Milling in Hexane

2.1.1 Ball mill - either 99.5 percent pure alumina ball mill or it should have a polyethylene or a polyurethane lining

2.1.2 Milling balls - 3/4 to 1 inch diameter 99.5 percent pure alumina balls

2.1.3 Ball charge - about 50 percent of the mill volume should be filled with milling balls (4000 grams of balls for a gallon size mill).

2.1.4 Milling balls to charge ratio - milling balls to charge ratio in terms of weight 14 to 1 (4000 gram balls to 285 gram batch).

2.1.5 Milling liquid - hexane, 4.66 cc per gram batch (or 2118 cc hexane per pound batch)

2.1.6 Milling speed - 71 percent of critical speed for 6.5 inch diameter mill or 74 rpm. For a larger mill the speed should be 60-65 percent of critical speed.

2.1.7 Milling time - 4 hours for a gallon size mill batch. It may be longer for a larger mill.

2.1.8 Hexane removal - the hexane should be evaporated at a low temperature under vacuum.

2.1.9 Ball separation - the milling balls should be removed from the batch by screening through a 40 mesh sieve. During screening the balls will pick up iron from the sieves. Therefore, the balls should be cleaned before reusing them. Alternatively, sieves made of plastic (nylon or polyethylene) mesh or plastic coated wire screens should be used.

2.1.10 Drying the batch - the batch should be dried at 150 C for at least 4 hours and stored in dry nitrogen until hot pressing.

2.1.11 Approving the batch - make small hot pressed samples and evaluate before releasing the batch to production.

2.2 Dry Milling x = 0.75 Sialon

2.2.1 Ball mill - either 99.5 percent pure alumina ball mill or the mill should have a polyethylene or polyurethane lining.

2.2.2 Milling balls - 3/4 to 1 inch diameter 99.5 percent pure alumina balls.

2.2.3 Ball charge - the alumina balls should occupy about 50 percent of mill volume (4000 gram balls for a gallon size mill).

2.2.4 Milling balls to charge ratio - milling balls to charge ratio in terms of weight 15.4 to 1 (260 grams of batch

2.2.5 Milling aid - triethanolamine, 0.2-0.4 weight percent of batch

2.2.6 Milling time - 8 to 10 hours

2.2.7 Milling speed - about 70 percent of the critical speed (74 rpm for 6.5 inch diameter mill). It should be about 60-65 percent of critical speed for larger mills.

2.2.8 Ball separation - see 1.9

2.2.9 Drying the batch - dry the batch at 110 C under vacuum overnight

2.2.10 Storage - store the batch under dry nitrogen until hot pressing

2.2.11 Approving the batch - make small hot pressed samples and evaluate before releasing the lot.

2.2.12 Recommended dry milling sequence

(a) Weigh the milling balls into the ball mill

(b) Add milling aid, triethanolamine

(c) Add Al_2O_3 and AlN

(d) Run the mill for about 10-15 minutes. This will help to distribute the small constituents evenly.

(e) Add GTE SN402 Si_3N_4 and run the mill for the required amount of time.

(f) Make sure the axis of the mill is exactly horizontal, otherwise, the batch will pack up on the low end of the mill.

(g) The alumina pick-up from the balls and the mill lining increases due to increased milling time and absence of milling liquid. Therefore, this increase should be determined and compensated in batch formulation.

Processing X = 0.35 Sibeon

1.0 Formulation and Batching

1.1 Raw Materials

- Processed GTE SN502 Si_3N_4
- Amorphous Cabosil SiO_2
- UOX grade brush BeO

1.2 Target Composition

General formula of β'-Sibeons

$Si_{6-x}Be_{x}O_{2x}N_{8-x}$

The chosen composition is x = 0.35

$Si_{5.65}Be_{0.35}O_{0.70}N_{7.30}$

The target composition in weight percentages

Si	Be	O	N		Si_3N_4	BeO	SiO_2
57.65	1.145	4.07	37.135	or	93.0	3.179	3.819

1.3 Formulation of the Batch

The formulation of the 0.35 Sibeon batch should be calculated to yield the target composition using the experimentally determined compositions of the raw materials and taking into account their weight losses and total impurity contents.

For the specific lots of raw materials used in this project, the weight percentages of the raw materials for c = 0.35 Sibeon batch.

- Processed GTE SN502 Si_3N_4 95.47 percent
- Cabosil SiO_2 1.34 percent
- UOX Grade Brush BeO 3.19 percent

1.4 Weighing the Raw Materials - weigh the raw materials in low humidity conditions or in dry boxes. The accuracy of the weighings should be at least for:

- Processed GTE SN502 Si_3N_4 ± 0.1 percent
- Cabosil SiO_2 ± 0.05 percent
- UOX Grade Brush BeO ± 0.05 percent

2.0 Milling the C = 0.35 Sibeon Batch

2.1 Wet Milling in Hexane

2.1.1 Ball mill - the ball mill should have either a polyethylene or polyurethane lining

2.1.2 Milling balls - 1/2 to 3/4 inch diameter Teflon balls or cylinders.

2.1.3 Ball charge - about 50 percent of the ball mill volume (2400 grams for a gallon size mill).

2.1.4 Milling balls to charge ratio - the milling balls to charge ratio, in terms of weight, should be about 9.6.

2.1.5 Milling liquid - the milling liquid is hexane, 5.6 cc of hexane per gram of batch (or 2540 cc per pound of batch).

2.1.6 Milling speed - 120 rpm (85 percent of critical speed for a 3.6 inch diameter quart size mill). The speed should be lower for larger size mills.

2.1.7 Milling time - the milling time is 12 hours.

2.1.8 Hexane removal - the hexane should be evaporated at a low temperature (25-30 C) under vacuum.

2.1.9 Ball separation - the Teflon balls should be separated from the batch by screening through a 40 mesh sieve. It would be preferable for the sieve to have a plastic mesh screen or a plastic coated wire mesh screen to prevent contamination of the batch.

2.1.10 Drying the batch - dry the batch at 150 C under vacuum and store under dry nitrogen until hot pressing.

2.1.11 Approving the batch - make small hot pressed samples and evaluate before releasing the lot to production.

Caution: The Sibeon batches should be handled in accordance with beryllium handling procedures due to their BeO content.

Hot Pressing Specifications

1.0 Preparation of Hot Pressing Furnace

1.1 Dies, punches, and plugs

1.1.1 Dies will be machined from ATJ (Union Carbide Corporation) graphite. Punches and plugs will be machined from HPD grade (POCO Corporation) graphite.

1.1.2 Dies shall be lined with two layers of 7 mil thick graphite foil (graphoil, Union Carbide Corporation). Also, two layers of graphoil shall be placed between the powder pressed and the top punch and the bottom plug.

