N O T I C E

THIS DOCUMENT HAS BEEN REPRODUCED FROM
MICROFICHE. ALTHOUGH IT IS RECOGNIZED THAT
CERTAIN PORTIONS ARE ILLEGIBLE, IT IS BEING RELEASED
IN THE INTEREST OF MAKING AVAILABLE AS MUCH
INFORMATION AS POSSIBLE

EFFECTS OF VARYING OXYGEN PARTIAL PRESSURE ON

MOLTEN SILICON - CERAMIC SUBSTRATE INTERACTIONS

FINAL REPORT

by P. Darrell Ownby, Harold V. Romero and Michel W. Barsoum
Ceramic Engineering Department
University of Missouri-Rolla
Rolla, Missouri 65401
April 1980

ABSTRACT

The objective of the University of Missouri - Rolla program under the Jet Propulsion Laboratory Low Cost Silicon Solar Array contract is to investigate the interaction of molten silicon with various die and container candidate materials under varying oxygen partial pressures. This has been done by making silicon sessile drop contact angle measurements on the candidate materials to determine the degree to which silicon wets these substances, and subsequently sectioning the post-sessile drop experiment samples and taking photomicrographs of the silicon-substrate interface to observe the degree of surface dissolution and degradation.

Several different materials supplied by JPL have been investigated in this manner, i.e., hot pressed silicon nitride (from both Kawecki Berylco, Inc. (KBI) and AVCO), CNTD silicon nitride coated on hot pressed silicon nitride (Chemetal-Eagle Picher), CVD silicon carbide coated on graphite (Ultracarbon), and Ω Sialon (Battelle). Of these materials, silicon did not form a true sessile drop on the Ultracarbon SiC on graphite due to infiltration of the silicon through the SiC coating or on the Ω Sialon due to the formation of a more-or-less rigid coating on the liquid silicon. The lowest sessile drop contact angle (i.e., the most wetting) was obtained on the CNTD coated Si_3N_4 with a value of 42°. The AVCO and CNTD coated materials showed the least amount of interaction with molten silicon.

The importance of oxygen partial pressure on the interaction of molten silicon with refractory materials having been established[*], the oxygen concentrations in the EFG silicon ribbon furnace at Mobil Tyco Solar Energy Corp., Waltham, Massachusetts, and in the JPL silicon sessile drop furnace at Pasadena, California, were measured using the portable thoria-yttria solid solution electrolyte oxygen sensor constructed at UMR for this purpose. Oxygen partial pressures of 10^{-7} and 10^{-8} atm. were obtained for the Mobil Tyco and JPL facilities, respectively. The measurements made at these two facilities are believed to represent non-equilibrium conditions.

---

[*] Eagle-Picher Fifth Quarterly Report to JPL on contract #DOE/JPL-954877-78/3.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES

INTRODUCTION

The objective of the Low Cost Silicon Solar Array (LSSA) program of the Jet Propulsion Laboratory (JPL) is to produce inexpensive silicon photovoltaic cells. An important consideration in achieving this objective is the types of materials to be used in forming the silicon into the required thin sheets, i.e., how these materials will affect and be affected by the silicon in the molten state. The University of Missouri-Rolla (UMR) has undertaken to make silicon sessile drop measurements on refractory materials supplied by JPL to determine their compatibility with molten silicon, and the extent to which molten silicon will degrade the refractory - molten silicon interface, as well as the effect of oxygen partial pressure on the molten silicon - refractory interaction.

Work done by UMR for Eagle-Picher Industries under subcontract to JPL for the LSSA project demonstrated the importance of very low amounts of oxygen on the molten silicon - refractory interaction.[1] The capability of routinely measuring oxygen partial pressures well below the equilibrium partial pressure for the formation of SiO_2 (about 2×10^{-19} atm. at 1700K) has been achieved using a thoria-yttria solid solution electrolyte oxygen cell. The cell was constructed so that, in addition to being used in the UMR laboratory for measuring oxygen partial pressures in sessile drop experiments,

it could be transported to other contractors' facilities where silicon sheets and ribbons are produced and the oxygen concentration in their silicon sheet and ribbon furnaces measured. Such measurements were carried out in the JPL EFG silicon ribbon furnace at the Mobil Tyco facility in Waltham, Massachusetts, and at the JPL silicon sessile drop furnace in Pasadena, California.

Sessile drop experiments were carried out at UMR on a variety of candidate die and container materials, including hot pressed silicon nitride, CVD coated silicon nitride, Sialon, and CVD coated SiC on graphite. These experiments consisted of in situ measurements of the contact angle between the liquid silicon and the substrate and subsequent examination of the silicon-substrate interface to determine the degree of interaction.

SESSILE DROP EXPERIMENTS

Silicon sessile drop experiments were conducted using a molybdenum wire wound tube furnace capable of reaching temperatures up to 2000K. The material to be tested was placed on an alumina "D" tube, then a 7 mm cube of silicon was placed on the sample. It was shown that it is desirable that the silicon cube not be in complete contact with the sample, because if it is, adsorbed oxygen under the silicon cube is not properly exposed to and equilibrated with the buffer gas and an oxygen promoted high degree of attack of the sample by the silicon occurs. In order that all faces of the silicon cube and the sample surface be equilibrated with the flowing

buffer gas, a small chip of silicon was used to tilt the cube (Fig. 1).

