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DEVELOPMENT AND EVALUATION OF DIE AND CONTAINER MATERIALS

Fifth Quarterly Progress Report for October 1—December 31, 1978

By
R. R. Willis
D. E. Niesz

January 15, 1979

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

Battelle Columbus Laboratories
Columbus, Ohio

U.S. Department of Energy

Solar Energy

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FIFTH QUARTERLY PROGRESS REPORT

(Covering the Period October 1, 1978, to December 31, 1978)

on

DEVELOPMENT AND EVALUATION OF DIE AND CONTAINER MATERIALS

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

to

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

January 15, 1979

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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

$X = 0.75$ β' Sialon (a silicon aluminum oxynitride) and Sibeon (silicon beryllium oxynitride) are promising die materials. In sessile drop tests in contact with molten silicon, beryllium contamination was <10 ppm and aluminum contamination 50 ppm.

A shaping die of the Sialon material has been successfully fabricated and delivered to JPL. This $X = 0.75$ β' Sialon exhibits an almost constant wetting angle of 37 degrees. The dissolution of aluminum in molten silicon is influenced by the oxygen content of the molten silicon and the material should be used under inert atmosphere conditions with a suitable crucible material that does not affect the Sialon-silicon equilibrium.

Dry milling studies for the preparation of Si_3N_4-Al_2O_3-AlN mixtures have been performed with butanol, acetic anhydride, oleic acid, and triethanolamine milling aids. Optimum mixing was achieved with 0.15 percent triethanolamine using a milling time of 8 hours.

Preliminary evaluation of Sibeon materials indicates that they are more resistent to molten silicon attack than $X = 0.75$ β Sialon. Silicon contamination from the beryllium was less than aluminum contamination even though the aluminum impurity level in the Sibeon was only 450 to 1300 ppm. Work designed to produce an aluminum-free Sibeon is described.

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

(a) The material must be mechanically stable to 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.

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

These silicon metal oxynitride ceramics are two silicon aluminum oxynitrides (Sialons) and one silicon beryllium oxynitride (Sibeon). Each material is a solid solution, not a discrete compound. The compositions of these silicon metal oxynitride solid solutions are represented by the following formulae:

$Si_{6-x}Al_xN_{8-x}$ 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, frequently called β' Sialon, is a solid solution between β Si_3N_4 and $Al_2O_3 \cdot AlN$. The second material referred to as O' Sialon is a solid solution between Si_2N_2O and Al_2O_3. The third material is a solid solution between β-Si_3N_4 and Be_2SiO_4. This solid solution has been designated β' Sibeon by the authors.

These materials will be prepared by the following reactions:

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

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

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

Summary of Past Work

In the initial phase of the program commercial high purity Si_3N_4, Al_2O_3, and SiO_2 powders were obtained and analyzed, and the preparation of AlN powder by a gas phase nucleation process was investigated. This process gave low yields of AlN powder and consequently commercial AlN powder was used in the preparation of β' Sialons.

Well controlled processing schedules were developed for the preparation of single phase β' and O' Sialons. These procedures were adopted after the importance of the nature of Si_3N_4 powder was discovered. The oxygen content, chlorine content, and particle size of the Si_3N_4 powder in each mixture were found to strongly affect reactivity and densification during hot pressing.

In contact with molten silicon O' Sialons formed an interface zone consisting of a Si_3N_4 layer and an amorphous layer of composition 90.7 percent silicon, 0.16 percent aluminum, and 9.14 percent oxygen and nitrogen. Thin aluminum precipitates also form in the silicon. The stability of β' Sialons in contact with molten silicon is dependent upon their aluminum content, a low aluminum content being desirable. X = 0.75 β' Sialon was selected as the optimum Sialon composition as it represented the lower limit of fabricability of a dense single phase material with a minimum of aluminum (5.35 atomic percent) in the Sialon solid solution. Preliminary evaluation of this Sialon suggested that the atmospheric conditions (argon or vacuum) affected its resistance to molten silicon attack.

Silicon beryllium oxynitrides were fabricated by hot pressing Si_3N_4-BeO-SiO_2 mixtures using three Si_3N_4 powders. Single phase materials were obtained with KBI, Inc., and Sylvania SN502 grade powders, but not with Sylvania SN402 grade powder. Preliminary evaluation of these silicon beryllium oxynitride materials after contact with molten silicon did not reveal any obvious attack.

Mass spectrometric studies of molten silicon in contact with SiO_2, BeO, Al_2O_3, Si_3N_4, mullite, x = 0.75 β' Sialon, and SiC were completed. Henry's Law constants for oxygen, beryllium, aluminum, and nitrogen at concentrations $\leq$5000 ppm were determined and the solubilities of oxygen, carbon, and nitrogen in molten silicon were found to be in good agreement with values given in the literature.