1.2 Degassing and Conditioning

1.2.1 All new graphite dies, punches, plugs, and graphoil liners shall be degassed and conditioned by heating the parts above 1900 C in vacuum (at least 5×10^{-4} mm Hg) for not less than 2 hours. After first hot pressing, the dies, punches, and plugs need not be degassed.

1.2.2 All new graphite susceptors and graphite felt insulation parts of the hot press shall be degassed and conditioned in place as in 1.2.1.

1.3 Temperature Monitoring

1.3.1 The hot pressing temperature shall be monitored by a W-26Re and W-5Re thermocouple. At least two thermocouples or a thermocouple and an optical pyrometer should be used as back up in case of thermocouple failure.

1.3.2 Thermocouple wires should be heavy guage (25-30 mil thick) for longevity.

1.3.3 Thermocouple protection tubes and insulators may be either a high purity alumina or beryllia ceramics.

2.0 Loading the Powder

2.1 Weigh the necessary amount of batch powder to produce 0.40 inch high billet. Allow about 7 to 8 percent weight loss for Sialons and 5 to 6 percent weight loss for Sibeons.

2.2 Load the powder into the graphoil lined die. Gently press the powder into the die in between to make room for loading the required amount.

Caution: The Sibeon batches should be handled according to beryllium handling specifications due to its BeO content.

2.3 Place the two layers of graphoil liners on top of the powder.

2.4 Insert the top graphite punch and press under 400-600 psi pressure.

3.0 Loading the Hot Press

3.1 Align the optical pyrometer hole on the side of the susceptor with the observation porthole of the vacuum chamber.

3.2 Place the loaded die into the susceptor. Make sure that the top of the bottom plug of the die is in the middle of the susceptor and at the same level as the tip of the W-Re thermocouple.

3.3 Bring the top ram in contact with the top punch without exerting pressure.

3.4 Set the dial gauge for ram travel

3.5 Clean the observation portholes.

3.6 Close the vacuum chamber and apply vacuum.

4.0 Hot Pressing Cycle

4.1 Mode I - Sialon, $x = 0.75$

4.1.1 Heat at a rate of 22-24 C per minute under vacuum (at least 5×10^{-4} mm Hg) until temperature reaches 1100 ± 100 C.

4.1.2 Admit 0.83 atmosphere pressure prepurified N_2 into the chamber at 1100 C.

4.1.3 Continue heating in N_2 atmosphere to 1550 C and hold for 25 ± 5 minutes at 1550 C to allow for the fuming of the volatile species.

4.1.4 Turn power off to cool - apply vacuum at 1300 ± 50 C.

4.1.5 Attain the vacuum of at least 5×10^{-4} mm Hg at 900 C.

4.1.6 Turn power on and start heating to 1755 C at a rate of about 25 C per minute.

4.1.7 Admit N_2 into chamber, 0.83 atmosphere at 1000 C.

4.1.8 Apply 4000 psi pressure at 1550 C and increase the pressure to 8000 psi as temperature rises to 1755 C.

4.1.9 Hold temperature at 1755 ± 10° and pressure 8000 ± 100 psi for 2 hours.

4.1.10 Cool to 1550 C at a rate of 8 C/minute.

4.1.11 Turn power off at 1550 C and allow to cool to room temperature naturally.

4.2 Mode II - Sibeon $x = 0.35$

4.2.1 Heat at a rate of 22-24 C per minute under vacuum (at least 5×10^{-5} mm Hg) until temperature reaches to 1100 ± 100 C.

4.2.2 Admit prepurified N_2 (0.83 atmosphere pressure) into the chamber at 1100 C.

4.2.3 Continue heating in N_2 atmosphere at a rate of 22-25 C per minute to 1775 C.

4.2.4 Apply 4000 psi pressure at 1550 C and increase the pressure gradually to 8000 psi as temperature reaches to 1700 C.

4.2.5 Hold temperature at 1775 + 10 or -5 C and pressure 8000 ± 100 psi for 1 hour.

4.2.6 Keeping pressure at 8000 psi , lower the temperature at a rate of about 15 C per minute to 1550 C.

4.2.7 At 1550 C turn the power off and release pressure.

4.2.8 Allow to cool to room temperature.

4.3 Mode III - Sibeon $x = 0.35$ (Mode III is similar to Mode I and it will produce sibeons with less impurities).

4.3.1 Heat at a rate of 22-24 C per minute under vacuum (at least 5×10^{-4} mm Hg) until temperature reaches 1100 ± 100 C.

4.3.2 Admit prepurified N_2 (0.83 atmosphere pressure) into the chamber at 1100 C.

4.3.3 Continue heating in N_2 atmosphere at 22-25 C per minute to 1550 C.

4.3.4 Hold temperature at 1550 C for 25 to 30 minutes to allow the volatile species to escape.

4.3.5 Turn power off and allow the furnace to cool to 950 C (rate of cooling 25 C/minute).

4.3.6 Apply vacuum at 1350 C as temperature drops to pull out the volatile species.

4.3.7 At 950 C the vacuum should reach at least 5×10^{-4} mm Hg pressure.

4.3.8 Backfill the furnace chamber with prepurified N_2 to 0.80 atmosphere pressure.

4.3.9 Start reheating to 1775 C at a rate of about 25 C/minute.

4.3.10 Apply 4000 psi pressure at 1550 C.

4.3.11 Increase pressure gradually to 8000 psi as temperature reaches 1700 C.

4.3.12 Hold temperature at 1775 plus 10 minus 5 C and pressure 8000 ± 100 psi for 1 hour.

4.3.13 Cool to 1550 C at a rate of about 15 C per minute. Keep pressure at 8000 psi.

4.3.14 Turn power off and release the pressure at 1550 C and allow to cool to room temperature.

5.0 Cleaning and Inspection

5.1 Take out the hot pressed samples from dies and remove any adherent graphoil by sand blasting.

5.2 Measure density and check the crystalline phases by x-ray diffraction.

5.3 At least one sample from each lot of batch should be tested for silicon compatibility and insepcted under metallographic microscope.