The buffer gas used to maintain the required low oxygen partial pressure in the sessile drop furnace was a H_2/H_2O mixture having a ratio of between $10^4/1$ and $10^6/1$ and a flow rate of about 700 cc/min. The hydrogen supply was from standard cylinders, routed first through a liquid nitrogen bath trap to condense out water, thus increasing the H_2/H_2O ratio and lowering the oxygen partial pressure, and then through the oxygen cell to determine the precise oxygen partial pressure, which was typically between 10^{-18} and 10^{-21} atm.

All samples, with the exception of the ultracarbon SiC coated graphite which will be discussed in a later paragraph, were polished to a uniform degree prior to the sessile drop experiments to eliminate the surface roughness variable, permitting comparison of the surface attack on each sample after sessile drop experiments had been carried out.

Heat-up time for the system after insertion of the sample was about 4 hours, so some effects were observed herein which were not seen by other experimenters whose systems come to temperature much more quickly. Information was desired about the molted silicon-refractory interaction over a long enough period to be considered characteristic of actual silicon sheet and ribbon production times, so the silicon sessile drop was usually maintained at 1700K for 8 hours.

---

* Equivalent to a linear flow rate of ~1 cm/sec. to assure equilibrium between sample and buffer.

Figure 1: Schematic diagram showing how a silicon cube is tilted using a silicon chip so all faces of the cube and the entire substrate surface are exposed to the flowing buffer gas prior to melting.

Silicon Cube

Silicon Chip

Substrate

"D" Tube
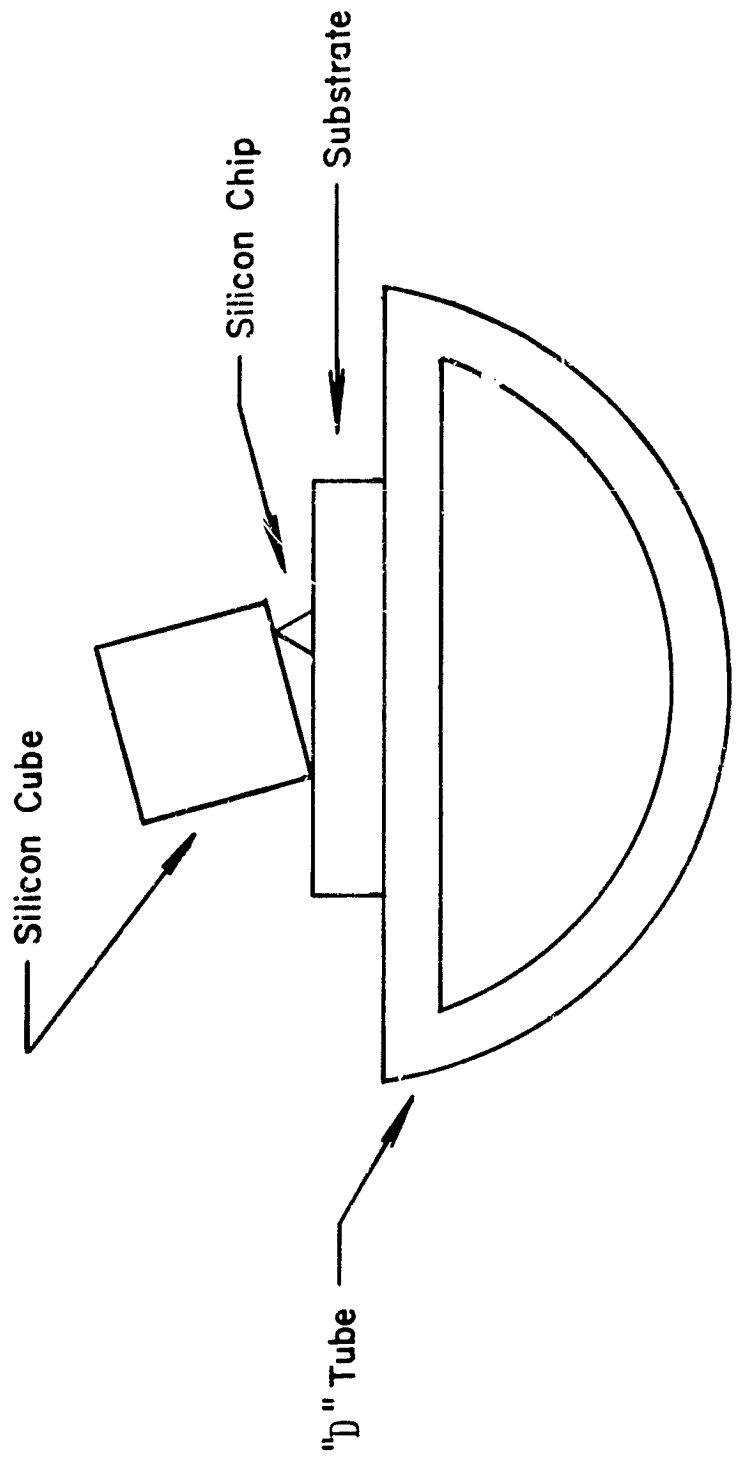
Silicon Nitride

Contact angles were measured as a function of time, and the results are plotted on the graph in Figure 2.

The CNTD Si_3N_4 coated on hot pressed silicon nitride (supplied by Chemetal - Eagle Picher) was used to verify reproducibility since this material had undergone similar testing in previous work for JPL at UMR. Both contact angle data (Fig. 2) and the character of the post sessile drop silicon - CNTD Si_3N_4 coating interface were in excellent agreement with the previous work.

The contact angle data for the AVCO hot pressed silicon nitride agreed favorably with the data on CNTD coated Si_3N_4, but the KBI hot pressed silicon nitride gave contact angles that decreased much more rapidly, this being indicative of much interaction between the molten silicon and the KBI substrate.