TECHNICAL DISCUSSION OF RESULTS THIS QUARTER

Studies of X = 0.75 β' Sialon

X = 0.75 β' Sialon (37.5 atom percent silicon, 5.35 percent aluminum, 5.35 percent oxygen, and 51.8 percent nitrogen) was previously chosen as the optimum composition along the Sialon solid solution between β Si_3N_4 and Al_3O_3N for two reasons. First, the aluminum content of the Sialon solid solution should be as low as possible in order to minimize molten silicon attack, and second, a dense material is required to reduce the surface area available to molten silicon attack. Other aluminum-containing phases in the Si-Al-O-N system such as O' Sialon and X phase(1)*

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* References are located on Page 24.

are less resistant to molten silicon attack than β' Sialon; consequently, it is imperative that the hot pressed β' Sialon material contain no other phases. X = 0.75 is considered to be the lower composition limit for practical fabrication purposes due to difficulties in obtaining high-density single phase materials with increasing Al_2O_3 content, and allowing for the SiO_2 content of the Si_3N_4 powder in the Si_3N_4-Al_2O_3 powder mixture. The process developed for fabricating single phase β Sialons has been described previously.(1)

(1) Wetting of X = 0.75 β' Sialon

The wetting (see Figure 1) of molten silicon on a polished surface (1 μm) of X = 0.75 β' Sialon in 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 1 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.

TABLE 1. WETTING ANGLE FOR MOLTEN SILICON
IN CONTACT WITH X = 0.75 β' SIALON
AT 1450 C IN 0.83 ATMOSPHERE 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

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:

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

$\delta = 702$ 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.$^{(2)}$ JPL prepared materials initially exhibited high wetting angles (80 to 110), but after 15 to 30 minutes, the wetting angle decreased to 45 to 55 degrees. The exact reason for the difference in behavior of the Battelle prepared 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.

(2) Capillary Rise Tests

From a hot pressed X = 0.75 β'-Sialon billet a 2.764 x 1.199 x 0.240 cm sample was cut. Two longitudinal slots with average widths of 0.1161 cm and 0.041 cm were cut along the length of the sample. The capillary rise test was made for one hour at 1445 C in 0.83 atmosphere pressure of argon, using a fused silica crucible to hold the molten silicon. After cooling, it was observed that the silicon had failed to rise in either capillary.

To observe exactly what happens when the silicon melts, a second experiment was made in a horizontal tube furnace used for sessile drop measurements, using a sample with dimensions 1.44 x 1.18 x 0.03 cm. The sample had a 0.0432-cm wide capillary slot with an effective height of 1.14 cm. The experiment was repeated in the same manner as the first test. After holding the temperature at 1440 C for 50 minutes, no rise occurred although the silicon was observed to be liquid. The argon was then pumped out of the chamber and as the vacuum approached about 100 microns pressure, bubbles were observed to burst out of the molten silicon. At about 2 to 3 μ the bubbling stopped, and the silicon began to rise in the capillary (see Figure 2). 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 oxygen from the silica crucible dissolved in the molten silicon and affected its surface tension at the silicon-Sialon interface. Assuming the oxygen concentration of the melt is 200 ppm(3) the partial pressure of SiO would be 2×10^{-5} atm (1.52×10^{-2} torr). At a vacuum level of 1 micron (1×10^{-3} torr) SiO would have been completely removed and the molten silicon consequently able to rise up the capillary slot.

(3) Relative Stabilities of X = 0.75 β' Sialon in Argon and Under Vacuum

Previous experiments in the Knudsen cell(4) suggest that loss of SiO vapor from the molten silicon allows the reactions 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 2 confirm these ideas, 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 2. 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