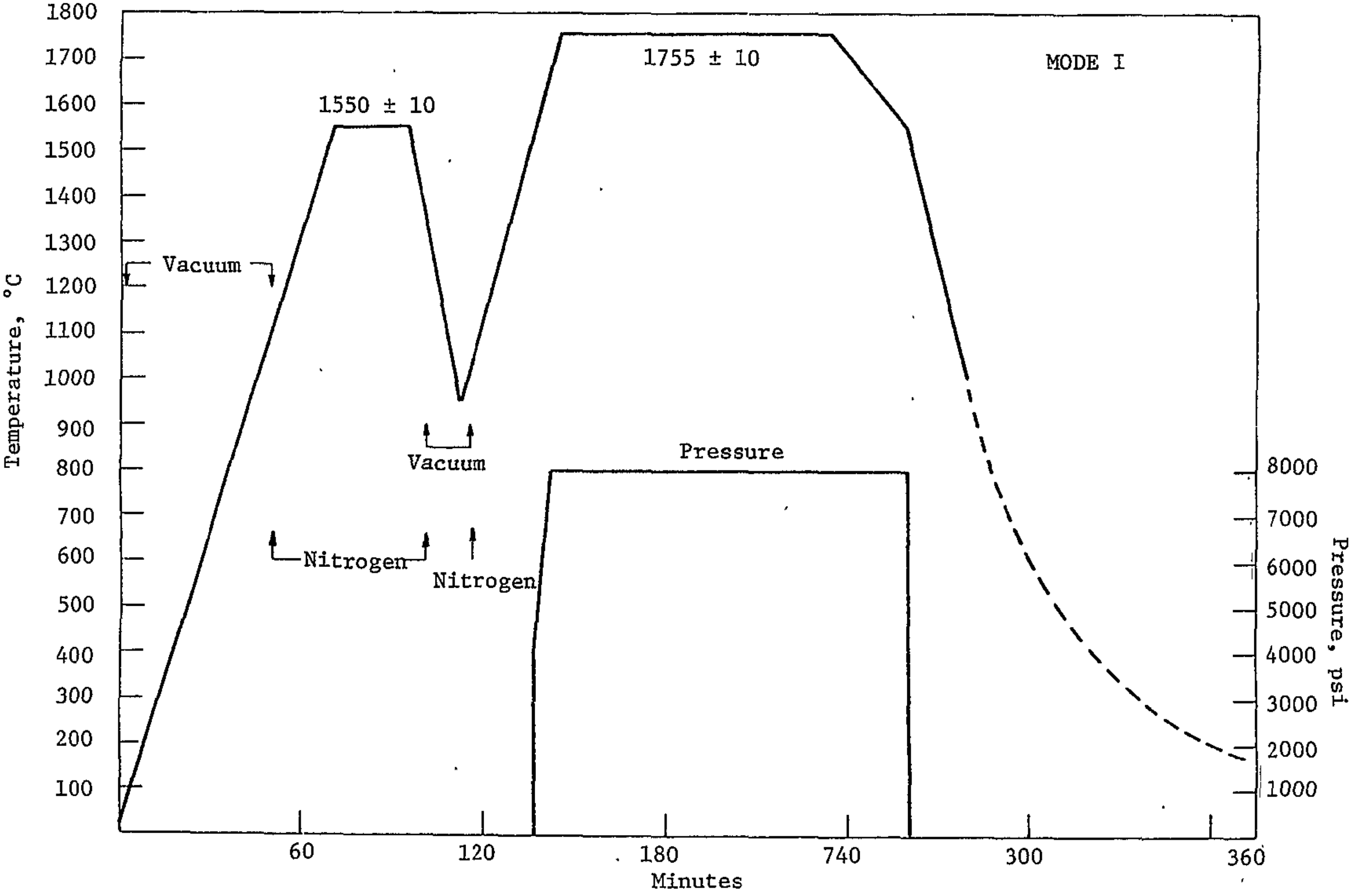

FIGURE A-1. HOT PRESSING CYCLE, SIALON X = 0.75

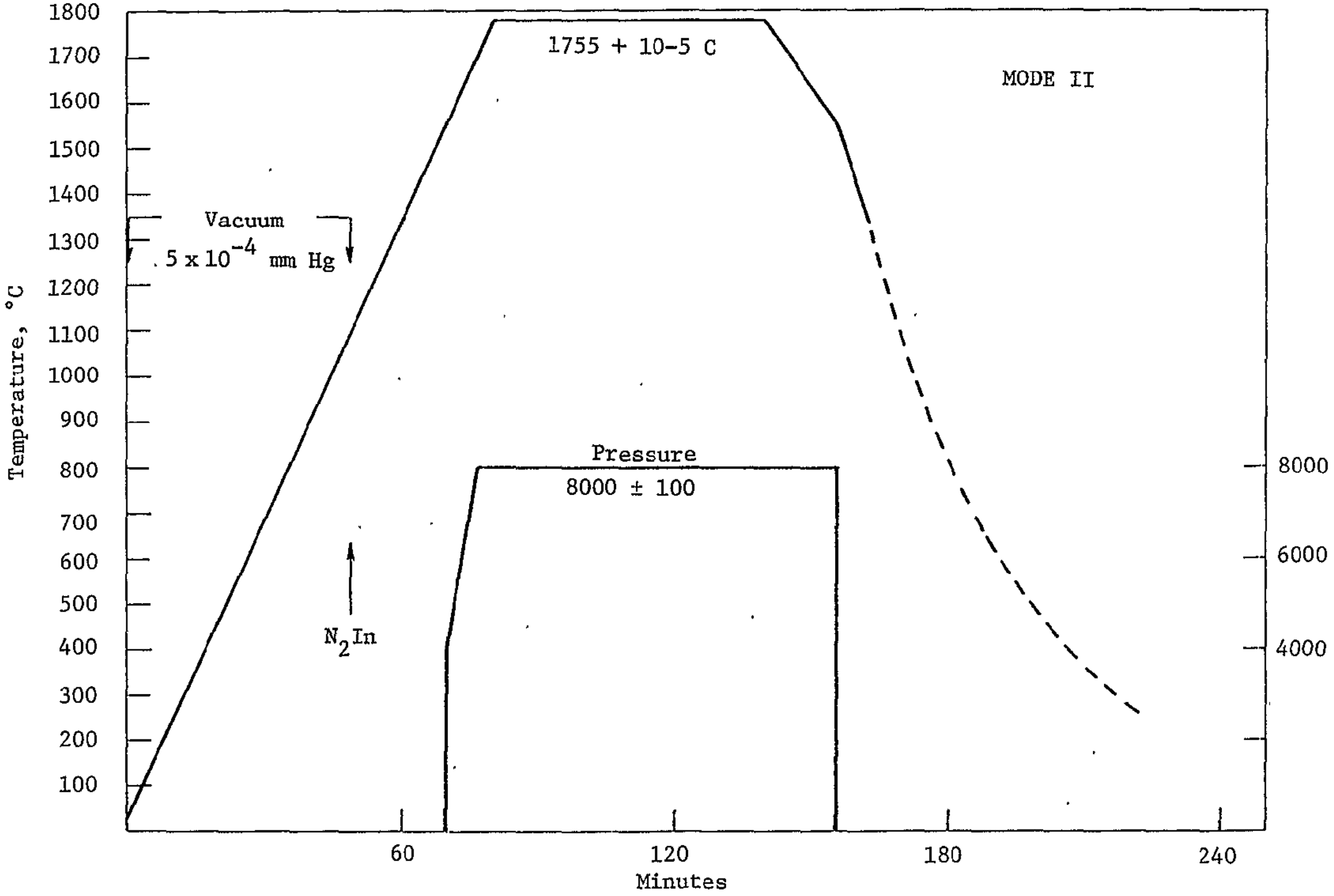

FIGURE A-2. HOT PRESSING CYCLE, SIBEON X = 0.35

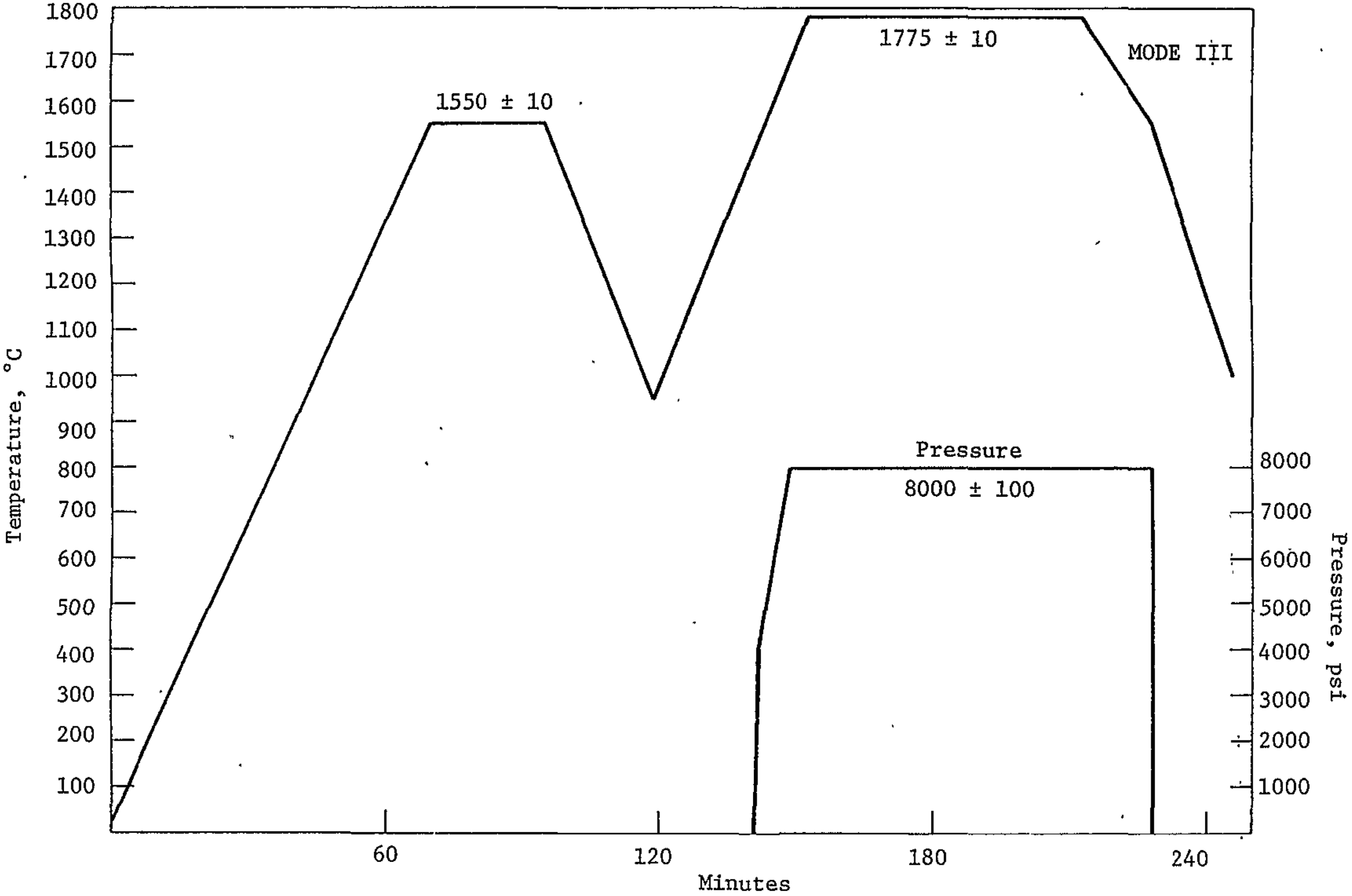

FIGURE A-3. HOT PRESSING CYCLE, SIBEON X = 0.35

Machining of Silicon Ribbon Drawing Die

The following procedure was used to diamond machine a die from a hot pressed billet. This procedure is not considered to be fully optimized.

To prevent chipping and breakage, the Sialon should be encapsulated in a machinable plastic*. Furthermore, the resin must be transparent and should be soluble in a suitable solvent (the solvent for Epon is Hisolv**).

(1) Rough cut the 2-5/8-inch diameter and approximately 0.500-inch thick hot pressed Sialon blank to 1.055 x 1.800 x 0.500 inch rectangular blank.

(2) Cast the rectangular blank into Epon resin and let it set overnight.

(3) Leaving 1/4 inch on the sides, cut the excess Epon parallel to the sides.

(4) Grind the excess Epon from one of the wide surfaces and 10-15 mils from the ceramic until white skin of the ceramic is removed. This will produce surface #1 (see Figure 14, Page 39).

(5) Grind the Epon down to a few millimeters thick from the other wide surface and make it parallel to the surface #1.

(6) Establish reference point A by marking off 0.460 inch from the top.

(7) Grind 20 mils material from surface #1 to produce surface #2.

(8) Produce surface #3 by cutting 70 degree angle on surface #1. Grind parallel to the wide edge.

