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DEVELOPMENT AND EVALUATION OF DIE AND CONTAINER MATERIALS

MASTER

Third Quarterly Progress Report, April 1—June 30, 1978

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By
R. R. Wills
D. E. Niesz

July 15, 1978

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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THIRD QUARTERLY PROGRESS REPORT

(Covering the Period April 1, 1978, to June 30, 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

July 15, 1978

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

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

by

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

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ABSTRACT

Mass spectrometric studies of molten silicon in contact with silicon nitride and silicon carbide show that the vapor pressure of silicon is lower over these materials than over the oxides (beryllium oxide, alumina, and silica) studied previously. Measured carbon and nitrogen contents are 6.4×10^{19} atoms/cm^3 and 3.3×10^{18} atoms/cm^3, respectively.

The fabrication of O' and β' Sialons was found to be strongly dependent upon the nature of the silicon nitride powder. A modified hot pressing procedure was adopted to allow volatilization of chlorine-containing species from the SN402 grade powder. Densification and conversion of the reactants to Sialon were retarded by the use of the calcined SN502 grade silicon nitride powder. O' and β' Sialons were hot pressed to 96-100 percent theoretical density.

β' Sialon of composition X = 1 appears to offer some promise as a candidate die material, but materials containing a higher alumina composition (X = 2.4 Sialon) or the phase known as X phase react with molten silicon. O' Sialons of compositions X = 0.1, X = 0.2, and X = 0.35 reacted with molten silicon, forming a complex interface zone. The concentration of thin precipitates in the silicon increased with the alumina content of the O' Sialon solid solution.

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DEVELOPMENT AND EVALUATION OF DIE AND CONTAINER MATERIALS

by

R. R. Wills and D. E. Niesz

INTRODUCTION

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

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

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

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

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

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

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

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

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

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

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

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

These materials will be prepared by the following reactions:

$$(1) \quad Si_3N_4 + AlN + Al_2O_3 \rightarrow \beta' \text{ Sialon}$$

$$(2) \quad Si_3N_4 + Al_2O_3 + SiO_2 \rightarrow O' \text{ Sialon.}$$

In the first 6 months 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.

High dense O' and β' Sialons were fabricated but these were not single phase materials because of substantial free aluminum in the commercial AlN powder and chlorine in the Si_3N_4 powder. Initial evaluation of these Sialon materials in contact with molten silicon at 1450 C indicated that chemical reaction occurred. Thin string-like precipitates found in the silicon after reaction with β' Sialon were considered to be due to the presence of a second phase in the material. Electron probe analysis of silicon in contact with O' Sialon did not detect any aluminum in the silicon, but two reaction zones were found at the interface.

Solution thermodynamics studies of molten silicon in contact with SiO_2, Al_2O_3, and BeO were completed. Henry's Law Constants for oxygen, beryllium, and aluminum at concentrations $\leq$5000 ppm were determined.

TECHNICAL DISCUSSION OF RESULTS THIS QUARTER

Solution Thermodynamics

Mass spectrometric studies of SiC and Si_3N_4 crucibles in contact with molten silicon have been completed this quarter. Evaluation of the data shows that the apparent vapor pressure of silicon is lower in the carbide and nitride crucibles than in the oxide crucibles. Table 1 summarizes the available data on the vapor pressure of silicon.

The difference among silicon vapor pressures suggests that either (1) there is interaction between the silicon and the crucible which reduces 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 for this program 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. The vapor pressure data obtained from the molten silicon in a silicon carbide crucible are listed in Table 2. Table 3 shows the impurities in the silicon determined by Spark Source Mass Spectrometry. These originated from the CVD silicon carbide crucible.

The carbon content of the silicon which had been molten (at 1700 K) in the silicon carbide crucible for 3 hours was determined to be 0.7 atomic percent. The analysis was carried out in the Leco Carbon Analyzer. Metallographic examination of the contact area (Figure 1 is a typical region) shows that the molten silicon penetrates into the silicon carbide and also erodes away the surface.

TABLE 1. VAPOR PRESSURE OF SILICON OVER THE TEST MATERIALS AT 1700 K

Literature Value (Stull & Sinke(1))	1.4×10^{-6} atm
Literature Value (JANAF(2))	1.1×10^{-6}
Literature Value (Hultgren, et al(3))	4.5×10^{-7}
Measured Si in Si_3N_4 Crucible	1.2×10^{-8}
Measured Si in SiC Crucible	4.6×10^{-9}
Measured Si in BeO Crucible(4)	2.0×10^{-7}
Measured Si in Al_2O_3 Crucible(4)	3.5×10^{-7}
Measured Si in SiO_2 Crucible(4)	4.3×10^{-7}

TABLE 2. VAPOR SPECIES FROM SILICON IN SiC AT 1700 K

Species	Pressure, atm
Si	4.6×10^{-9}
Si_2C	3.8×10^{-9}
Si_2	1.3×10^{-9}
Si_4	9×10^{-11}
Si_2C_2	4×10^{-13}

TABLE 3. IMPURITIES IN SILICON FROM INTERACTION WITH SILICON CARBIDE CRUCIBLE

Element	Concentration, ppm
Na	250
Mg	20
Al	100
S	20
Cl	100
Ca	42
Cr	30
Fe	50
Zn	14

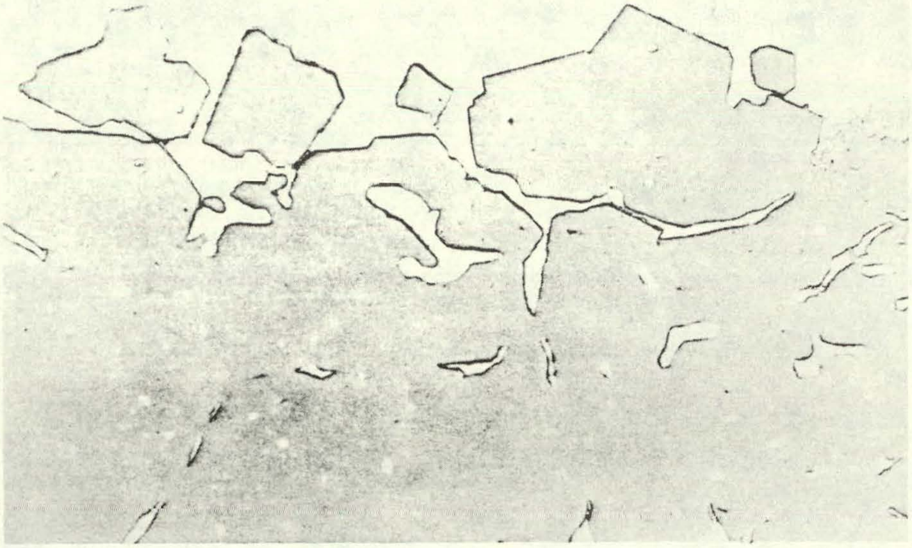

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FIGURE 1. Si-SiC INTERFACE AFTER 3 HOURS AT 1700 K

The dark area is the SiC and the light area is Si. Note the penetration of the Si into the SiC.

The mechanism of attack by the molten silicon thus 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(5) has shown that at the melting point of silicon the concentration of dissolved carbon is 1.3×10^{19} atoms/cm^3. Since the measured carbon content in the above experiment was 6.4×10^{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.

Investigation into the behavior of molten silicon in a silicon nitride crucible has been complicated by fabrication processes. The crucible lid with the orifice could not be fabricated from Si_3N_4, so a BeO crucible lid was used. The data were obtained by the mass spectrometer from a Knudsen cell with a Si_3N_4 body and a BeO lid. The molten silicon (at 1700 K) was held in contact with the crucible for 3 hours. The vapor species observed are listed in Table 4. Table 5 shows the impurities in the silicon melted in a Si_3N_4 crucible as determined by SSMS. These originated from the CVD Si_3N_4 crucible. Another experiment was also conducted to check the vapor species from Si_3N_4 itself. Table 6 shows the vapor species and pressures. The nitrogen content of the silicon was determined to be 360 ppm atomic by placing a piece of the silicon in a tungsten cell in the mass spectrometer and monitoring the nitrogen released when molten silicon reacts with the tungsten. The total nitrogen signal was integrated and correlated to the silicon monoxide calibration by making cross section corrections. The nitrogen content corresponds to a solubility in liquid silicon of 3.3×10^{18} atoms/cm^3 which is in close agreement with the value 6.0×10^{18} determined by Yatsurugi, et al.(6) using activation analysis.