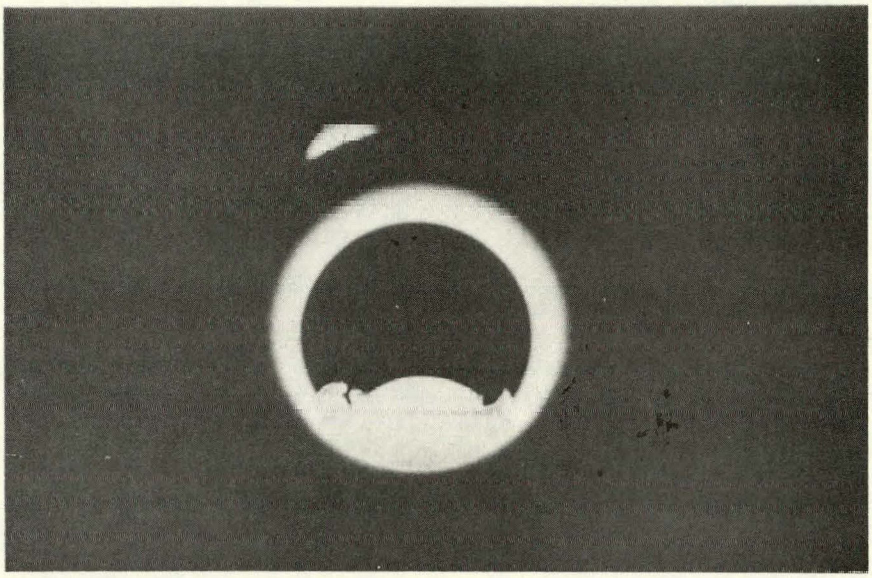


FIGURE 1. WETTING OF MOLTEN SILICON ON X = 0.75 β' SIALON IN 0.85 atm ARGON

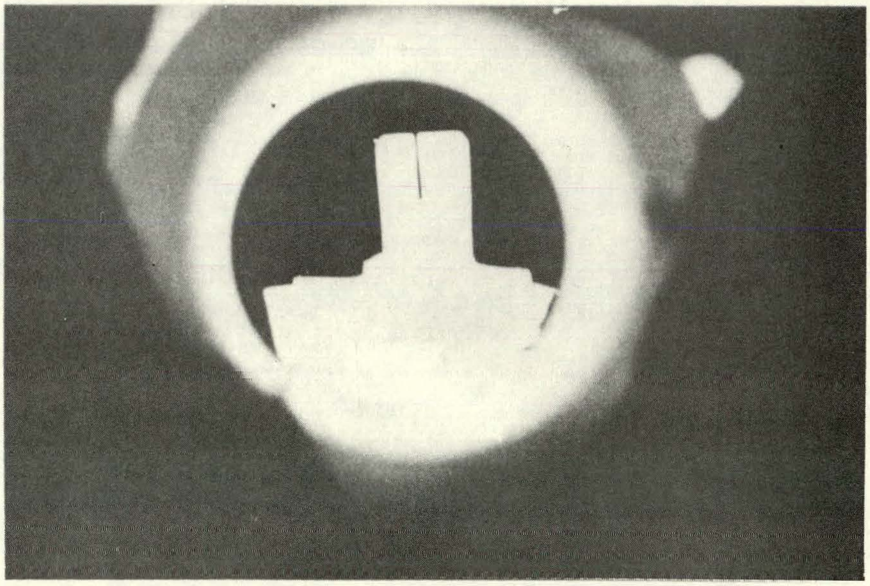


FIGURE 2. INITIAL CAPILLARY RISE IN 0.43 cm SLOT IN X = 0.75 β' SIALON

The data in Table 2 imply that aluminum is homogeneously distributed throughout the silicon, but this is not the case. Figure 3 shows the X-ray image of aluminum in silicon after it had been in contact with X = 0.75 β' Sialon in the Knudsen cell. Four particles or clusters of precipitates are evident, the remainder of the light dots being due to background.

(4) Machining of X = 0.75 β' Sialon Die

Several billets of X = 0.75 β' Sialon of dimenions 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 4 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. Therefore, the Sialon was cast in Epon resin so that it could be clamped better during machining. The first die has been machined and delivered to JPL (see Figure 5). In this die the dimensions of the one-piece die design (see Figure 4) 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 6).

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 Appendix. The fabrication of additional dies for delivery to JPL will be used to optimize this machining sequence and to minimize the overall number of steps.

(5) Dry Milling of 0.75 β' Sialon

Powder mixing has so far been carried out using n-hexane medium, primarily from the standpoint of convenience in laboratory-scale iteration

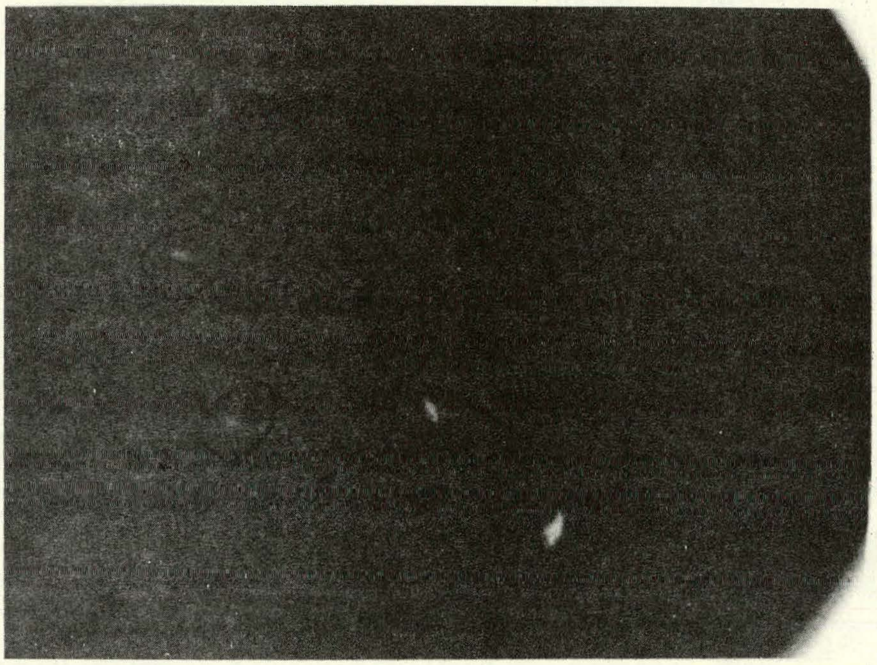


FIGURE 3. X-RAY IMAGE OF ALUMINUM IN SILICON. SILICON HELD IN CONTACT WITH X = 0.75 β' SIALON IN KNUDSEN CELL. LIGHT SPECKLES DUE TO BACKGROUND.