Contact angle vs. time graphs for two silicon sessile drop experiments on identical KBI hot pressed Si_3N_4 samples are shown in Figure 3 to demonstrate the importance of allowing the system to come to equilibrium before melting the silicon. In the first run, the system was taken to 1700K directly, and the silicon melted without a pre-melt hold time. The sessile drop that was formed had a contact angle well above 90°, which decreased to 46° after 8 hours. In the next run, the system was held at 1650K for 3 hours, then raised past the silicon melting temperature. This time the initial contact angle was well below 90°. Photomicrographs of the interface between the KBI silicon nitride and

Figure 2: Contact angle vs. time and pO2 for silicon sessile drops on silicon nitride: (a) Kawecki-Berylco (KBI) hot pressed, (b) KBI hot pressed with no premelt hold, (c) AVCO hot pressed, (D) CNTD coated.
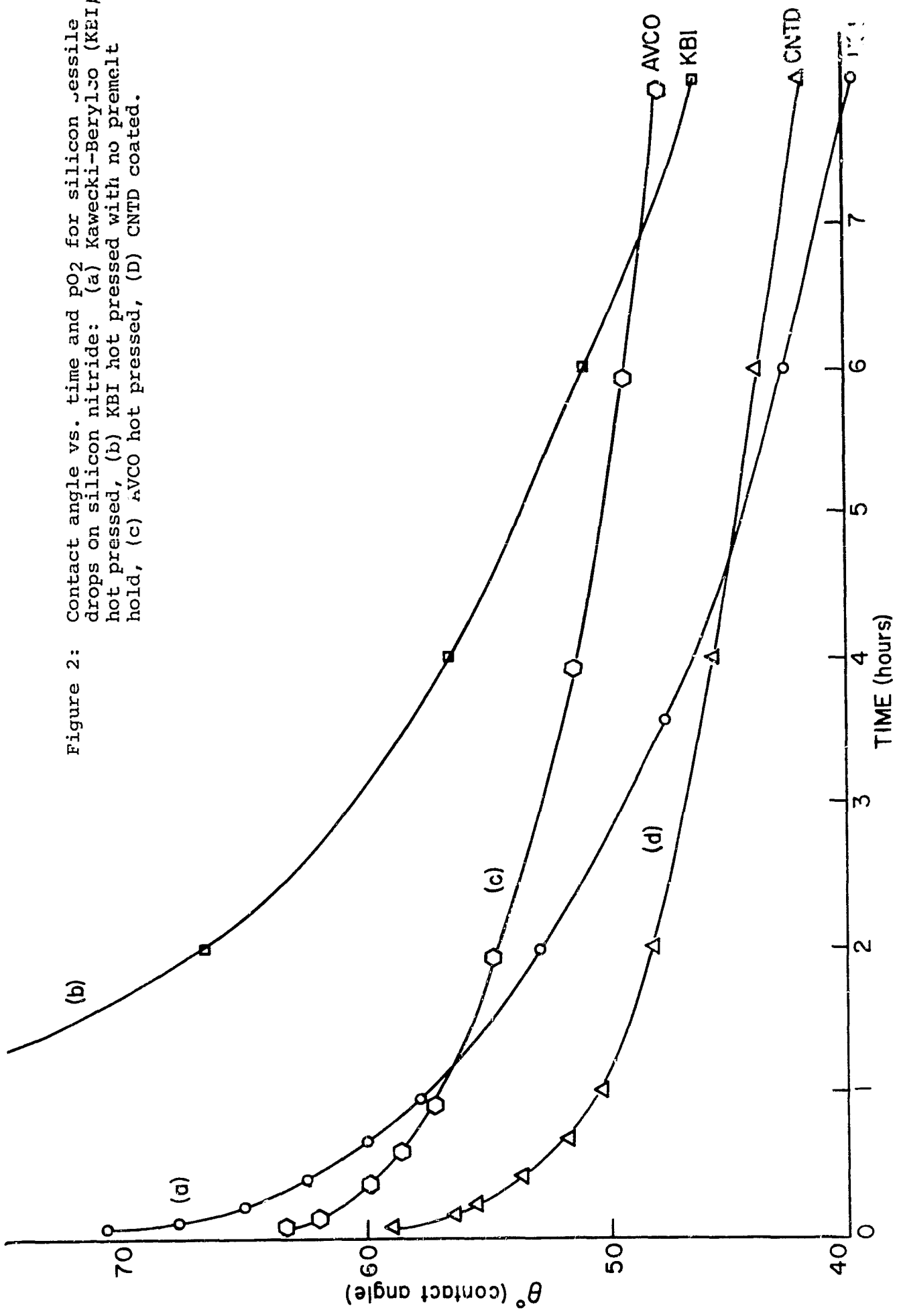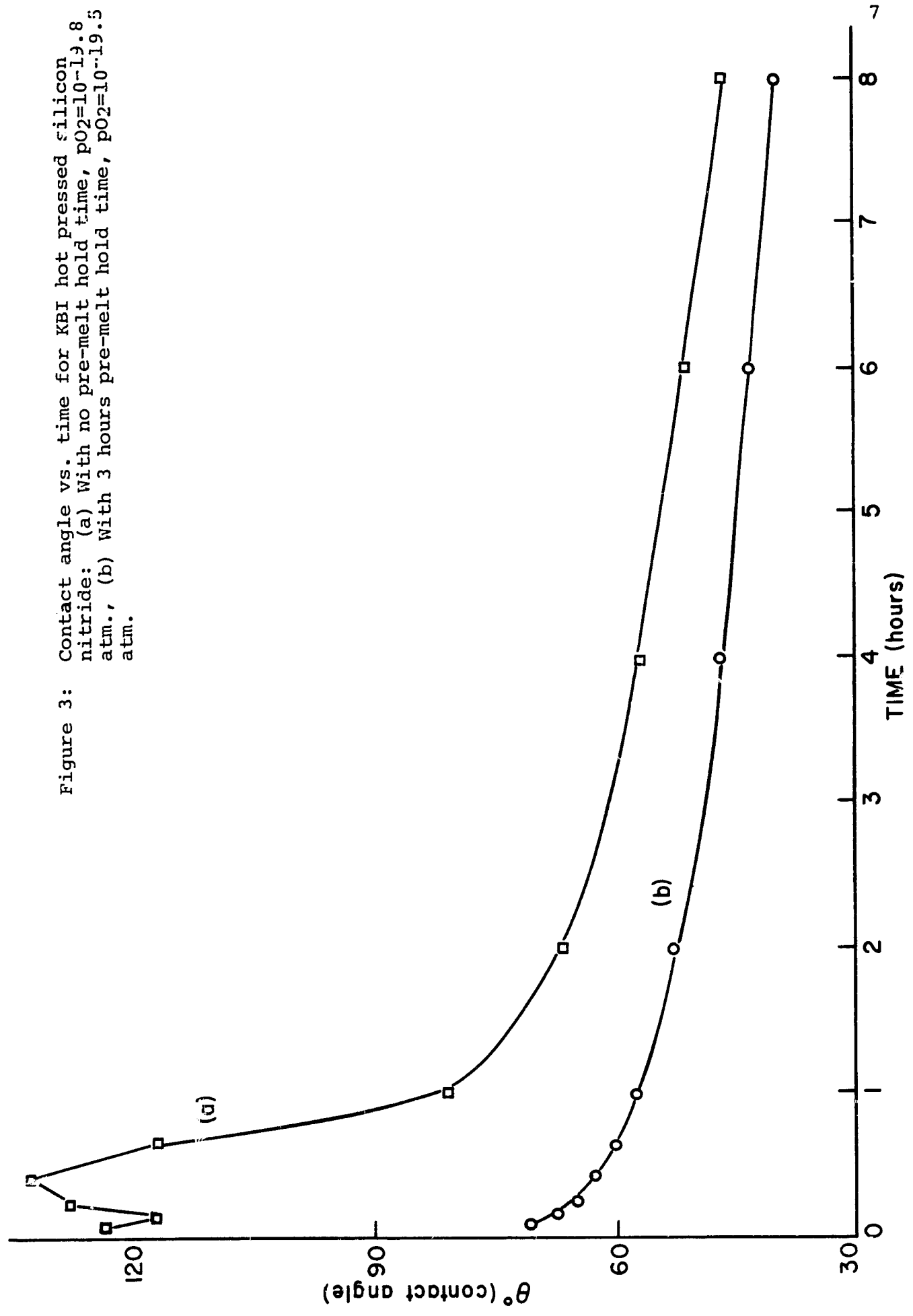
Figure 3: Contact angle vs. time for KBI hot pressed silicon nitride: (a) With no pre-melt hold time, $pO_2=10^{-19.8}$ atm., (b) With 3 hours pre-melt hold time, $pO_2=10^{-19.5}$ atm.