(9) Encapsulate surfaces #1, 2, and 3 with Epon to half thickness without covering the other half.

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* Epon Resin 815. Supplied by Ceilcote Company, Inc., 140 Sheldon Road, Berea, Ohio 44017.

** Hisolv - Hightemp Resins, Inc., 225 Greenwich Avenue, Samford, Connecticut.

(10) Grind the Epon on surfaces #1, 2, and 3 flat and parallel to the opposite face and bring the excess Epon from the sides to the original dimensions.

(11) Grind the opposite surface to surfaces #1, 2, and 3 and bring the thickness of sample to 0.255 inch. This will produce surface #4.

(12) Repeat Steps 6, 7, and 8 to produce surfaces #5 and 6.

(13) Again cast surfaces #4, 5, and 6 into Epon to half thickness of the sample. Then grind Epon flat and parallel to the opposite surface.

(14) Adjust the width by grinding the sides to final dimensions.

(15) Grind the top surface to produce 0.029 inch surface.

(16) Cast both side surfaces into Epon to produce 1/4-inch thick excess Epon layer and 1/4-inch high.

(17) Grind the Epon on the side flat and parallel to the edges of the sample.

(18) Grind the top 4.00 inch radius surface by cylindrical grinding on an automatic milling machine.

(19) Cut the two 10-mil wide and 20-mil deep notches on the surface with 10-mil diamond wheel.

(20) Recast the top surface 1/2-inch thick Epon.

(21) Grind the excess Epon to make parallel to the original surfaces.

(22) Cut the 60-mil deep top slot. Then cut the 250 mil deep side slot using 15 mil diamond blade.