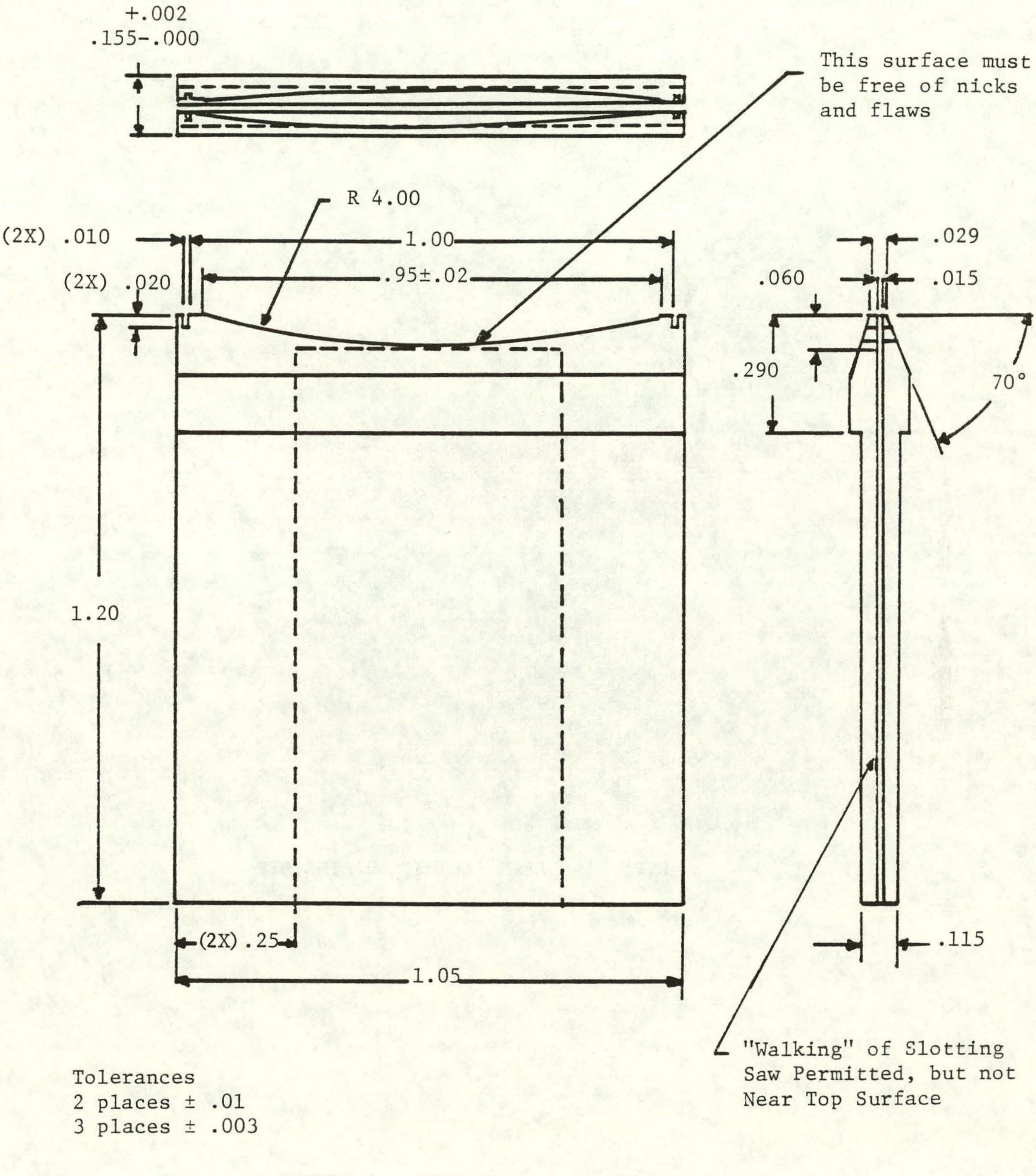


FIGURE 4. ORIGINAL ONE-PIECE DIE DESIGN

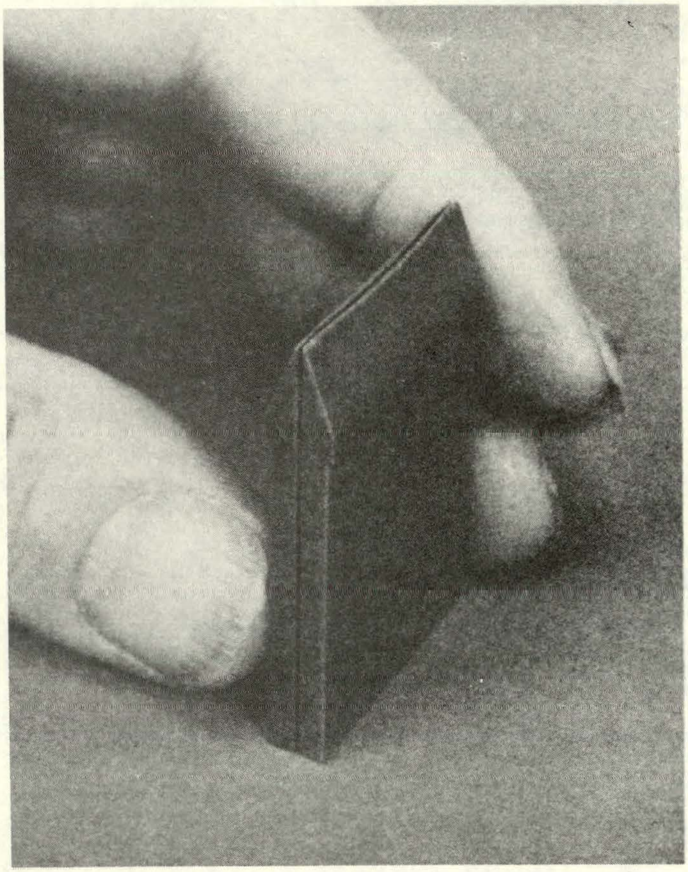
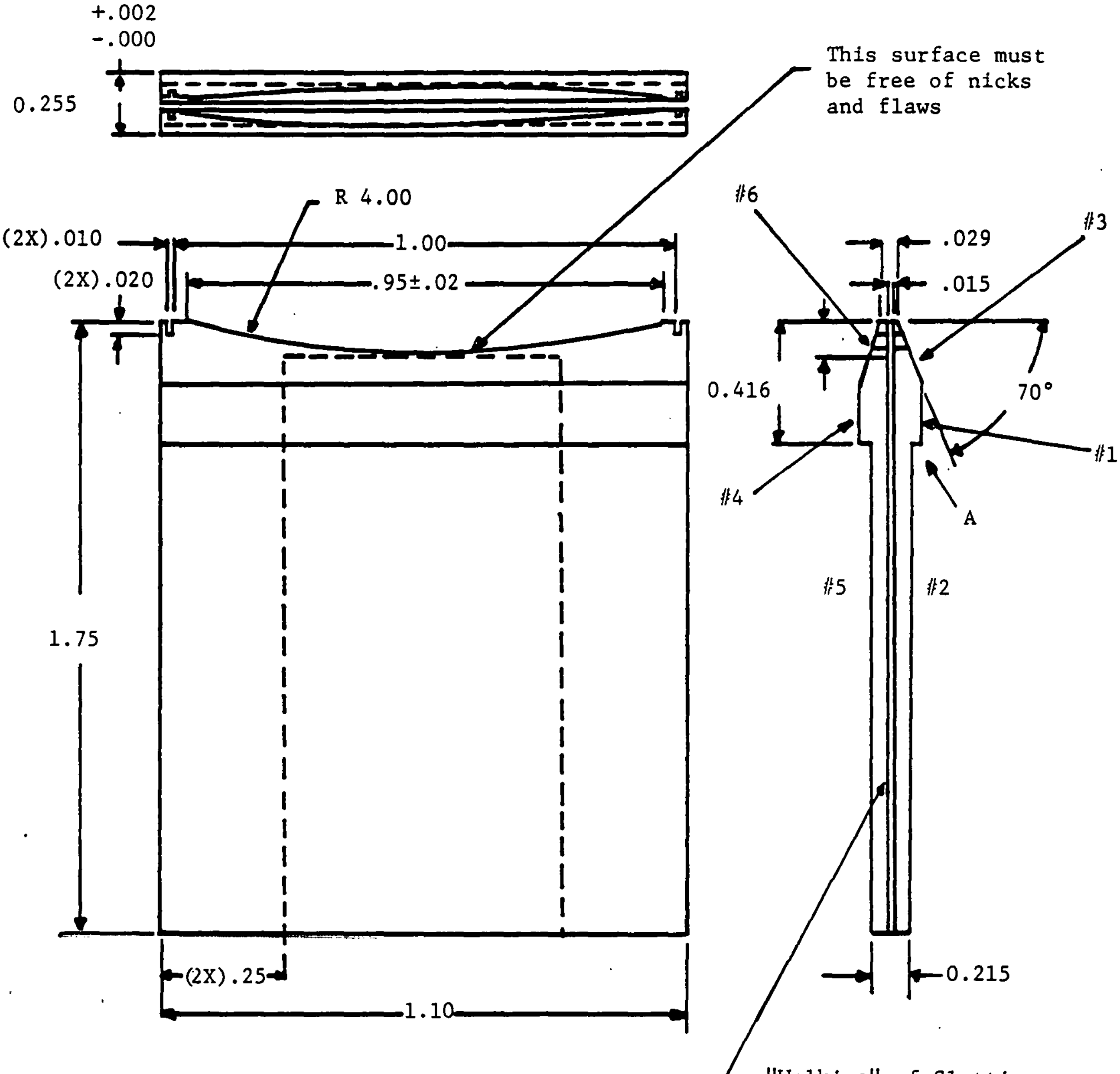


FIGURE 5. X = 0.75 β' SIALON CERAMIC SHAPING DIE



Tolerances
2 places ± .01
3 places ± .003

FIGURE 6. MODIFIED ONE-PIECE DIE DESIGN
SURFACE NUMBERS ARE REFERRED TO IN THE APPENDIX

studies. However, in developing a specified manufacturing process, the preferred commercial practice for advanced ceramics is dry milling.

Dry milling studies have been performed with butanol, acetic anhydride, oleic acid, and triethanolamine milling aids. Optimum mixing in alumina mills was achieved with 0.16 weight percent triethanolamine using a milling time of 8 hours. After removal of triethanolamine at 100 C in vacuum, a powder sample was hot pressed to 99 percent theoretical density. X-ray diffraction analysis confirmed that the material was single phase β' Sialon. After 1 hour's contact with molten silicon in an argon atmosphere, the silicon-Sialon interface was examined by optical microscopy. No reaction was observed.

This dry milling process will be used to prepare a large batch of powder for subsequent hot pressing to form X = 0.75 β Sialon. A die will then be machined from the hot pressed billet, and delivered to JPL.

Studies of Silicon Beryllium Oxynitride (Sibeon)

In the last quarterly report, initial studies of the fabrication of Sibeon materials were described together with their compatibility with molten silicon.