the silicon (Fig. 4) show that the silicon attack is more pronounced in the sample that did not experience a pre-melt hold time (Fig. 4a) than in the case where the sample was held for 3 hours prior to melting (Fig. 4b).

The AVCO hot pressed silicon nitride sample (Fig. 5) does not show any evidence of the infiltration of silicon below the silicon-silicon nitride interface, although there is about the same degree of irregularity of the interface as compared to the KBI material. Of the hot pressed materials without coating, the AVCO material exhibited properties (both contact angle and resistance to silicon attack) that were comparable to the CNTD material and superior (i.e., lower, more stable molten silicon contact angle and less interaction) to any other hot pressed Si_3N_4 tested.

Silicon Carbide Coated Graphite

When a silicon sessile drop experiment was made on a polished sample of silicon carbide coated graphite supplied by Ultracarbon (Fig. 6), the silicon did not melt into a smooth drop, but showed facets, such as would occur if the faces of the silicon cube had merely spread out with the molten silicon underneath. There was no change in this configuration for nearly 1 3/4 hours, when it was observed that the drop had completely disappeared. After cooling and sectioning, it could be seen that the silicon had completely penetrated the coating and was absorbed into the graphite substrate (Fig. 7). To eliminate the possibility that the silicon carbide coating had been too thin after polishing