APPENDIX B

PREPARATION OF THE $Si_2N_2O-Al_2O_3$ SILICON ALUMINUM OXYNITRIDE SOLID SOLUTION

PREPARATION OF THE Si_2N_2O-Al_2O_3 SILICON ALUMINUM OXYNITRIDE SOLID SOLUTION

by

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ABSTRACT

Dense high purity Si_2N_2O-Al_2O_3 silicon aluminum oxynitride (O' Sialon) has been prepared by reactive hot pressing of a Si_3N_4-Al_2O_3-SiO_2 mixture. The formation of a single phase material was found to be critically dependent upon the Si_3N_4 powder in the Si_3N_4-Al_2O_3-SiO_2 starting mixture. It is suggested that evolution of a chlorine-nitrogen containing species may enhance the reactivity of Si_3N_4 in this reaction. Densities of O' Sialons are very similar to that of Si_2N_2O (2.82 g/cm^3), the widely quoted value in the ceramics literature of 3.1 g/cm^3 for the density of Si_2N_2O being incorrect.

PREPARATION OF THE $Si_2N_2O-Al_2O_3$ SILICON ALUMINUM OXYNITRIDE SOLID SOLUTION

by

I. Sekercioglu and R. R. Wills

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Columbus Laboratories

Silicon oxynitride, Si_2N_2O, possesses good oxidation resistance, excellent corrosion resistance to molten metals and siliceous slags, and has high electrical resistivity according to studies by Washburn.(1) Fully dense single phase Si_2N_2O, however, is difficult to fabricate because the chemical reactions occurring in the Si-N-O system are quite sluggish. The optimum properties of Si_2N_2O are consequently not realized since Si_2N_2O ceramic bodies contain either significant amounts of second phases or substantial porosity.

Si_2N_2O forms a Sialon (silicon aluminum oxynitride) solid solution with Al_2O_3, designated O' Sialon by Jack.(2) In contrast to Si_2N_2O, O' Sialon should be capable of being fabricated into a high density single phase material since liquid phase sintering is known to occur in the Si-Al-O-N system. Figure 1(3) shows the solid-liquid equilibria in this sytem.

Three possible preparation routes could be used. These are:

(1) $Si_2N_2O + Al_2O_3 \rightarrow O'$ Sialon

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

(3) β' Sialon* + $SiO_2 \rightarrow O'$ Sialon

Reaction (2) was chosen to prepare O' Sialon because the liquidus in the system $Al_2O_3 - SiO_2$ (1595 C) offers better potential for achieving densification and reactivity than those that will form during reactions (1) and (3).

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* β' Sialon is a solid solution of Al_3O_3N in $\beta-Si_3N_4$.

EXPERIMENTAL

High purity Si_3N_4*, Al_2O_3**, and SiO_2*** powders were first vacuum dried at 200 C and then stored in sealed containers under a nitrogen atmosphere. This storage procedure was adopted to ensure that the characteristics and reactivity of each powder remain unchanged throughout the study. Physical, chemical, and structural features of these powders were determined by spark source mass spectrographic analysis, oxygen analysis (for the two Si_3N_4 powders), surface area measurements, thermal gravimetric analyses (TGA), particle size distribution measurements, compaction curves, and transmission electron microscopy. The oxygen analysis data (SN402 grade Si_3N_4 2.90 weight percent; SN502 grade 1.38 weight percent) and the TGA data (see Figure 2) were used in calculating the starting compositions of mixtures needed to produce single phase O' Sialons. Allowance was thus made for weight loss according to the TGA data and also for the oxygen content of each Si_3N_4 powder. No allowance was made for the impurity content (see Table 1) of each powder.

Powders were mixed by ball milling in a high purity Al_2O_3 ball mill using high density high purity Al_2O_3 balls and "Nanograde" hexane.**** Powder batches (500 g) were milled in 1500 cm^3 hexane for 4 hours using 4000 g of Al_2O_3 balls, dried at 190 C over a 24 hour period, and stored under nitrogen in sealed jars. No significant change in the composition was found as a result of this milling operation. Powder samples (18 g) were subsequently cold pressed at 56 MN/m^2 (8000 psi) prior to being loaded into a graphite die set. A protective BN layer was used to prevent reaction with the graphite during hot pressing. Hot pressing was performed both in vacuum and under nitrogen atmosphere, the final temperature and pressure conditions being 1750 C and 70 MN/m^2 (10,000 psi for 1 hour).

Standard x-ray diffraction techniques, optical metallography, and SEM microscopy were used to characterize crystalline phases and microstructural features of the hot pressed samples.

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* SN402 and SN502 grades, GTE Sylvania, Inc.

** Grade RC-HP-DBM Reynolds Metal Company

*** -325 mesh powder, Atomergic Chemical Company.

**** American Hospital Supply Company.

RESULTS AND DISCUSSION

The O' Sialon solid solution can be represented by the formula $Si_{2-x}Al_xN_{2-x}O_{1+x}$, where x ($\leq 0.4$) represents the number of silicon atoms replaced by aluminum. The results given in this section are expressed in terms of this nomenclature.

Preliminary hot pressing trials with x = 0.1 O' Sialon in vacuum using SN402 grade Si_3N_4 powder indicated that excessive volatilization, which occurred between approximately 1470 C and 1650 C, resulted in nonuniform samples exhibiting high weight losses ($\sim$25 percent). Because of these high weight losses, all further hot pressings were performed in 0.8 atmospheres nitrogen.

The general densification behavior was similar for mixtures containing either SN402 grade Si_3N_4 or SN502 grade Si_3N_4 powder. In both cases densification was largely complete before 1750 C was reached. Considerable "fuming" was observed between 1470 C and 1650 C with samples containing the SN402 grade Si_3N_4 powder, but not from powder compacts containing SN502 grade Si_3N_4.

Figure 3 shows that O' Sialon prepared from a SN402 grade Si_3N_4-Al_2O_3-Si mixture contains excessive free silicon. The presence of substantial free silicon is due to the loss of nitrogen, but nitrogen itself would not be expected to be evolved in such a large amount at 1750 C. Loss of nitrogen is apparently associated with chlorine removal during hot pressing of Si_3N_4 since the chlorine content of the hot pressed material (see Table 2) is considerably lower than the 5000 ppm concentration present in the SN402 grade Si_3N_4 powder. In addition, samples hot pressed from mixtures containing the SN502 grade Si_3N_4 (chlorine content 500 ppm) exhibited virtually no "fuming". These samples did not contain any free silicon (see Figure 4). "Fuming" is consequently considered to be due to the evolution of a nitrogen and chlorine containing species such as NCl_3 or NOCl.