(1) Spark Source Analyses of Sibeon Materials

Mixing of Si_3N_4, BeO, and SiO_2 powders was carried out in polyethylene jars with alumina balls in n-hexane. Although mixing was performed only for 4 hours, aluminum was picked up during this process (see Table 3). Batch number HP50 used KBI, Inc. High Purity Grade Si_3N_4 powder that contains 200 ppm aluminum, and consequently, aluminum contamination during milling amounted to 250 ppm. Batch number HP49 consisted of GTE Sylvania, Inc. SN502 grade Si_3N_4, BeO, and SiO_2. The higher aluminum contamination (1300 ppm) of this powder mixture is due to a larger charge of alumina balls in the mill (HP49 was milled with 300 g Al_2O_3; HP50 with 100 g Al_2O_3). As discussed in the following sections, aluminum contamination of these Sibeon materials is undesirable,

TABLE 3. MASS SPECTROGRAPHIC ANALYSES OF SIBEONS

	Sample Designation(a)	
Element	HP49 Sibeon 7.52m percent Be_2SiO_4	HP50 Sibeon 3.44m percent Be_2SiO_4
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 3. (Continued)

Element	Sample Designation[(a)] HP49 Sibeon 7.52m percent Be_2SiO_4	HP50 Sibeon 3.44m percent Be_2SiO_4
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.

and work is under way to produce a dense single-phase aluminum-free Sibeon material.

(2) Compatibility with Molten Silicon

Sibeon materials were exposed to molten silicon at 1450 C for 1 hour under an argon atmosphere. Preliminary analysis by optical metallography at low magnification did not show any attack of the ceramic.(4) Prior to mass spectrographic analysis (see Table 4), the silicon samples were cleaned in acetone, hydrofluoric acid, hydrochloric acid, and absolute alcohol.

The most significant impurity shown in Table 4 is chlorine, which probably originated from the hydrochloric acid wash. Aluminum, picked up from the ball milling of the Sibeon mixtures, is the other major impurity. It is particularly interesting to note that, although the Sibeon samples contain substantially more beryllium than aluminum impurity, higher aluminum concentrations were detected in the silicon. For example, in the silicon sample held in contact with Sibeon sample HP49 (see Table 4), beryllium was not detected (<0.01 ppm), whereas 100 ppm aluminum was found. These data indicate that, in contact with molten silicon, the Sibeon solid solution is much more stable than the Sialon solid solution. Data obtained by Palm and Greskovich(5) on the oxidation and creep of Sibeon also suggest that the Sibeon solid solution is more stable than the Sialon solid solution. From oxidation and creep experiments they concluded that diffusion coefficients for beryllium and oxygen were lower than for any other element found in hot-pressed silicon-nitride based materials. This greater stability of the Sibeon solid solution is probably related to the stronger chemical bonding in BeO than in Al_2O_3.

The above data clearly demonstrate that Sibeon is an extremely promising die material. However, a high-purity aluminum-free material is needed before a meaningful evaluation can be conducted.

TABLE 4. MASS SPECTROGRAPHIC ANALYSES OF SILICON FROM COMPATIBILITY TESTS (parts per million weight)

	Sample Designation	
Element	HP49 Sibeon 7.52m percent Be_2SiO_4	HP50 Sibeon 3.44m percent Be_2SiO_4
Li(a)	-	0.1
Be	<0.01	10
B(b)	<4	<8
F	<4	<10
Na	8	16
Mg	≤5	≤20
Al	100	50
Si	Major	Major
P(c)	≤20	≤10
S	2	6
Cl	160	160
K	0.4	0.4
Ca	≤10	≤10
Sc	≤2	≤2
Ti	2	0.1
V	<0.05	<0.05
Cr	<1	<0.6
Mn	30	10
Fe	20	3
Co	<0.2	<0.06
Ni	<0.2	<0.2
Cu	35	<0.2
Zn	<0.2	<0.2
Ga	<0.5	<0.3
Ge	<1	<0.4
As	<0.2	<0.1
Se	<2	<0.5
Br	<0.3	<0.3
Rb	<0.4	<0.2
Sr	<0.1	<0.1
Y	<0.3	<0.2
Zr	<0.3	<0.3
Nb	<0.3	<0.2
Mo	<2	<0.7
Ru	<0.3	<0.3
Rh	<0.2	<0.2
Pd	<2	<0.4

(a) Photoplate slipped. Unable to obtain masses 6 and 7 on sample HP49.

(b) Samples pulverized in Boron/Carbide Mortar.

(c) Memory from previous sample.