These experiments indicate that the nitrogen pressures above Si_3N_4 are less than the nitrogen pressure above Si_3N_4 containing molten silicon. This phenomenon indicates that molten silicon is pulling (dissolving) nitrogen from the crucible, and may also account for the reduction in the silicon vapor pressure.

TABLE 4. VAPOR SPECIES FROM SILICON IN Si_3N_4 CRUCIBLE WITH BeO LID AT 1703 K

Species	Pressure, atm
N_2	7×10^{-7} atm
Si	1.2×10^{-8}
Si_2N	1.1×10^{-8}
SiO	6×10^{-9}

TABLE 5. IMPURITIES IN SILICON FROM INTERACTION WITH SILICON NITRIDE CRUCIBLE

Element	Concentration, ppm
Na	25 ppm
Al	50
Ca	40
Cr	10
Fe	50
Ni	100

TABLE 6. VAPOR SPECIES FROM Si_3N_4 CRUCIBLE WITH BeO LID AT 1723 K

Species	Pressure
N_2	9×10^{-8} atm
Si	2×10^{-10}
SiO	3×10^{-8}

Metallographic examination of the silicon nitride crucible and molten silicon contact surface shows that the molten silicon is dissolving the silicon nitride crucible. Figure 2 shows the interaction after molten silicon was in contact with the crucible for 3 hours. Another area of the crucible, which was in contact with the molten silicon, was scraped to remove the silicon and silicon nitride particles. Microscopic examination of the particles recovered from the crucible wall scrapings showed mostly silicon chips with a few transparent chips which x-ray diffraction camera showed to be αSi_3N_4. The data for both SiC and Si_3N_4 are summarized in Table 7.

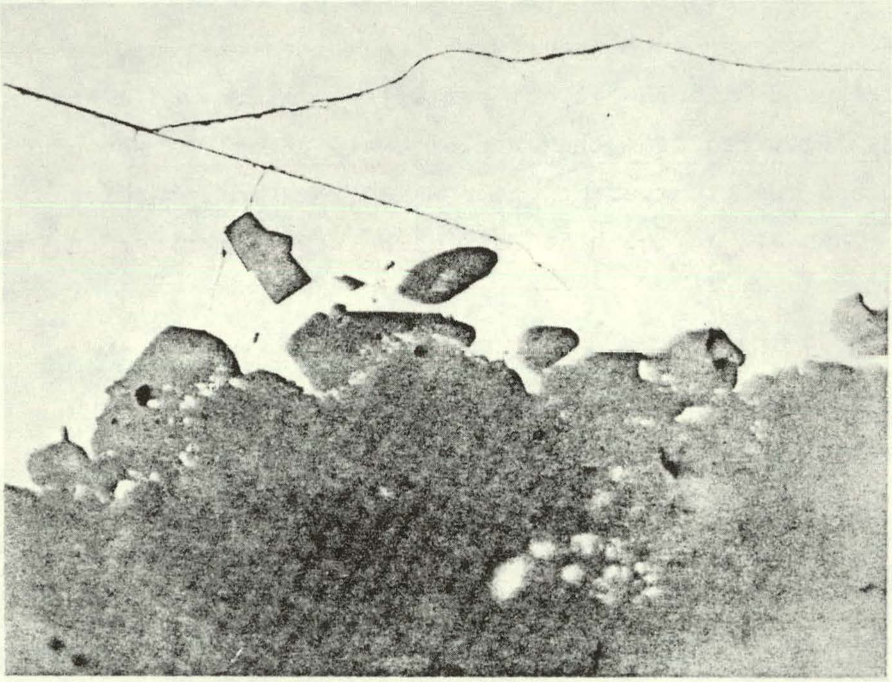
Processing and Fabrication of Sialons

Characterization of Powders

In the second quarterly report the deleterious effect of free aluminum metal in a batch of AlN powder (supplied by Atomergic Chemetal, Inc.) on the fabrication of β' Sialons was described. The formation of aluminum rich precipitates in silicon was considered to be due to the presence of an unidentified aluminum rich phase contained in the matrix of β' Sialon. This unknown phase undoubtedly formed as a result of the free aluminum metal in the starting mixture.

A new batch of -200 mesh AlN powder was obtained from Cerac, Inc., and analyzed before use. Sieve analysis (see Table 8) showed that the majority of the powder is less than 44μm particle size (-325 mesh). In order to determine the presence of free aluminum metal, a sample of each of the above size fractions was cast into a clear resin, and polished. Free aluminum metal, previously found in the core of the AlN particles, was not detected in this batch of AlN powder by examination under an optical microscope.

The powder was milled in two batches of 900 grams each. Each batch was milled for 8 hours in a high purity Al_2O_3 ball mill containing 950 cm^3 of hexane and 4000 grams of Al_2O_3 balls. After milling, the powder was dried under vacuum at 1500 C, separated from the Al_2O_3 balls, and stored under nitrogen in sealed containers. The average particle size of this powder is 5μm (see Figure 3). The particles themselves are irregular in shape (see Figure 4).



500X

FIGURE 2. Si-Si_3N_4 INTERFACE AFTER 3 HOURS AT 1700 K

The dark area is the Si_3N_4 and the light area is the Si. A piece like the island which is separated from the rest of the crucible is similar to that which was observed as αSi_3N_4 in the XRD experiment.

TABLE 7. SUMMARY OF THERMODYNAMICS DATA

	SiC Crucible	Si_3N_4 Crucible
Psi	4.6×10^{-9} atm	1.2×10^{-8} atm
PN_2		7×10^{-7}
[C]	0.7 atomic %	
[N]		360 ppm atomic
Henry's Law k		1.9×10^{-3}
A Si$^{(a)}$	10^{-2}	0.26
A $N_2^{(b)}$		2×10^{-4}

(a) The activity (A) of the silicon is defined as $psi/p^{o}si$ = $= 4.6 \times 10^{-9}/4.5 \times 10^{-7} = 10^{-2}$, where

psi = measured pressure of silicon above silicon in silicon carbide crucible at 1700 K

$p^{o}si$ = vapor pressure of silicon as an ideal monatomic gas at 1700 K.

(b) The activity of the N_2 is calculated from $PN_2/P^{o}N_2$, where PN_2 is the measured nitrogen pressure and $P^{o}N_2$ is calculated from JANAF data for the reaction

$$Si_3N_{4(c)} \rightarrow 3\ Si_{(2)} + 2N_{2(g)}\ .$$

The calculated N_2 pressure is 3×10^{-3} atm.

TABLE 8. SIEVE ANALYSIS OF -200 MESH AlN POWDER[a]

Mesh Size	Percent Friction
+140	7.1
+200	12.7
+270	11.7
+325	7.1
-325	62.0

(a) Batch supplied by Cerac, Inc.