A modified processing cycle was devised which sharply reduced the free silicon content of Sialon (see Figure 5) prepared using SN402 grade Si_3N_4 powder. This consisted of first heating to 1500-1550 C under vacuum in the hot press to enable the volatile species to be removed easily. The temperature was then allowed to fall to 1000 C and nitrogen admitted to chamber before increasing the temperature and hot pressing. It is believed that nitrogen renitrides the silicon in the temperature range 1000-1300 C before hot pressing is initiated.

The replacement of SN402 grade Si_3N_4 by the SN502 grade powder markedly affected the reactivity of the Si_3N_4-Al_2O_3-SiO_2 mixtures. The results in Table 3 for x = 0.1, x = 0.2, and x = 0.35 O' Sialons indicate that high density materials were obtained but that these were not single phase materials. The second phases in Table 4 are considered to be β' Sialon rather than β-Si_3N_4 because the solution-precipitation reaction occurring in this system necessitates that Si_3N_4 dissolves in a Si-Al-O-N liquid, and consequently β' Sialon is more likely to be an intermediate compound than β Si_3N_4.

While some slight difference in the metallic impurity content of the two Si_3N_4 powders exists, this is so small that it is unlikely that it accounts for the difference in their reactivity. Both particle size and oxygen content could also be factors controlling the rate of reaction. While it is known that the sintering of β' Sialon is controlled by the SiO_2 content of the Si_3N_4 powder,(4) it is difficult to believe that this is true for O' Sialon when a considerable amount of SiO_2 forms part of the initial mixture. Although the disparity in particle sizes (average particle sizes: SN402 0.8μ, SN502 2.3 μ) may be the reason for the observed difference in reactivities, the possibility that the loss of the chlorine containing species at 1500 C "activates" the Si_3N_4 in some manner cannot be disregarded. It is difficult to even speculate about what this activation process might be without knowing the exact identity of the volatile species.

Figure 5 indicates that the density of the single phase x = 0.1 O' Sialon is close to the theoretical. Yet Washburn(1) cites Forgeng's(5) value for the density of Si_2N_2O as 3.1 g/cm^3. On this basis the x = 0.1 O' Sialon material would only be 90 percent theoretically dense. There appears to be an error by Washburn since Forgeng and Decker(5) do not calculate the density of Si_2N_2O in their paper. Using the lattice parameter data of Forgeng and Decker, and also of Brosset and Idrestedt,(6) the average value for the density of Si_2N_2O is claculated to be 2.82 g/cm^3. The densities of O' Sialons will be very close to that of Si_2N_2O since the unit cell dimensions increase only very slightly with increasing Al_2O_3 content.(3) The density of single phase hot pressed x = 0.1 O' Sialon (2.80 g/cm^3) is consequently considered to be very close to the theoretical value.

ACKNOWLEDGMENT

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TABLE 1. IMPURITY CONTENTS OF Si_3N_4, Al_2O_3, AND SiO_2 POWDERS

Element	SN402 Si_3N_4	SN502 Si_3N_4	Al_2O_3	SiO_2
Li	<0.004	0.01	<0.002	0.2
Be	<0.004	<0.003	<0.02	<0.002
B	<0.06	<0.02	0.06	2
F	0.1	<0.1	0.4	0.1
Na	10	5	40	100
Mg	<10	5	20	≤20
Al	<10	60	Major	100
Si	Major	Major	50	Major
P	1	0.2	20	3
S	<1	0.6	4	1
Cl	5000	500	100	20
K	≤0.2	0.6	0.8	20
Ca	≤6	12	6	60
Sc	0.2	0.3	<0.1	<0.1
Ti	<2	7	<0.3	20
V	<0.2	0.2	<1	0.5
Cr	2	10	2	<1
Mn	<3	0.2	0.4	<1
Fe	<1	10	50	30
Co	<0.3	0.4	0.01	<1
Ni	<1	0.2	1	<2
Cu	<4	0.7	0.2	≤2
Zn	<2	0.5	2	<2
Ga	<2	0.4	100	1
Ge	<1	<0.1	<0.7	<0.03
As	<0.2	0.2	≤0.04	≤0.3
Se	<3	<2	<0.2	<0.05
Br	4	0.2	0.1	0.1
Rb	<0.2	0.2	<0.1	<0.4
Sr	<1	0.3	<0.2	5
Y	<0.1	3	<0.04	2
Zr	<0.04	60	<0.2	3
Nb	<0.1	<0.2	<0.02	<0.2
Mo	12	400	≤0.2	2
Ru	<0.2	<0.1	<0.1	<0.1
Rh	<0.02	<0.7	<0.03	<0.06
Pd	<0.7	<0.4	<0.2	<3
Ag	<0.2	<0.03	<0.1	<0.2
Cd	<0.2	<0.06	<0.3	<0.2
In	<0.06	<0.04	<0.04	<0.4

TABLE 1. (Continued)

Element	SN402 Si_3N_4	SN502 Si_3N_4	Al_2O_3	SiO_2
Sn	<0.4	<0.2	≤0.2	0.2
Sb	<0.1	<0.05	<0.07	<0.1
Te	<0.2	<0.2	<0.06	<0.3
I	<0.06	<0.1	<0.1	<0.2
Cs	<0.2	<0.2	<0.2	<0.1
Ba	<0.1	<0.03	<0.1	4
Ce	<0.1	<0.2	<0.04	<1
Pr	<0.1	<0.03	<0.02	<0.2
Nd	<0.2	<0.1	<0.2	<0.4
Sn	<0.2	<0.1	<0.2	<0.2
Eu	<0.1	<0.1	<0.1	<0.1
Gd	<0.1	<0.1	<0.1	<0.3
Tb	<0.02	<0.01	<0.03	<0.06
Dy	<0.2	<0.05	<0.1	<0.6
Ho	<0.04	<0.02	<0.03	<0.2
Er	<0.1	<0.04	<0.1	<0.4
Tn	<0.2	<0.1	<0.3	<0.06
Yb	<0.2	<0.1	<0.1	<0.1
Ta	<0.07	<0.1	<2	<3
W	<0.1	<0.1	<0.1	<0.1
Re	<1	<0.03	<0.06	<0.06
Os	<0.1	<0.05	<0.1	<0.07
Ir	<0.4	<0.1	<0.2	<0.1
Pt	<0.2	<0.04	<0.1	<0.1
Au	<0.06	<0.01	<0.03	<0.03
Hg	<0.1	<0.05	<0.1	<0.1
Tl	<0.2	<0.04	<0.1	<0.04
Pb	0.2	<0.06	0.2	2
Bi	<0.06	<0.03	<0.03	<0.04
Th	<0.04	<0.03	<0.03	<0.1
U	<0.1	<0.03	<0.2	<0.1

TABLE 2. 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 3. DENSITIES AND PHASE COMPOSITIONS OF HOT PRESSED O' SIALON MATERIALS