TABLE 4. (Continued)

	Sample Designation	
Element	HP49 Sibeon 7.52m percent Be_2SiO_4	HP50 Sibeon 3.44m percent Be_2SiO_4
Ag	<0.4	<0.2
Cd	<1	<0.4
In	<0.4	<0.1
Sn	<1	<0.4
Sb	<0.3	<0.3
Te	<0.4	<0.4
I	<0.1	<0.1
Cs	<0.5	<0.5
Ba	<0.3	<0.7
L	<0.1	<0.2
Ce	0.5	<0.5
Pr	<0.2	<0.3
Nd	<1	<1
Sm	<0.5	<0.5
Eu	<0.3	<0.3
Gd	<0.6	<0.6
Tb	<0.2	<0.2
Dy	<0.6	<0.6
Ho	<0.2	<0.2
Er	<0.5	<0.5
Tm	<0.3	<0.3
Yb	<0.6	<0.6
Lu	<0.2	<0.2
Hf	<0.6	<0.6
Ta	<0.5	<0.3
W	<1	<0.6
Re	<0.3	<0.3
Os	<0.7	<0.5
Ir	<0.5	<0.3
Pt	<0.6	<0.6
Au	<0.2	<0.2
Hg	<0.6	<0.6
Tl	<0.4	<0.3
Pb	0.4	<0.4
Bi	<0.2	<0.2
Th	<0.2	<0.2
U	<0.3	<0.3

(3) Processing of High Purity Sibeon

Removal of the aluminum contamination problem referred to in the previous section was initially tackled by ball milling using Teflon® cylinders instead of alumina balls. However, we have noticed a small percentage of inclusions and strong agglomerates in the SN502 grade Si_3N_4 powder that are not broken down using these light-weight Teflon® cylinders. During hot pressing, these agglomerates do not react (see Figure 7) and unreacted αSi_3N_4 is detected in the X-ray diffraction spectra of the Sibeon materials.

The data in Table 5 show the sieve analysis of SN502 grade Si_3N_4 powder. Although the powder is nominally a submicron powder, 3-1/2 percent would not pass through a -325 mesh sieve. Large agglomerates and inclusions are evident in the two coarser fractions (see Figures 8 and 9).

TABLE 5. SIEVE ANALYSIS OF SN502 GRADE Si_3N_4 POWDER

Mesh Size	Percent by Weight
+60	0.4
+100	0.3
+200	0.1
+325	2.7
-325	96.5

Current efforts to fabricate a high-purity Sibeon material are directed toward milling -400 mesh screened SN502 grade Si_3N_4 and KBI, Inc. High Purity Grade Si_3N_4 powder with appropriate amounts of BeO and SiO_2 using Teflon® cylinders and sintered Si_3N_4* balls. All powder batches will be hot pressed and the best fabrication route chosen for producing high-purity single-phase dense Sibeon material.

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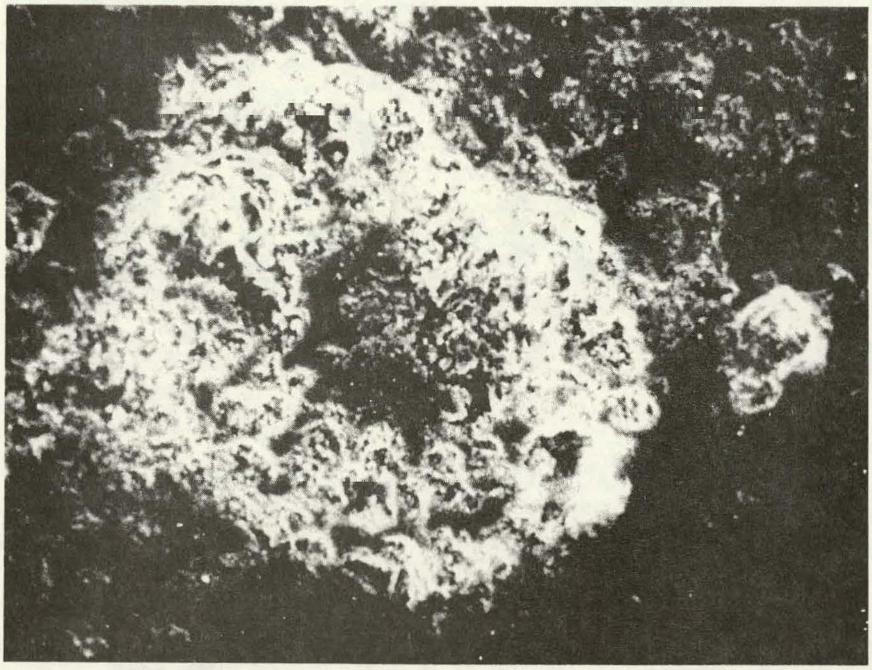
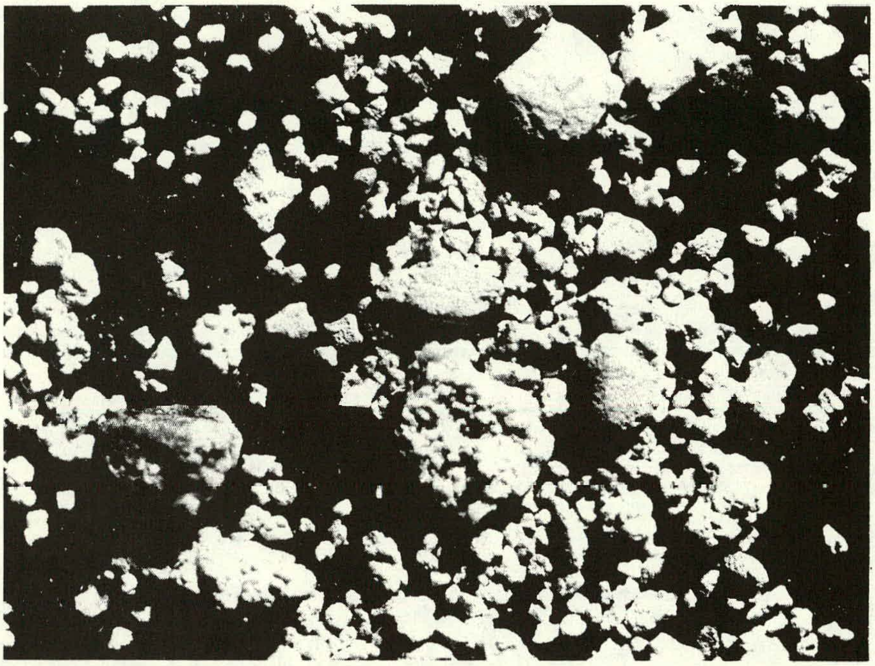
* GTE Sylvania, Inc.