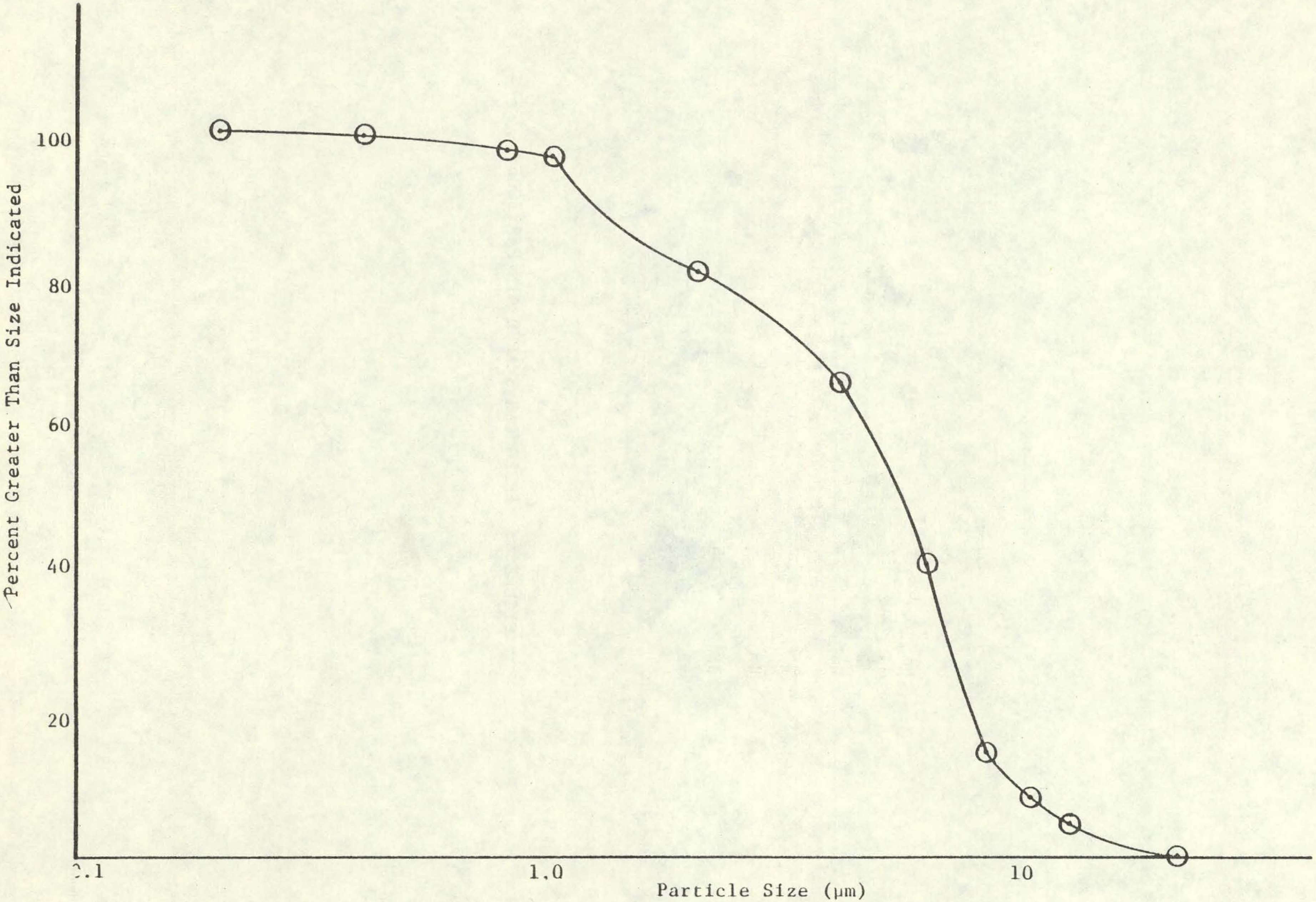


FIGURE 3. PARTICLE SIZE DISTRIBUTION OF MILLED AlN POWDER

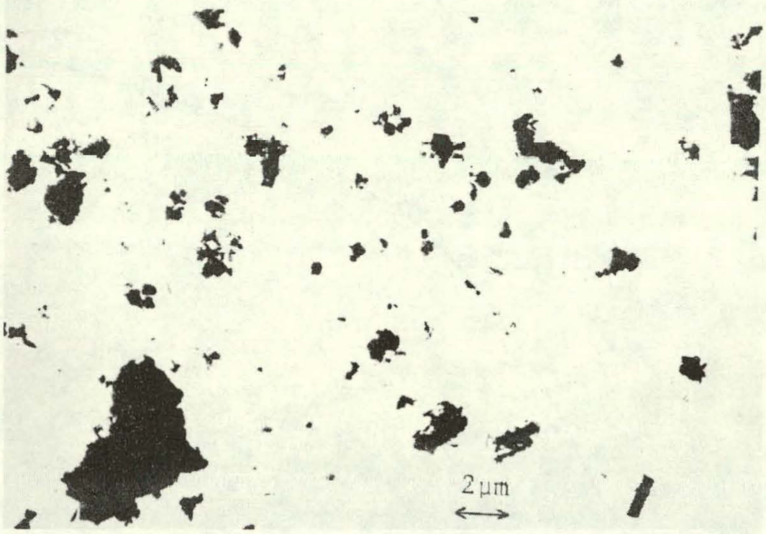


FIGURE 4. IRREGULAR SHAPED AlN PARTICLES

Chemical analysis shows that the powder contains 1.48 percent oxygen and 0.06 percent carbon, similar to the previous batch of AlN powder. Major metallic impurities (see Table 9) are Na (100 ppm), Mg (100 ppm), Fe (300), and Ca (60 ppm). These impurity levels which are slightly less than in the previous batch of AlN powder may prove to be unacceptably high, but this will not be known until extensive evaluation of β' Sialons in contact with molten silicon has been completed.

Previous hot pressing work with O' and β' Sialon mixtures containing SN402 grade Si_3N_4 powder indicated that significant weight losses were incurred as a result of the evaluation of chlorine containing species. To overcome this problem, SN502 grade Si_3N_4 powder was obtained from GTE Sylvania, Inc. This powder (see Figure 5) is produced by calcining the SN402 powder at 1500 C in ZrO_2 crucibles. Calcination not only reduces the chlorine content of the powder but also reduces the oxygen content (SN502 1.38 percent oxygen, 500 ppm chlorine; SN402 2.90 percent oxygen, 5000 ppm chlorine). Certain metallic impurities, however, are present in higher concentrations than in the SN402 powder. Mo, Al, and Zr in particular (see Table 10) are present at relatively high concentration levels. It is believed that the increase in Zr content is due to the use of ZrO_2 crucibles in the calcination process, but it is not known why the Al and Mo impurity levels increased so much.

Fabrication of O' Sialons

In the last quarterly report, a well controlled process schedule for fabricating high purity O' Sialons was described. It was shown that very little change in composition and impurities occurred in processing and fabricating the starting powders into a dense ceramic body. However, as a result of volatilization during hot pressing, O' Sialon samples contained appreciable amounts of elemental silicon.

Two approaches were adopted to overcome this problem. First, the hot pressing cycle was modified to endeavor to eliminate this free silicon. The green compact, composed of SN402 Si_3N_4, Atomergic SiO_2, and Reynolds Al_2O_3, was first heated to 1200 C under vacuum and then heated to 1500 C under a nitrogen atmosphere. After evaluation of the volatile species (15-20 minutes), the

TABLE 9. MASS SPECTROGRAPHIC ANALYSES OF AlN$^{(a)}$ AND $Si_3N_4$$^{(b)}$

Element	AlN	Si_3N_4	Element	AlN	Si_3N_4
Li	30	0.01	Pr	<0.2	<0.03
Be	<0.4	<0.003	Nd	<0.4	<0.1
B	5	0.2	Sm	<0.3	<0.1
F	<0.7	< 0.1	Eu	<0.1	<0.1
Na	100	5	Gd	<0.3	<0.1
Mg	100	5	Tb	<0.1	<0.01
Al	Major	60	Dy	<0.3	<0.05
Si	300	Major	Ho	<0.1	<0.02
P	10	0.2	Er	<0.2	<0.04
S	20	0.6	Tm	<0.4	<0.1
Cl	10	500	Yb	<9.3	<0.1
K	15	0.6	Ta	<1	<0.1
Ca	15	12	W	7	<0.1
Sc	<0.2	< 0.3	Re	<0.3	<0.03
Ti	12	7	Os	<0.4	<0.05
V	0.3	0.2	Ir	<0.3	<0.1
Cr	25	10	Pt	<0.3	<0.04
Mn	4	0.2	Au	<0.1	<0.01
Fe	300	10	Hg	<0.3	<0.05
Co	1	0.4	Tl	<0.1	<0.04
Ni	6	0.2	Pb	2	<0.06
Cu	20	0.7	Bi	5	<0.03
Zn	20	0.5	Th	<0.1	<0.03
Ga	60	0.4	U	<0.1	<0.03
Ge	<2	<0.1			
As	0.6	0.02			
Sc	<1	<2			
Br	2	0.2			
Rb	30	0.2			
Sr	2	0.3			
Y	<0.1	3			
Zr	1	60			
Nb	<0.1	<0.2			
Mo	2	400			
Ru	<0.6	<0.1			
Rh	<0.5	<0.7			
Pd	<0.2	<0.4			
Ag	<0.5	<0.03			
Cd	<0.5	<0.06			
In	<0.3	<0.04			
Sn	3	<0.2			
Sb	<0.3	<0.05			
Te	<0.2	<0.2			
I	30	<0.1			
Cs	0.3	<0.2			
Ba	20	<0.03			
Ce	<0.3	<0.2			

(a) AlN supplied by Cerac, Inc.