Figure 4: Photomicrograph of KBI hot pressed silicon nitride-silicon interface after 8 hours at 1430°C.
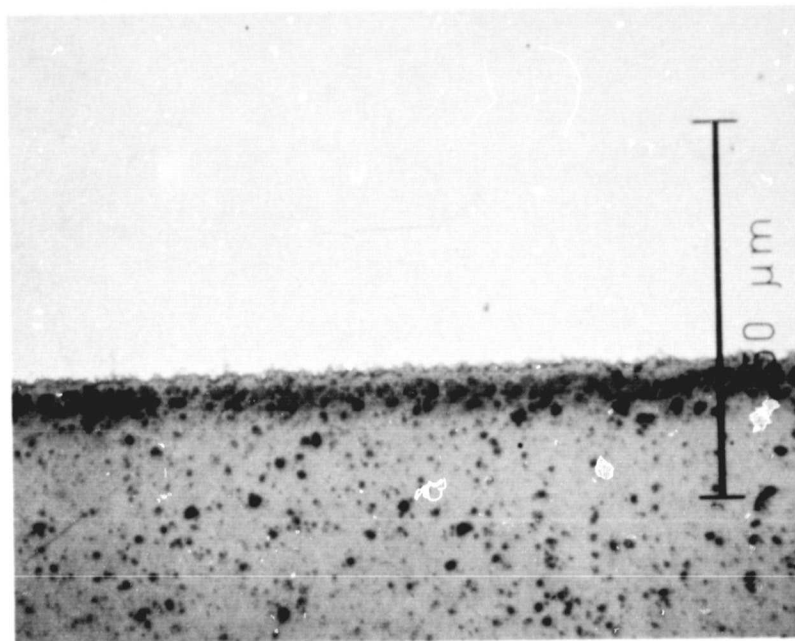
(a) With no pre-melt hold time, $pO_2 = 10^{-19.8}$ atm.
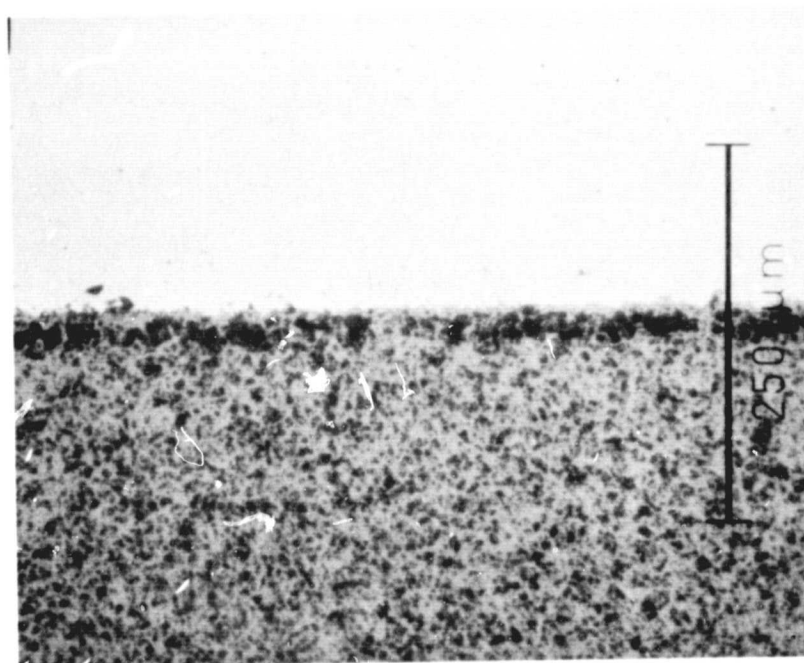
(b) With 3 hours pre-melt hold time, $pO_2 = 10^{-19.9}$ atm.

Figure 5: Photomicrograph of silicon - AVCO hot pressed silicon nitride interface after 8 hours at 1430°C with a $pO_2 = 10^{-19.9}$ atm.

Figure 6: In situ photographs at 1430°C of silicon sessile drop experiment on polished Ultracarbon silicon carbide coated graphite with pO_2 = $10^{-19.9}$ atm.
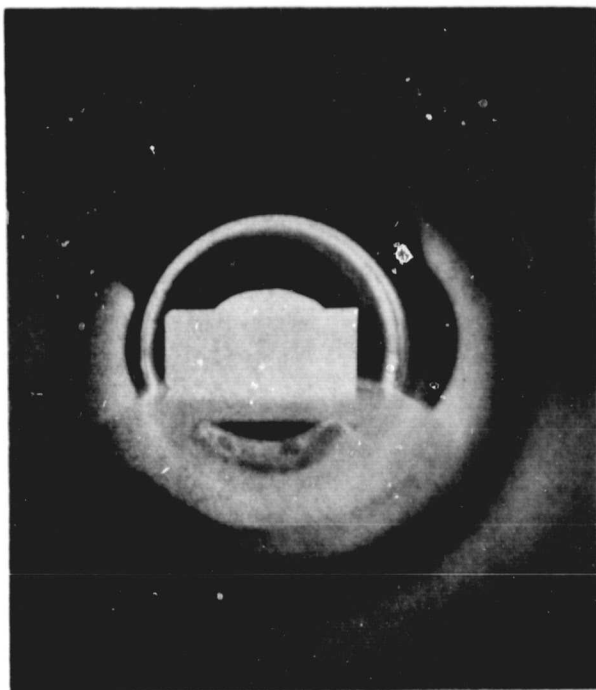
(a) 1 hour after silicon melt.

(b) 1 hour, 45 minutes after silicon melt.
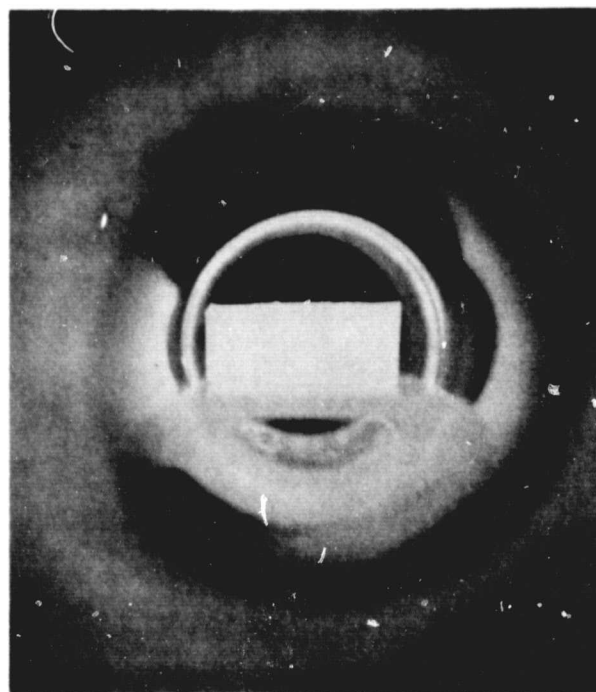
Figure 7: Photomicrograph of post-sessile drop section of polished Ultracarbon silicon carbide coated graphite after 1 3/4 hour experiment at $pO_2 = 10^{-19.9}$ atm. showing infiltration of silicon below SiC coating.