Processing Conditions	Density (g/cm^3)	O' Sialon Composition	Phase Analysis
(1) SN402 Si_3N_4 Powder + Al_2O_3 + SiO_2	2.79	x = 0.1	O' Sialon + excessive silicon
Simple Hot Pressing Cycle	2.81	x = 0.2	
(2) SN402 Si_3N_4 Powder + Al_2O_3 + SiO_2 Modified Hot Pressing Cycle	2.80	x = 0.1	O' Sialon only
(3) SN502 Si_3N_4 Powder + Al_2O_3 + SiO_2	2.82	x = 0.1	O' + αSi_3N_4
Simple Hot Pressing Cycle	2.84	x = 0.2	O' + β' Sialon
	2.88	x = 0.35	O' + β' Sialon

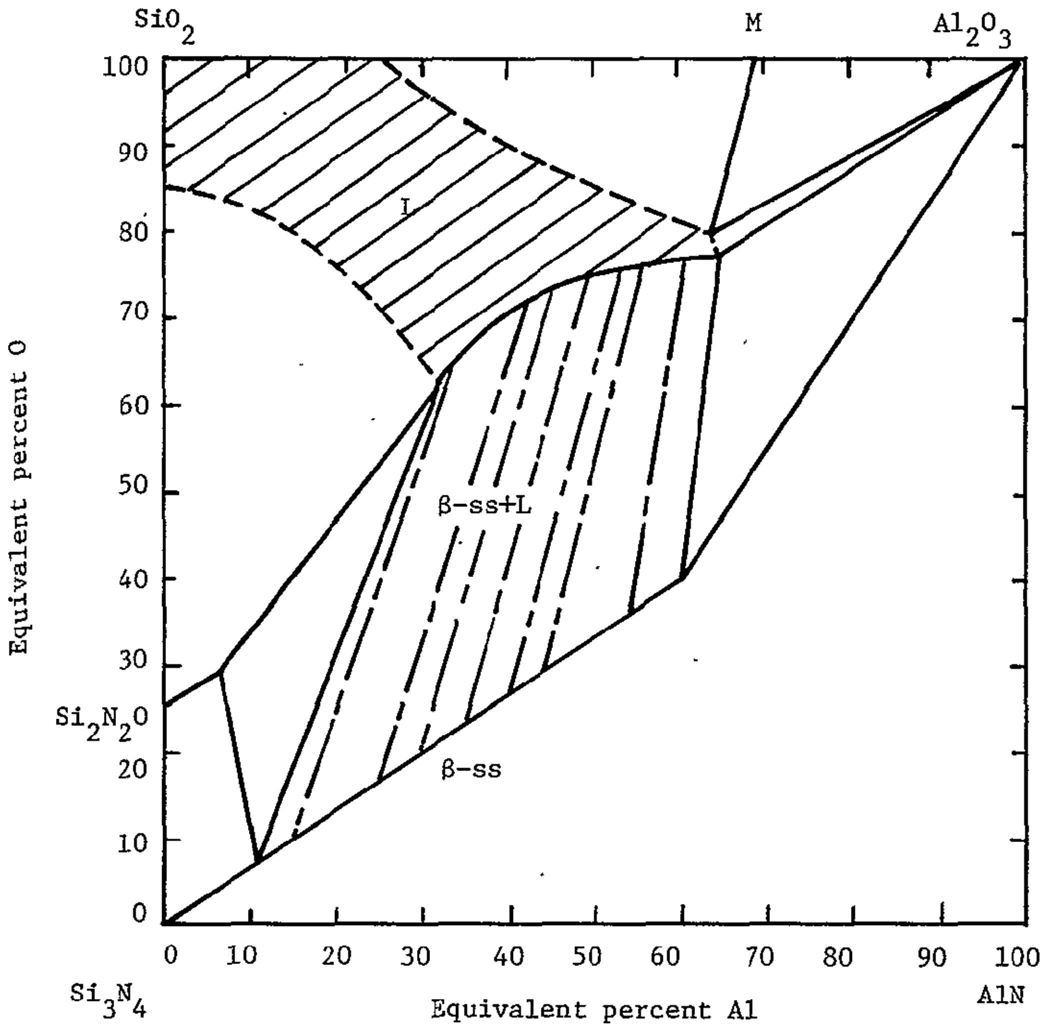

FIGURE B-1. PART OF ISOTHERMAL SECTION OF THE SYSTEM Si_3N_4-AlN-SiO_2-Al_2O_3 AT 1750 C SHOWING SOLID-LIQUID EQUILIBRIA; β-ss=β-Si_3N_4-BASED SOLID SOLUTION, M = MULLITE ($3Al_2O_3 \cdot 2SiO_2$), L = LIQUID. DIAGRAM FROM NACK, ET AL(3)