(b) Si_3N_4 SN502 grade supplied by GTE Sylvania, Inc.

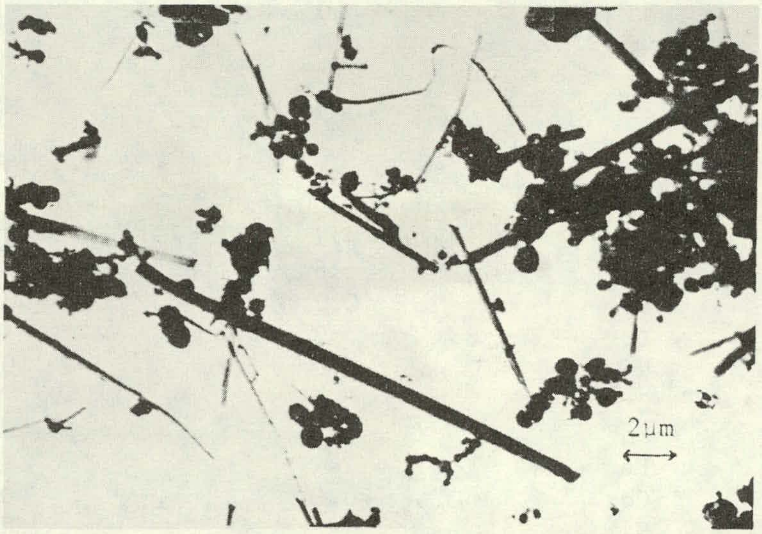


FIGURE 5. SN502 GRADE Si_3N_4 POWDER CONTAINING αSi_3N_4 NEEDLES

TABLE 10. MASS SPECTROGRAPHIC ANALYSES OF SN402 AND SN502 Si_3N_4 POWDERS (ppmw)

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

TABLE 10. (Continued)

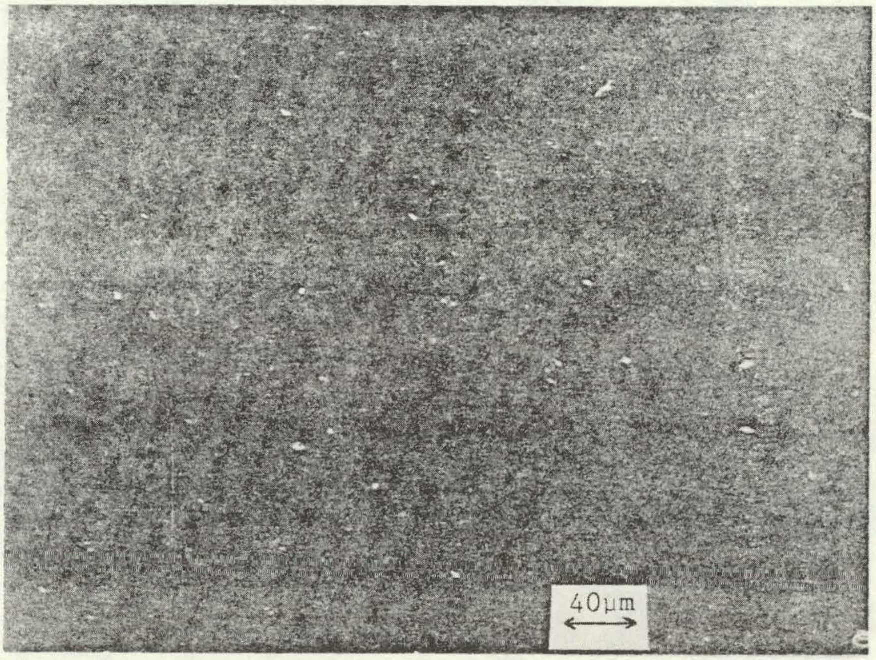
Element	SN402 Si_3N_4	SN502 Si_3N_4
Ce	<0.1	<0.2
Pr	<0.1	<0.03
Nd	<0.2	<0.1
Sn	<0.2	<0.1
Eu	<0.1	<0.1
Gd	<0.1	<0.1
Tb	<0.02	<0.01
Dy	<0.2	<0.05
Ho	<0.04	<0.02
Er	<0.1	<0.04
Tn	<0.2	<0.1
Yb	<0.2	<0.1
Ta	<0.07	<0.1
W	<0.1	<0.1
Re	<1	<0.03
Os	<0.1	<0.05
Ir	<0.4	<0.1
Pt	<0.2	<0.04
Au	<0.06	<0.01
Hg	<0.1	<0.05
Tl	<0.2	<0.04
Pl	0.2	<0.06
Bi	<0.06	<0.03
Th	<0.04	<0.03
U	<0.1	<0.03

temperature was reduced to <1000 C and the nitrogen and volatile species were pumped out of the chamber. The sample was then hot pressed at 1750 C for 1 hour under atmospheric nitrogen. The density of the sample (X = 0.1 O') was 2.80 g/cm^3, identical to that obtained for the same batch of powder hot pressed using the previous simpler hot pressing procedure. Clearly, allowing the volatile species to evolve has not noticeably affected the formation and lifetime of the transient liquid phase. If it had, the sample would not have pressed to as high a density. X-ray diffraction analysis indicated a single-phase material. As expected, the free elemental silicon content (see Figures 6 and 7) is considerably reduced by using this modified hot pressing cycle.

The second approach involved the replacement of SN402 Si_3N_4 in the starting mixtures by the calcined SN502 grade powder. As this grade of Si_3N_4 powder was considered to be less reactive than the SN402 grade (due to its larger particle size and lower oxygen content), the SiO_2 powder was first milled for 8 hours to break up the weak agglomerates in the powder and to reduce its average particle size (see Figure 8). During milling the powder also picked up 0.6 weight percent Al_2O_3 from the mill.

Mixtures of Si_3N_4, Al_2O_3, and SiO_2 corresponding to X = 0 O' Sialon (Si_2N_2O), X = 0.1, X = 0.2, and X = 0.35 O' Sialons were hot pressed at 1750 C for 1-2 hours under a nitrogen atmosphere. The results in Table 11 indicate that high density materials were obtained but that these were not single-phase materials. The densities of these samples and their conversion to O' Sialon generally correlate with the amount of Al_2O_3 in the original powder mixture because increasing the Al_2O_3 concentration enhances liquid phase sintering and diffusion processes. The original problem of excessive volatilization was not experienced, weight losses being reduced to 1-3 percent.

The fabrication of O' Sialons is thus strongly dependent upon the nature of the Si_3N_4 powder. If SN402 grade Si_3N_4 powder is used, high density material containing considerable free silicion is produced as a result of weight losses incurred during the hot pressing cycle. By allowing the volatile species to evolve at 1500 C and renitriding the sample before hot pressing at 1750 C, the free silicon content can be reduced considerably. Alternatively the volatilization problem can be overcome by using SN502 Si_3N_4 powder, but the lower reactivity of this powder prevents complete conversion to O' Sialon.