to be impervious to the liquid silicon, another experiment using an unpolished sample was tried. This time, a stable drop was never established, but the silicon was absorbed into the substrate as rapidly as it melted (Fig. 8). Photomicrographs of the sectioned sample, Figure 9, show that the SiC coating has many pores through which the silicon could flow, and the silicon has spread out uniformly through the surface of the graphite underneath the silicon carbide coating. It appears that the graphite would have to be saturated with silicon, forming a dense SiC layer before this material would be impervious to further liquid silicon penetration. Siltec Corporation is successfully using this type of Ultracarbon material in a non-liquid silicon environment transfer tube application. With rapid heat-up, JPL has obtained short time silicon sessile drop data on this material.

Sialon

As has been mentioned above, it was considered important in the silicon sessile drop experiments to allow all surfaces to come to equilibrium with the low oxygen partial pressure in the flowing hydrogen buffer gas. The experiments were carried out with the sample just below the melting temperature of silicon from one to three hours so equilibrium could be reached prior to melting. This same procedure was applied to the experiments on β Sialon (supplied by Battelle) with even longer equilibration times. Surprisingly, the silicon cube never melted (Fig. 10a) even though the temperature was raised
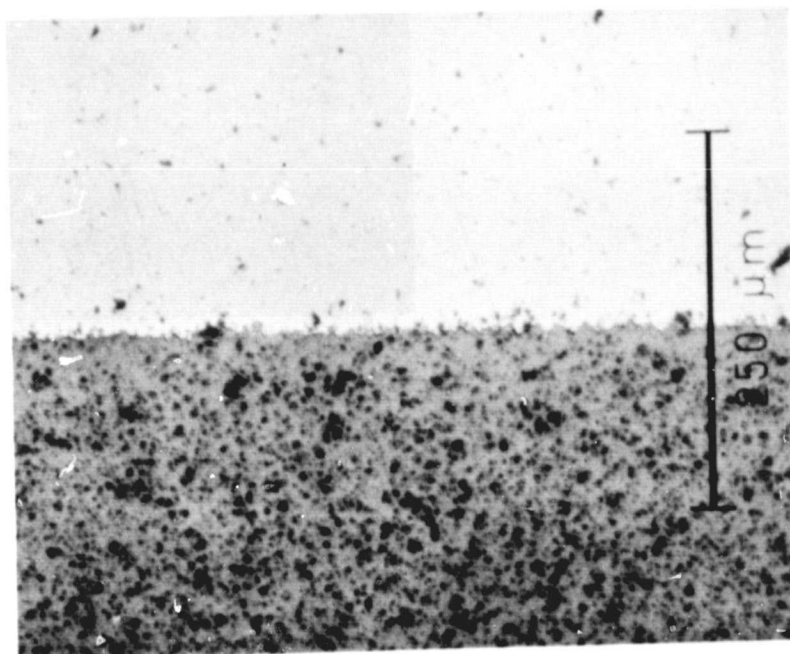
Figure 8: In situ photographs at $1430^{\circ}C$ of silicon sessile drop experiment on unpolished Ultracarbon silicon carbide coated graphite with $pO_2 = 10^{-20.2}$ atm. after:
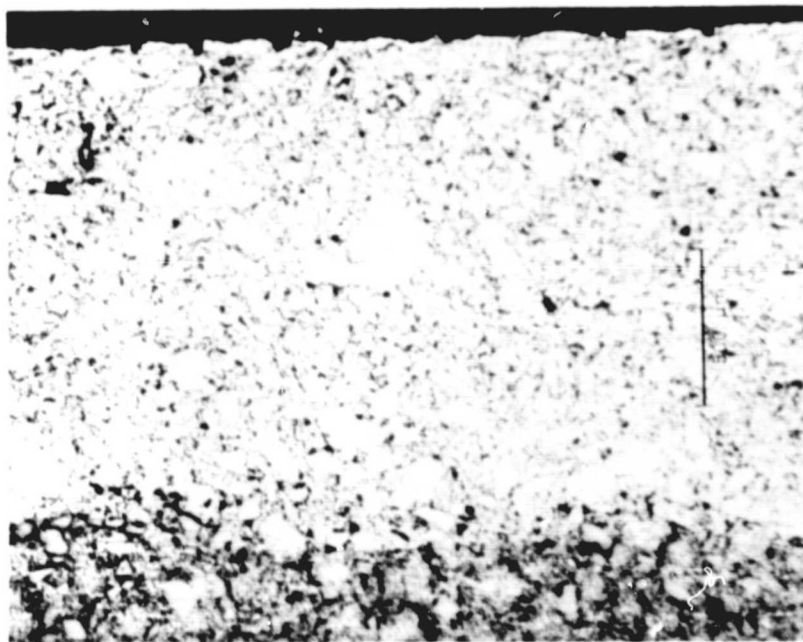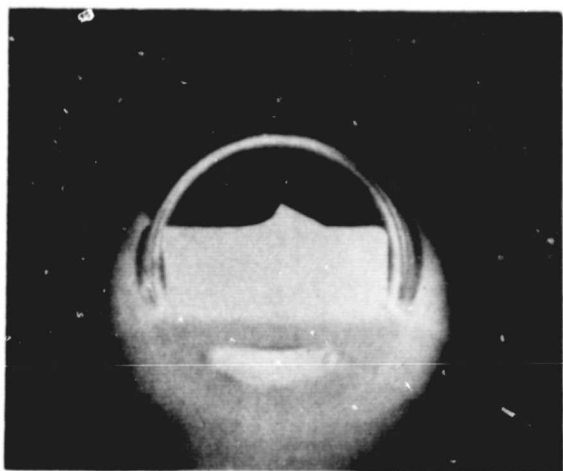