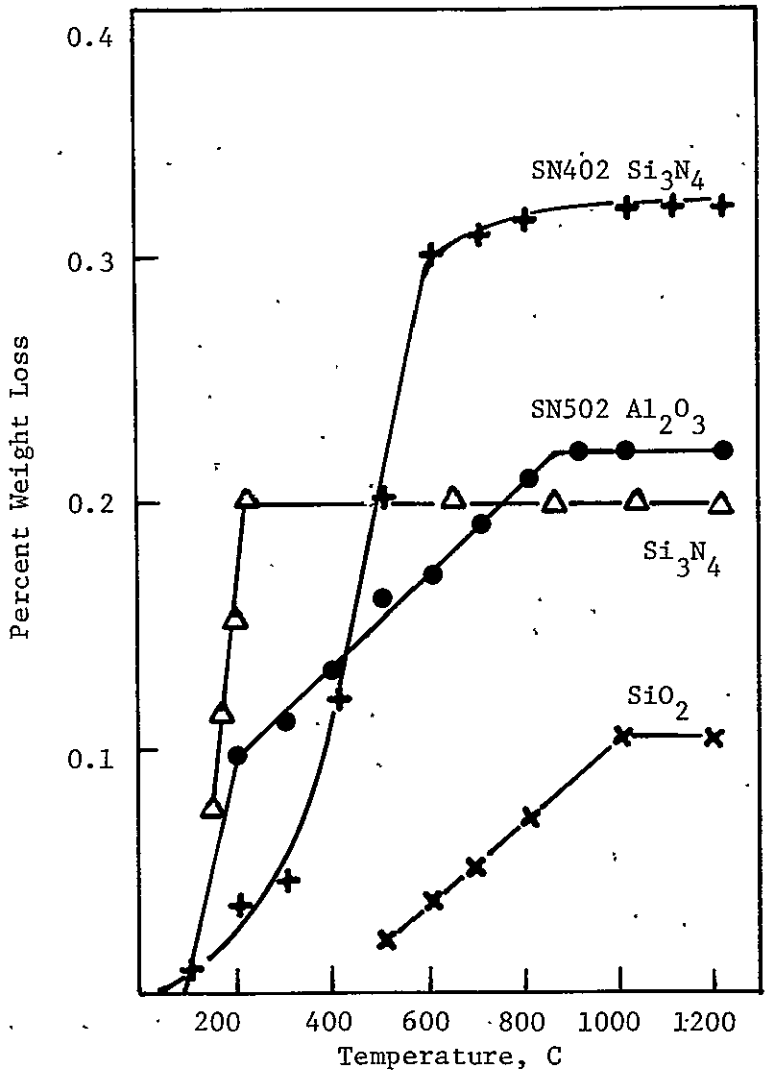

FIGURE B-2. THERMOGRAVIMETRIC ANALYSIS OF VACUUM DRIED Si_3N_4, Al_2O_3 AND SiO_2 POWDERS

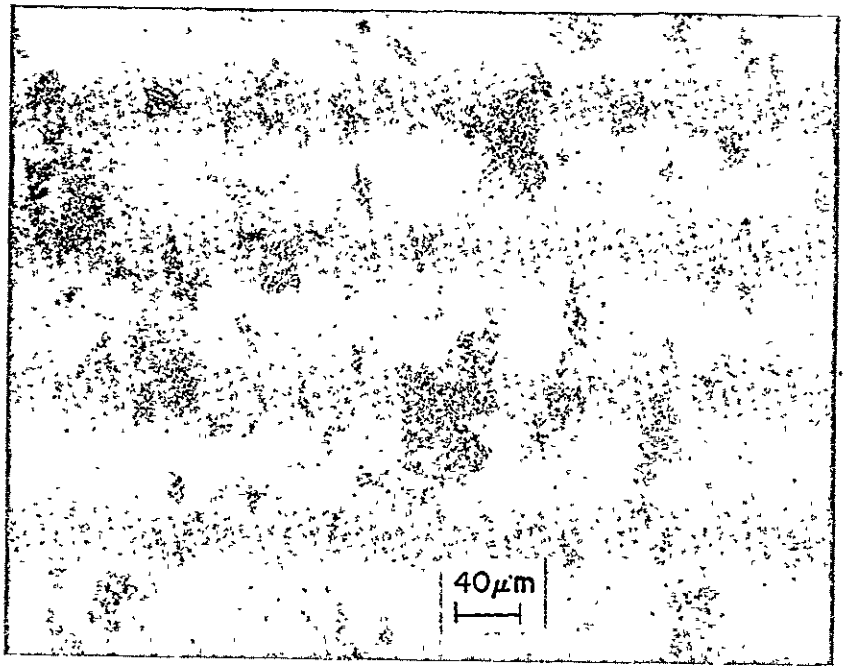

FIGURE B-3. O' SIALON SAMPLE CONTAINING EXCESSIVE SILICON. SAMPLE PREPARED FROM SN402 GRADE Si_3N_4-Al_2O_3-SiO_2 MIXTURE BY SIMPLE HOT PRESSING CYCLE.

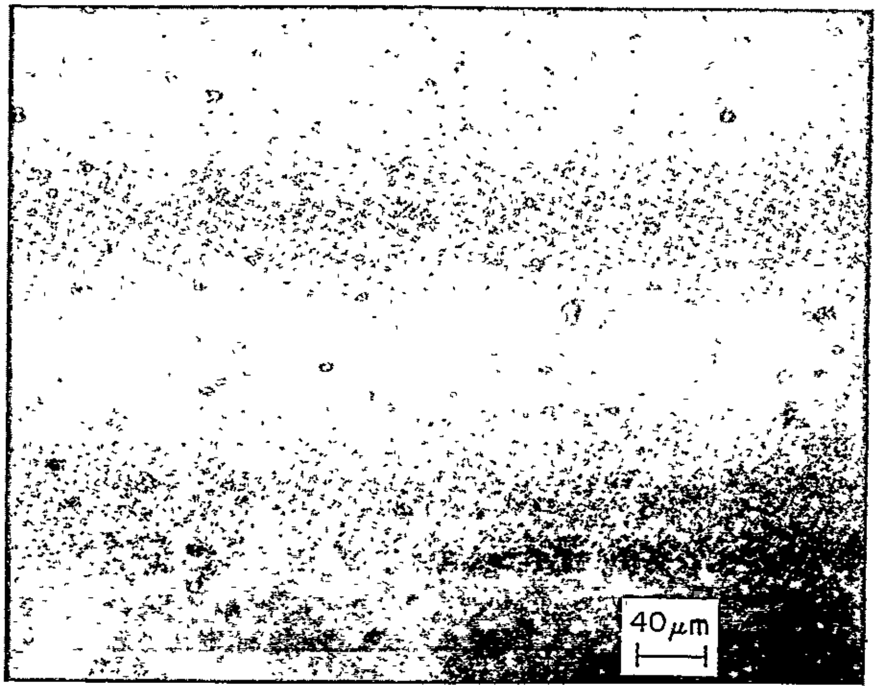

FIGURE B-4. O' SIALON SAMPLE CONTAINING β' SIALON. FABRICATED USING SN502 GRADE Si_3N_4-Al_2O_3-SiO_2 MIXTURE BY SIMPLE HOT PRESSING CYCLE.

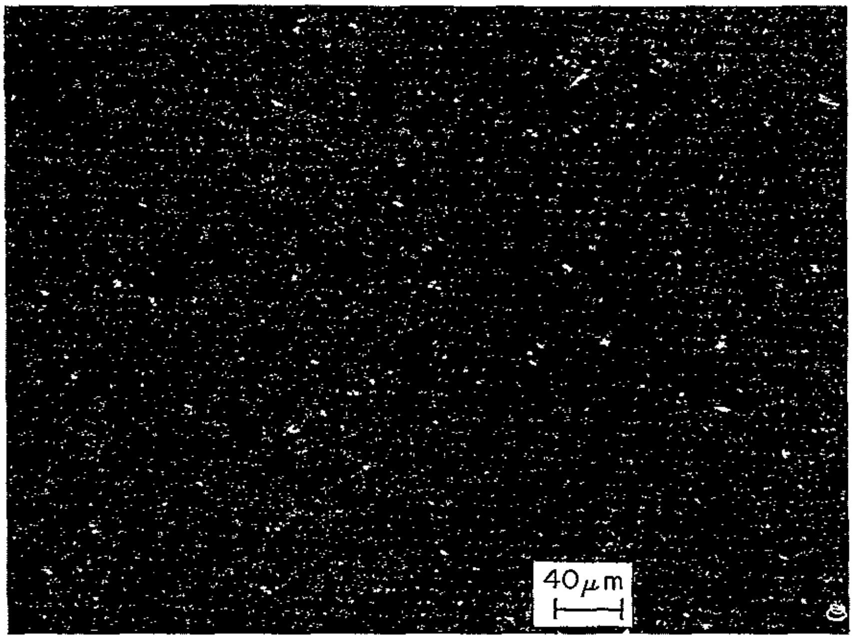

FIGURE B-5. REDUCED SILICON CONTENT OF O' SIALON FABRICATED BY MODIFIED HOT PRESSING CYCLE.