5J127

FIGURE 6. REDUCED SILICON CONTENT OF O' SIALON FABRICATED BY MODIFIED HOT PRESSING CYCLE

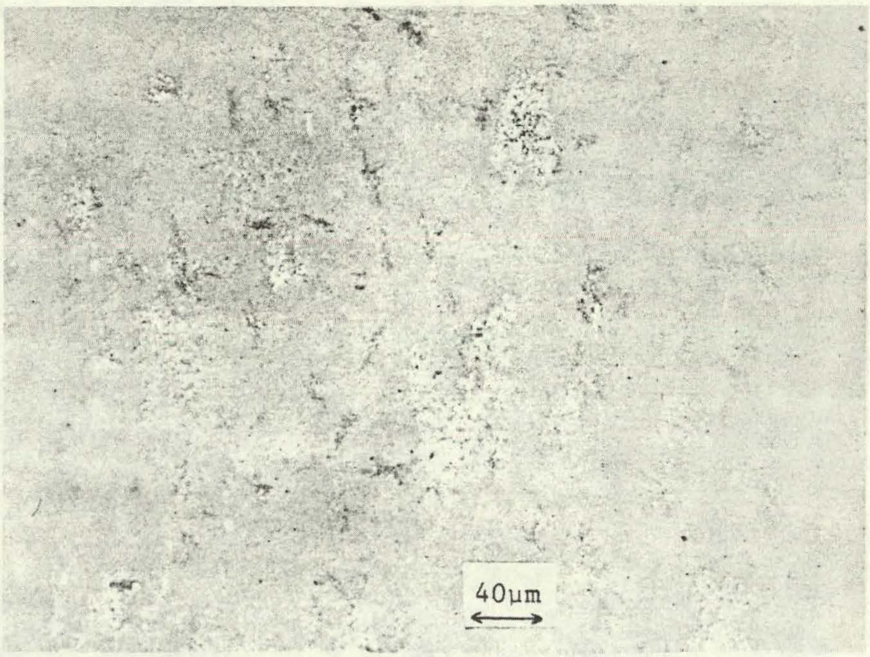


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FIGURE 7. TYPICAL MICROGRAPH OF O' SIALON FABRICATED BY SIMPLER HOT PRESSING CYCLE

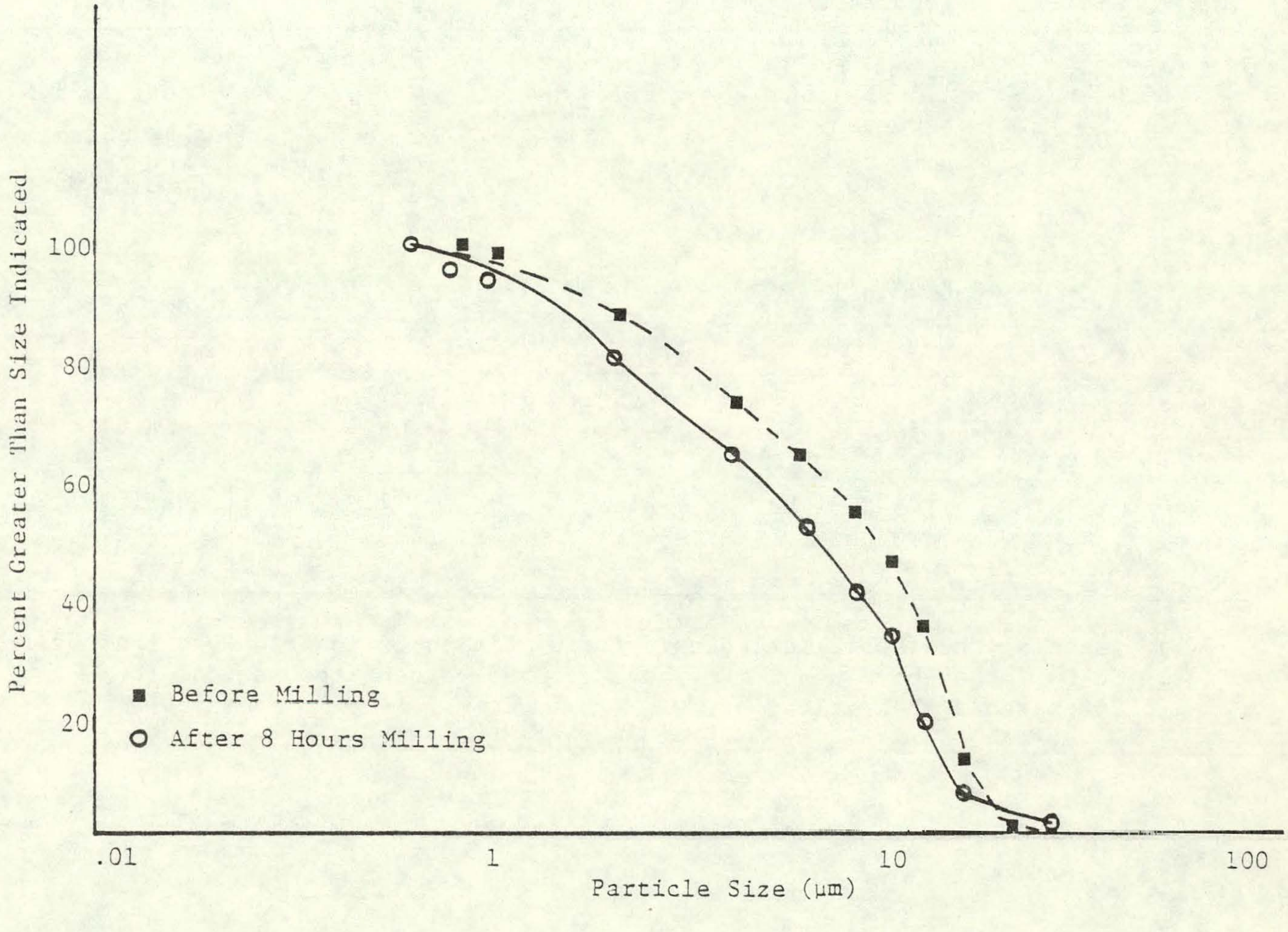


FIGURE 8. PARTICLE SIZE DISTRIBUTION OF SiO_2 POWDER BEFORE AND AFTER MILLING

TABLE 11. PHASE ANALYSIS, DENSITY, AND WEIGHT LOSS OF HOT PRESSED O' SIALONS

Composition	Processing Conditions	Density(a) (g/cm^3)	Weight Loss (percent)	X-Ray Diffraction Analysis
Si_2N_2O X = 0 O'	1740 C, 1 hr 6500 psi	2.72	1.0	Mostly αSi_3N_4 Some βSi_3N_4 Some Si_2N_2O
X = 0.1 O'	1745 C, 1 hr 6500 psi	2.82	3.0	Mostly O' Some αSi_3N_4
X = 0.2 O'	1745 C, 1 hr 6500 psi	2.84	1.3	Mostly O' Some β'
X = 0.35 O'	1745 C, 1 hr 7000 psi	2.88	2.0	Mostly O' Some β'

(a) Assuming the theoretical density of O' Sialon is identical to that of Si_2N_2O, the above densities range from 95 percent theoretical to 100 percent theoretical.

Thermal Expansion of O' Sialon

At the request of JPL, the linear thermal expansion of O' Sialon was determined up to 1000 C using an Orton Automatic Recording Dilatometer. The data shown in Figure 9 were obtained on a sample of X = 0.1 O'. Although the thermal expansions of Si_2N_2O and O' Sialon (a Si_2N_2O-Al_2O_3 solid solution) are expected to be identical, there is a difference in the two curves in Figure 9. This is primarily because the Si_2N_2O sample used by Washburn(8) contained only 68 percent Si_2N_2O, the remainder of the sample being mainly Si_3N_4. In contrast the O' Sialon sample was a single phase material. The curve for X = 0.1 O' Sialon thus represents the true expansion behavior of Si_2N_2O. The figure also shows the excellent match in thermal expansion of O' Sialon and silicon.

Fabrication of β' Sialons

Previous work(4) in fabrication of β' Sialons had shown that free aluminum metal in the AlN powder was responsible for the appearance of an unknown second phase in the hot pressed samples. After characterization of the new batch of AlN powder, trial hot pressings were carried out with X = 1 and X = 2.4 β' Sialons using either SN402 grade or SN502 grade Si_3N_4 powder with AlN and Al_2O_3. The results are summarized in Table 12.