(a) 4 min.
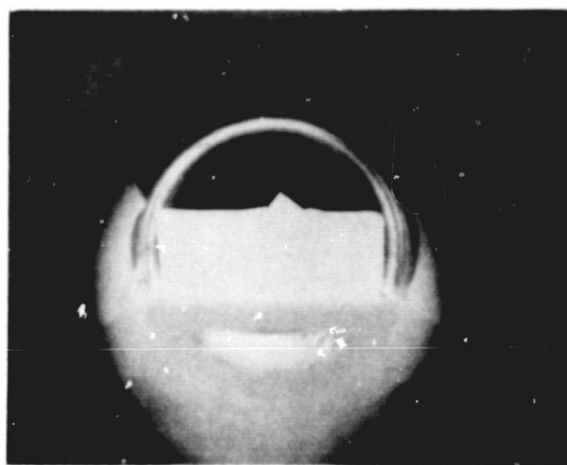
(b) 6 min.
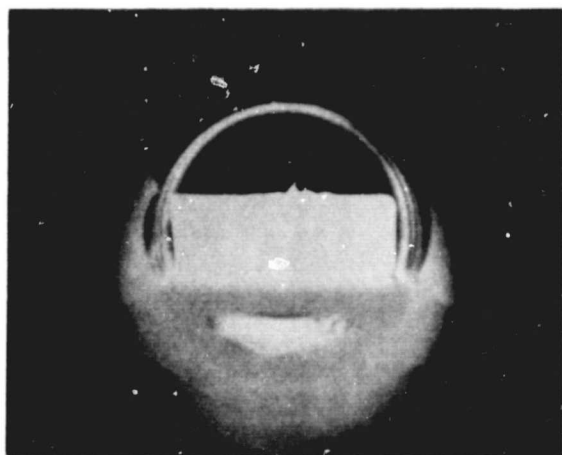
(c) 8 min.
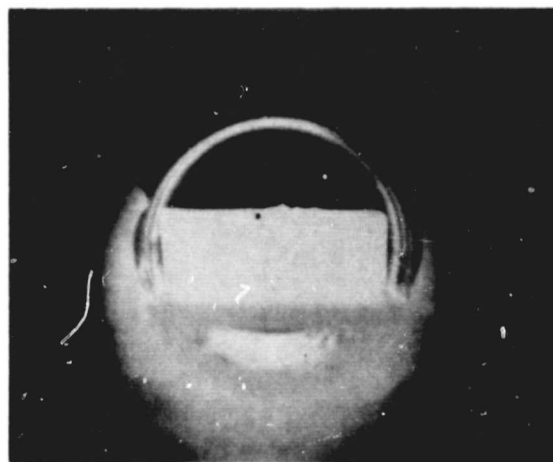
(d) 1 hour.