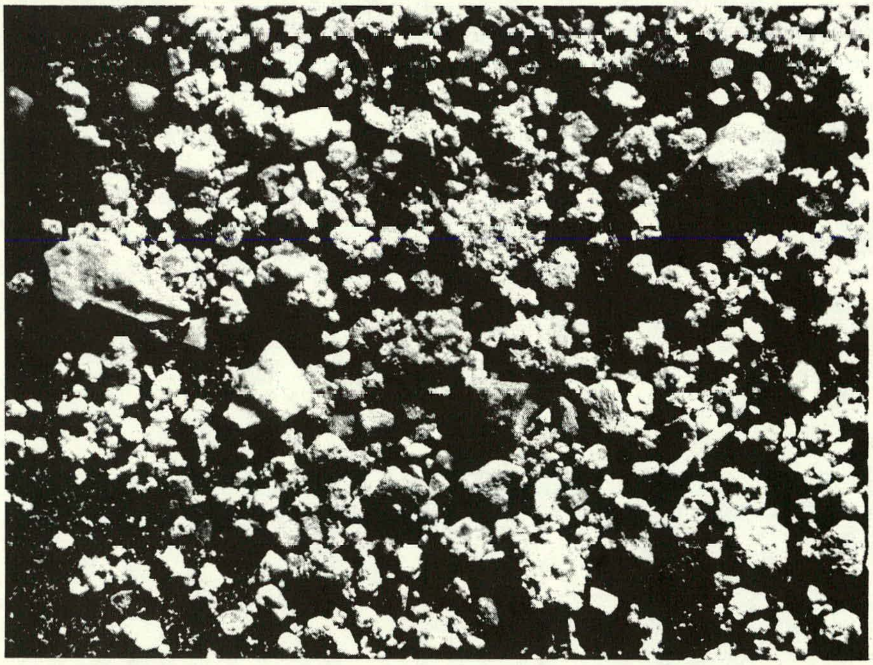
350X 21306

FIGURE 7. LARGE UNREACTED ALPHA SILICON NITRIDE PARTICLE IN HOT PRESSED SIBEON PROCESSED USING TEFLON® CYLINDERS



X7 7J324

FIGURE 8. +60 MESH FRACTION OF SN502 Si_3N_4 POWDER CONTAINING LARGE AGGLOMERATES AND INCLUSIONS



X7 7J325

FIGURE 9. +100 MESH FRACTION OF SN502 Si_3N_4 POWDER CONTAINING LARGE AGGLOMERATES AND INCLUSIONS

MANUFACTURING COST ESTIMATE

The main steps in the fabrication of β' Sialon and Sibeon ceramic shaping dies are powder mixing, hot pressing, and machining. Preliminary analyses indicate that the number of dies that can be obtained from a hot pressed billet together with the cost of machining will affect the unit die cost substantially. Ceradyne, Inc., and Norton Company, two companies having considerable experience in series uniaxial hot pressing, have agreed to give cost estimates for the manufacture of 10^5 dies per year.

WORK NEXT PERIOD

The following activities are planned for the next work period:

(1) Fabrication and evaluation of aluminum-free Sibeon

(2) Fabrication of X = 0.75 β' Sialon die from powder mixture prepared using dry milling procedure

(3) Fabrication of Sibeon die

(4) Preparation of manufacturing cost estimate and process specifications

(5) Preparation of draft final report.

NEW TECHNOLOGY

Silicon beryllium oxynitride as a ceramic shaping die for forming silicon ribbon has been registered as an item of new technology.

REFERENCES

(1) R. R. Wills and D. E. Niesz, "Development and Evaluation of Die and Container Materials", JPL Contract No. 954876, Second and Third Quarterly Reports.

(2) LSSA Project Task Report, "Compatibility Studies of Various Refractory Materials in Contact with Molten Silicon", DOE/JPL-1012-77/6, JPL Publication 78-18.

(3) R. R. Wills and D. E. Niesz, "Development and Evaluation of Die and Container Materials", JPL Contract No. 954876, First Quarterly Report (1977).

(4) R. R. Wills and D. E. Niesz, "Development and Evaluation of Die and Container Materials", JPL Contract No. 954876, Fourth Quarterly Report (1977).

(5) J. A. Palm and C. D. Greskovich, "Silicon Nitride for Airborne Turbine Applications", Final Report Contract N00019-77-C-0259 (1978).

APPENDIX A

MACHINING OF FIRST 1.00 INCH WIDE SILICON-RIBBON DRAWING SIALON DIE

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 6).

(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.

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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.

(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.

(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.

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