The first sample of X = 2.4 β', prepared using SN502 grade Si_3N_4 powder, was hot pressed at 1750 C for 2-1/2 hours at 8000 psi. The sample exhibited a density gradient from the outer surface to the inner core, the average density of the sample being 2.5 g/cm^3 and the inner darker region being approximately fully dense (3.09 g/cm^3). Both inner and outer regions were single phase β' according to the X-ray diffraction patterns. Based on previous experience(7) it was realized that the insufficient liquid was being formed to allow complete densification. A batch of the powder mixture was consequently mixed in propan-2-ol for 30 minutes to slightly increase the thickness of the SiO_2 layer on each Si_3N_4 particle. As expected, this allowed the sample to be hot pressed to a higher density (3.0 g/cm^3). X-ray diffraction analysis again showed this to be a single phase material.

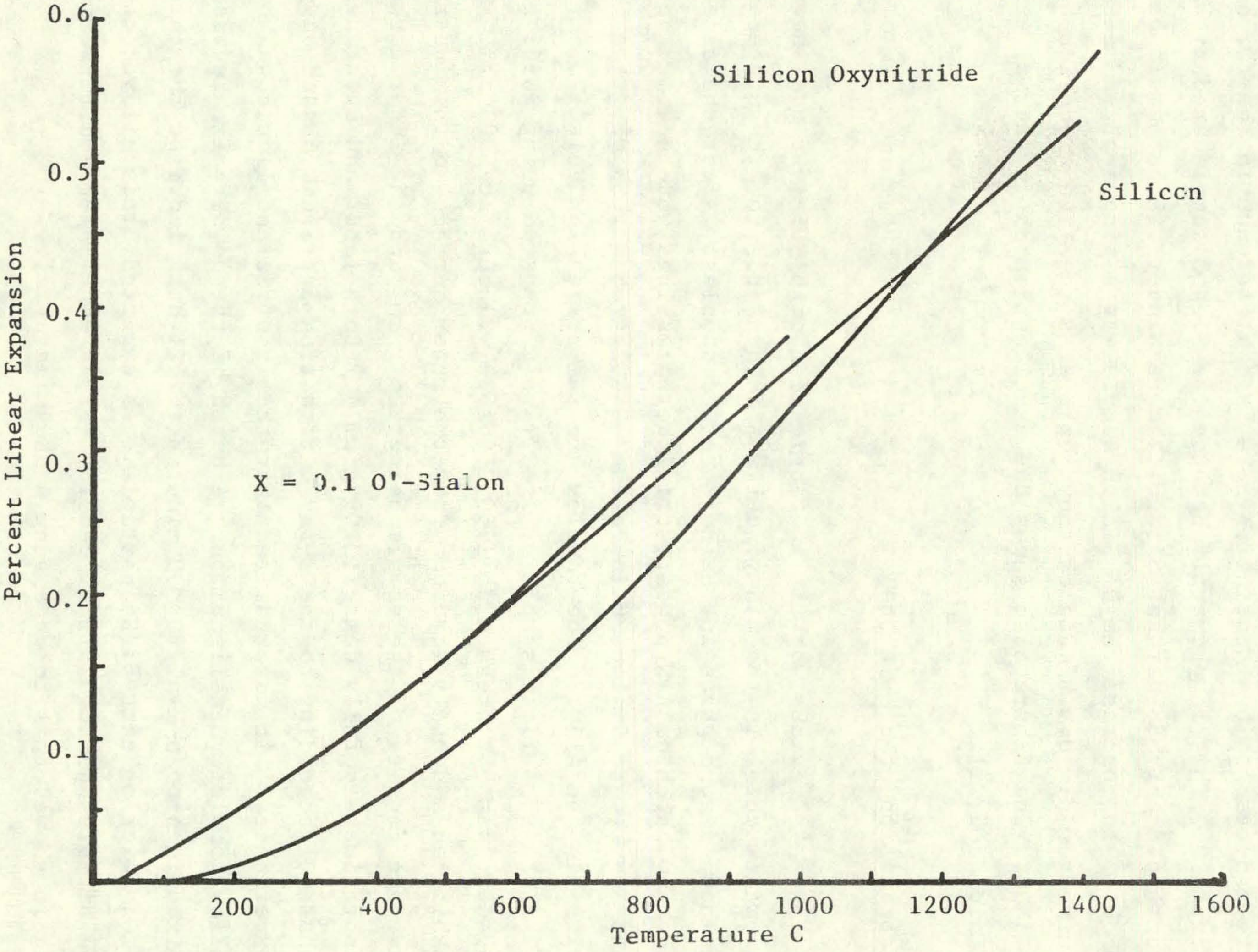


FIGURE 9. LINEAR THERMAL EXPANSION OF SILICON AND O'-SIALON AND SILICON OXYNITRIDE(8)

TABLE 12. FABRICATION OF β' SIALONS

Sample Preparation	Density (g/cm^3)	Weight Loss (percent)	Phase Analysis (X-Ray)
X = 2.4 β', SN402 Si_3N_4	3.10	5	Single phase
X = 1.0 β' SN402 Si_3N_4	3.13	7	Single phase
X = 2.4 β', SN502	2.56	8	Single phase
X = 2.4 β', SN502(a)	3.0	3.5	Single phase

(a) After milling, the Si_3N_4, Al_2O_3, AlN mixture was mixed in propan-2-ol for 30 minutes.

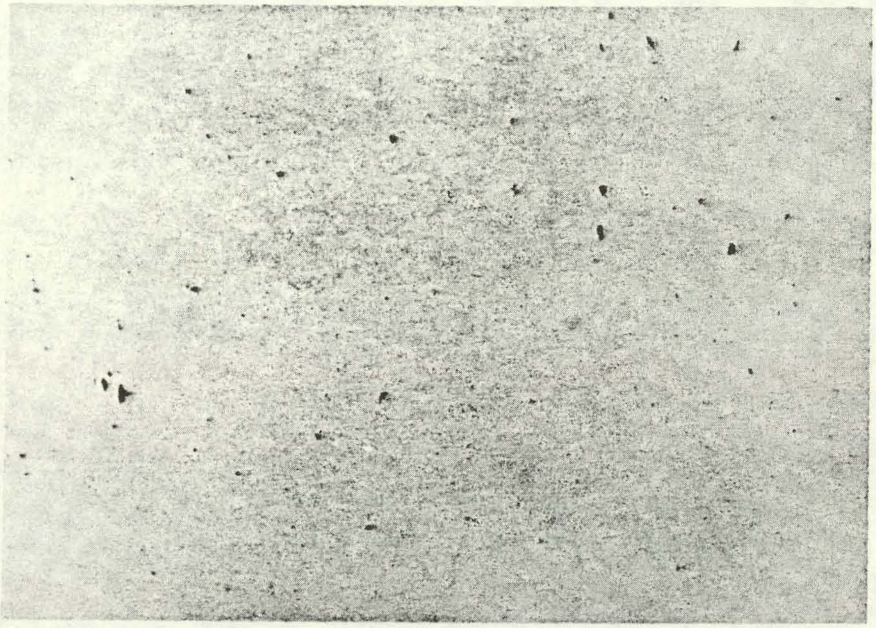
Hot pressing trials with SN402 grade Si_3N_4 powder in the starting mixture have also been completed. The hot pressing cycle, as described in the fabrication of O' Sialons, was adjusted to allow for volatilization of gaseous species. Final hot pressing conditions were 1750 C at 8000 psi for 2 hours. Optical micrographs of these materials are shown in Figures 10 and 11. Both materials appear to contain small amounts of free silicon, but only β' Sialon could be seen in the X-ray diffraction patterns of these materias.

Compatibility with Molten Silicon

O' Sialons

Samples of X = 0.1, X = 0.2, and X = 0.35 O' Sialons (see Table 11) were held in contact with molten silicon at 1450 C for 6 hours. A reaction zone (see Figure 12), similar to that reported previously, was found on all the samples. This reaction zone is slightly thicker than observed previously because of the longer contact period (6 hours instead of 1 hour). At some parts of the silicon-ceramic interface the reaction zone consists of three regions, the additional third region being being the black areas (see Figure 13) formed inside the dark gray area. Regions 1 and 2 were previously analyzed(4) by electron probe analysis and found to contain 0.15 percent Al and 90.7 percent Si and 0.16 percent Al and 63.6 percent Si, respectively. The remaining elements 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 certainly no known crystalline material of this composition and consequently Region 1 is probably a metastable amorphous material.

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). This conclusion is supported by the observations of Duffy et al.(9) that CVD "silicon oxynitride" forms Si_3N_4 at the interface with silicon. It should be pointed out, however, that CVD "silicon oxynitride" is not the compound Si_2N_2O, but an amorphous material of general composition SiO_xN_y.



100X 6J004

FIGURE 10. OPTICAL MICROGRAPH OF X=10 β' SIALON

Black spots are pullouts.

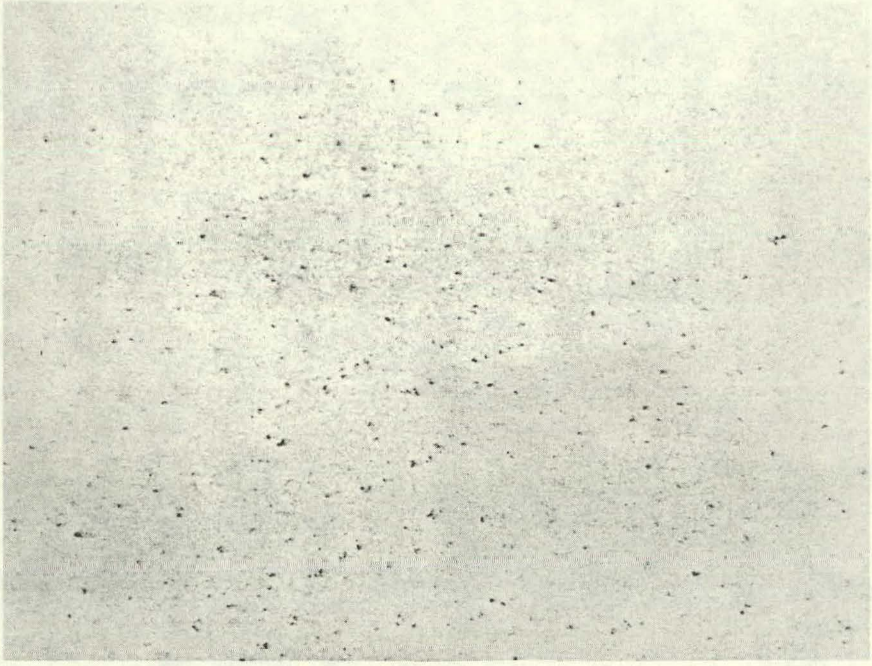


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FIGURE 11. OPTICAL MICROGRAPH OF X=2.4 β' SIALON

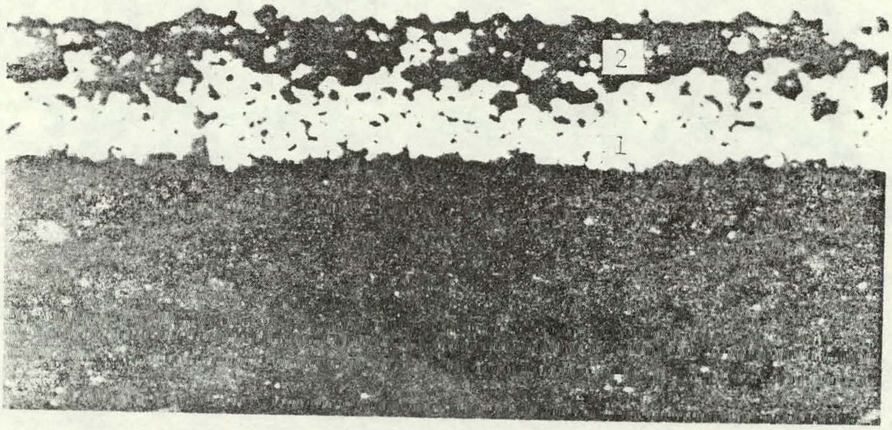

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FIGURE 12. TYPICAL REACTION ZONE AT INTERFACE OF O' SIALON AND SILICON

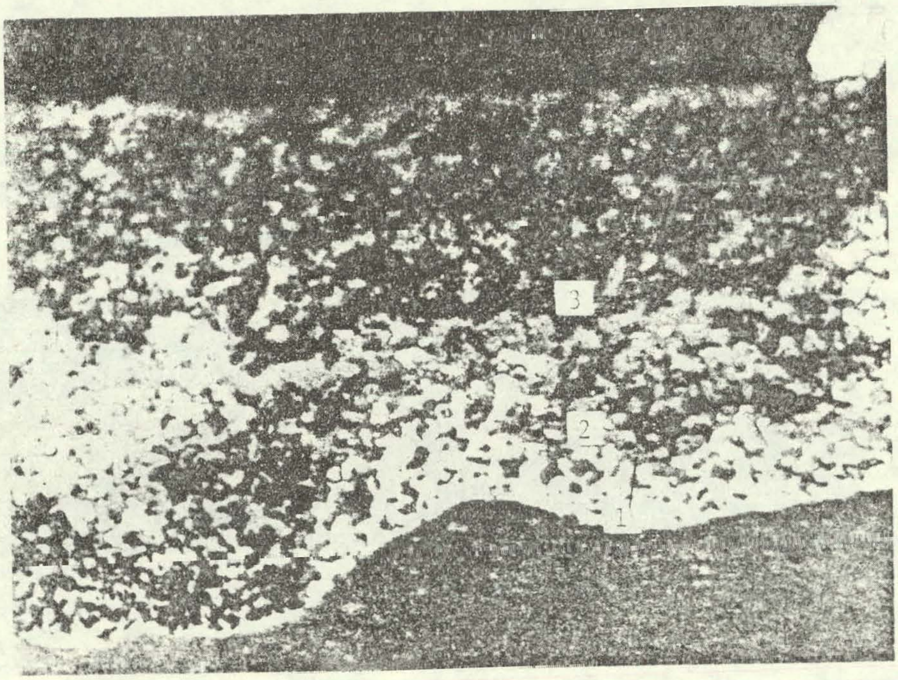

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FIGURE 13. THREE PHASE REACTION ZONE AT SILICON - O' SIALON INTERFACE

In addition to the reaction zone O' Sialon samples gave rise to the formation of string-like precipitates (see Figure 14) in the silicon. The concentration of these precipitates increased with Al_2O_3 content of the O' Sialon solid solution. Both aluminum and silicon were detected in these precipitates by energy-dispersive X-ray analysis, but further work is needed to determine the exact identity of these precipitates.

The evaluation of O' Sialons has employed samples of different Al contents, samples containing small amounts of unidentified phases and samples containing some β' Sialon, but in all cases the general behavior has been similar. It would thus appear that grain boundary phases or secondary phases are not responsible for the reaction zone formed at the silicon-ceramic interface but rather that the O' Sialon solid solution is simply not stable under these conditions. For this reason, development and assessment of this as a die and crucible material has ceased.

β' Sialons

β' Sialons (X = 1, X = 2.4), prepared from SN402 Si_3N_4 powder and Al_2O_3 and AlN powders using the modified hot pressing procedure, were held in contact with molten silicon at 1450 C for 1 hour. In addition, a sample of β' Sialon containing X* phase (a Sialon of approximate composition $Si_3N_4 \cdot 6Al_2O_3 \cdot 3SiO_2$) was also evaluated.

The results for the X = 1 Sialon are encouraging in that very little reaction was found at the interface (see Figure 15). Furthermore, no precipitates were observed in the silicon. In contrast, both the X = 2.4 Sialon sample and the two phase Sialon + X phase sample gave rise to the familiar thin precipitates (see Figure 16) in the silicon. Both samples show reaction at the interface, X = 2.4 Sialon exhibiting a reaction across the entire contact area (see Figure 17) whereas reaction with the Sialon + X phase sample is localized (see Figure 18). In both cases, it appears that the silicon has infiltrated into the bulk of the ceramic by dissolving part of the microstructure. The localized attack of the β' Sialon + X phase sample can be rationalized on the

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* Prepared from a mixture of 80 weight percent Si_3N_4, 20 weight percent Al_2O_3 by T. R. Wright and D. E. Niesz, NASA Report No. CR-134690.

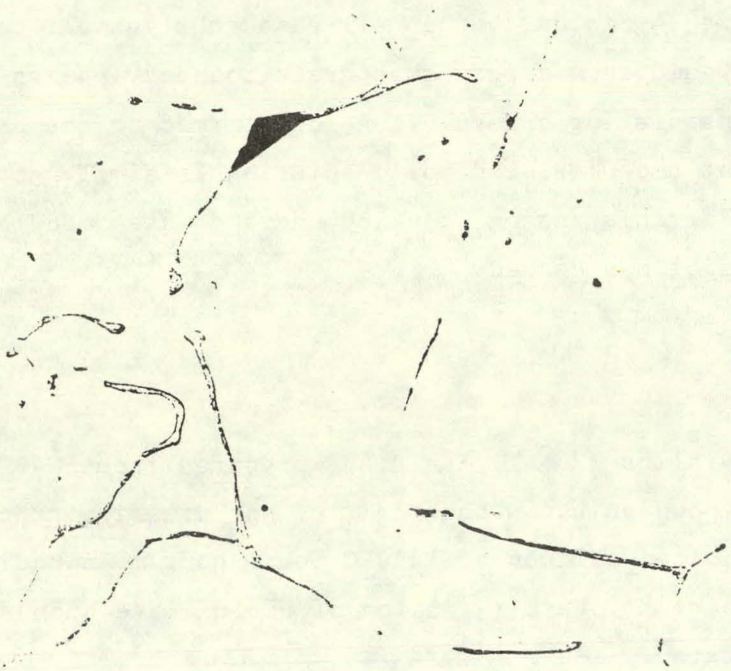

FIGURE 14. PRECIPITATES FORMED IN SILICON AFTER CONTACT WITH X=0.35 O' SIALON FOR 6 HOURS

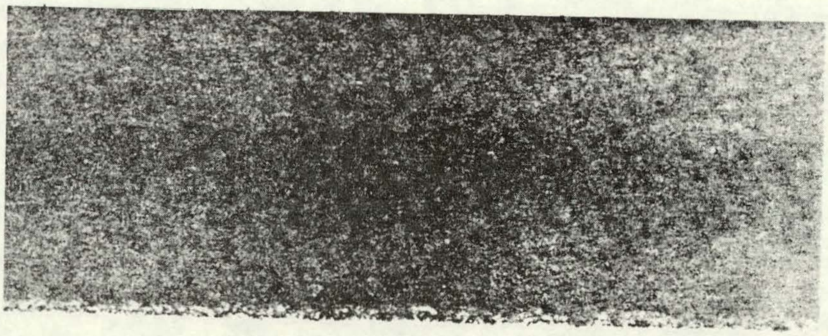

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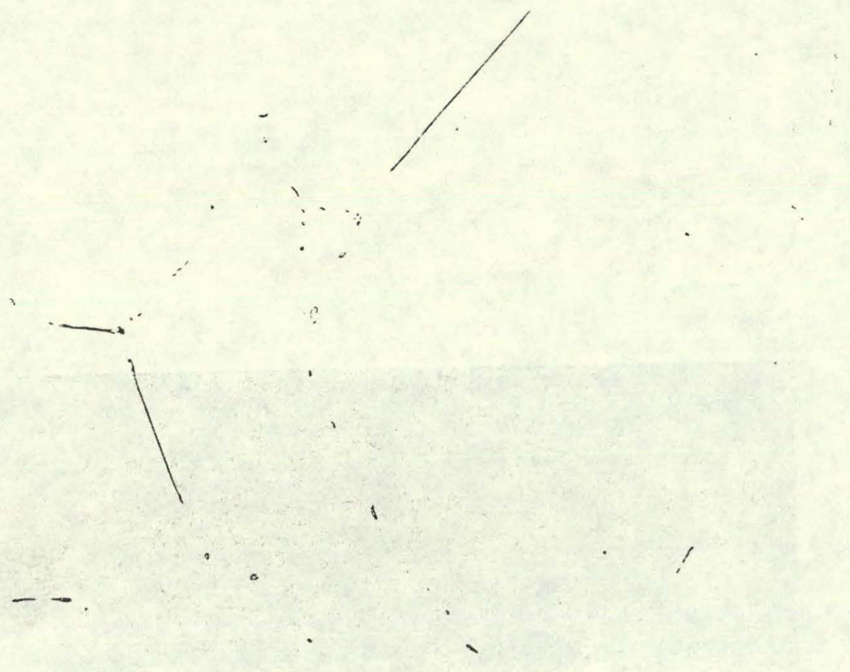
FIGURE 15. INTERFACE BETWEEN X=1 β' SIALON AND SILICON



100X

6J008

FIGURE 16. ALUMINUM RICH PRECIPITATES IN SILICON AFTER CONTACT WITH X=2.4 SIALON AND β' SIALON + X PHASE AT 1450 C FOR 1 HOUR

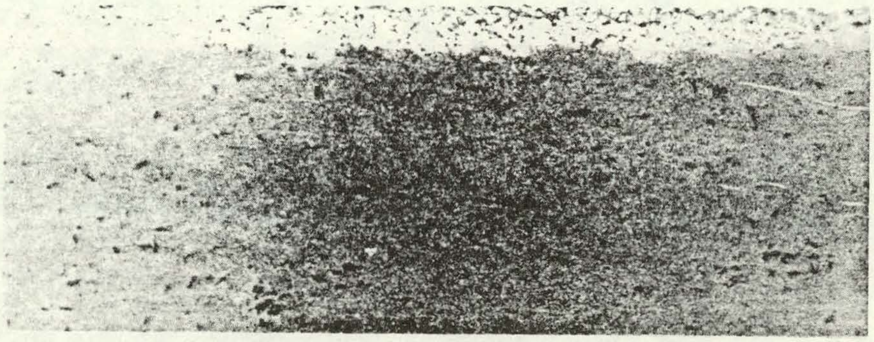


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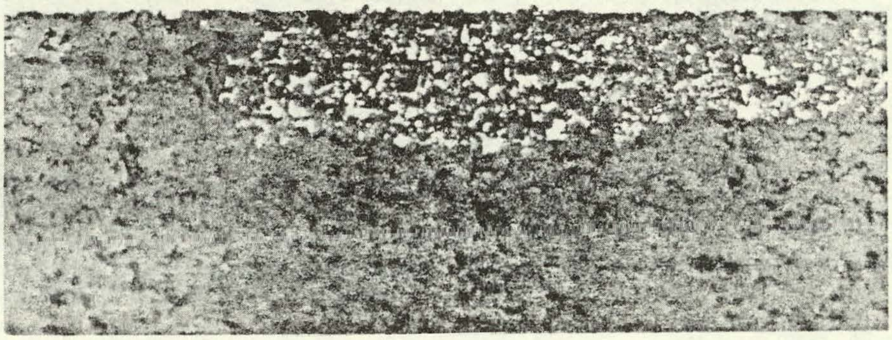
FIGURE 17. INTERFACE BETWEEN X=2.4 β' SIALON AND SILICON



500X T54

FIGURE 18. LOCALIZED ATTACK OF β' SIALON + X PHASE BY MOLTEN SILICON

basis of preferential attack of the high alumina content X phase. The alumina content of the β' Sialon phase in this sample is nearer to that of X = 1 β' Sialon than to X = 2.4 β' Sialon, and consequently based on the results for X = 1 β' Sialon, very little reaction occurs in regions of the sample consisting of the β' Sialon phase.

The above results indicate that the presence of the second phase (X phase) is detrimental to the stability of β' Sialon materials in contact with molten silicon. Further, the concentration of aluminum in the β' Sialon solid solution is important. The X = 1 β' Sialon exhibited very little reaction under the test conditions, and additional work will be conducted with this composition as well as with compositions of lower aluminum content.

PLANS FOR WORK NEXT QUARTER

(1) Determine the interaction of mullite with molten silicon.

(2) Fabricate silicon beryllium oxynitride materials. Assess their compatibility with molten silicon.

(3) Continue evaluation of X = 1 β' Sialon (contains 10 wt.% Al).

(4) Fabricate β' Sialons containing less than 10 wt.% Al. Assess their chemical stability in contact with molten silicon.

(5) Assess the sinterability of promising materials.

NEW TECHNOLOGY

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

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