Figure 9: Photomicrographs of post-sessile drop section of unpolished Ultracarbon silicon carbide coated graphite after 1 hour at $pO_2=10^{-20.2}$ atm. showing infiltration of silicon below SiC coating.
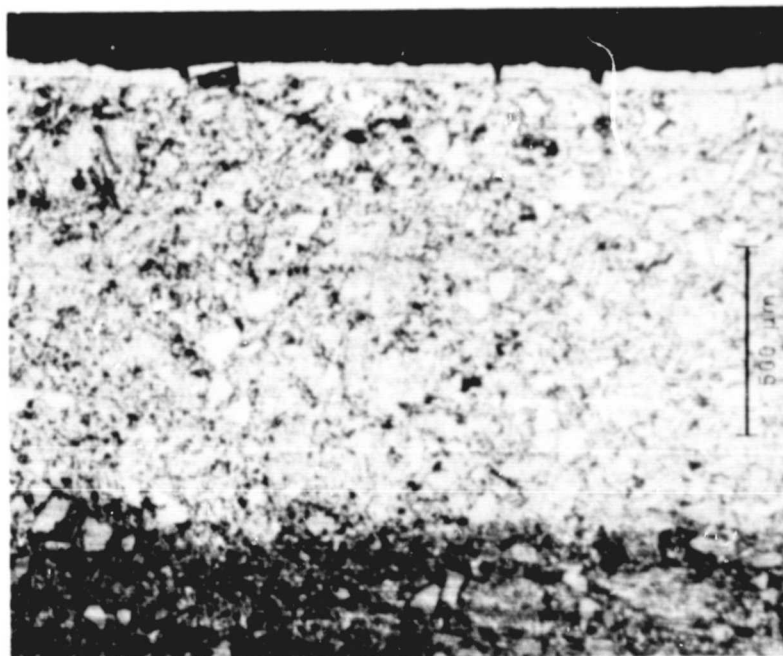
(a) Under original position of the silicon.
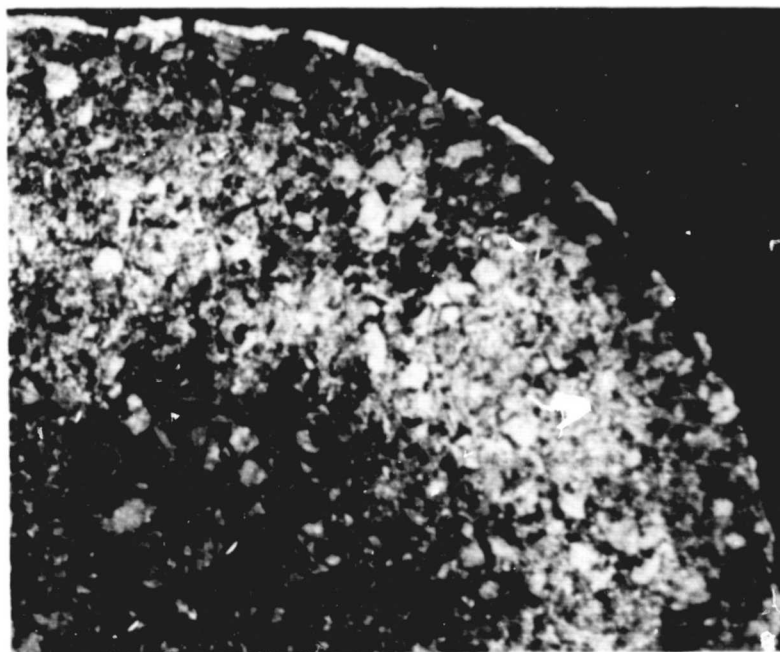
(b) At the edge of the sample.
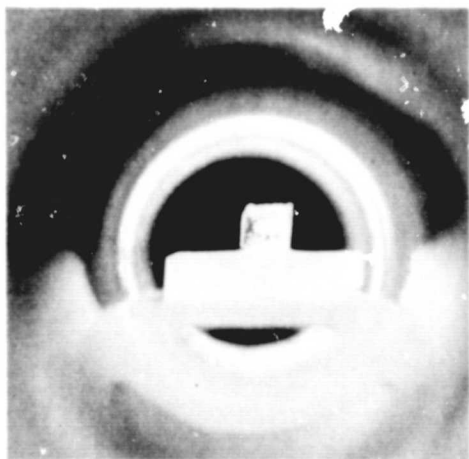
(a) 9 hours,
$pO_2 = 10^{-19.7}$ atm.
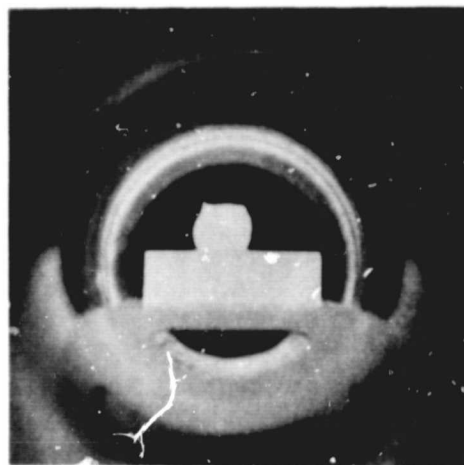
(b) 5 hours
$pO_2 = 10^{-20.2}$ atm.

Figure 10:   In situ photographs of silicon sessile drop experiments on Ω Sialon 25 min. after reaching melting temperature for sample held just below melting temperature for:
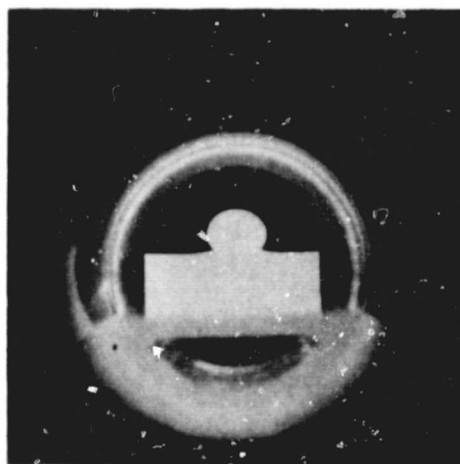
(c) 1.5 hours
$pO_2 = 10^{-20.2}$ atm.

to well above the silicon melting temperature. In subsequent experiments (Fig. 10b, 10c), the length of time the system was allowed to remain just below the melting temperature was reduced until it was possible to achieve an apparent sessile drop with a contact angle greater than 90°. However, in every case when the system was again cooled below the melting point, liquid silicon was observed to protrude from the cooling drop as if breaking through a skin (Fig. 11), even in the case where it appeared that a clean silicon sessile drop had formed. When the silicon was examined with a scanning electron microscope, it was found that there was indeed a skin over parts of the silicon (Fig. 12) having a high concentration of calcium (Fig. 13). The surface of the β Sialon also had a white powdery coating, x-ray analysis of which showed a structure quite different from the original Sialon. There is ample evidence in the alumina literature[2-10] that calcium present in only very small amounts as an impurity can migrate to grain boundaries and surfaces to quite high concentrations, which appears to be the case in these experiments. This is one example of an effect which would not be observable if a rapid heat-up rate were used. It is likely, however, that a skin over the silicon having a high concentration of calcium would be present even though it appeared that a clean sessile drop formed on the β Sialon when heated rapidly. The "contact angle" in this case would not represent that of a clean silicon drop in equilibrium.
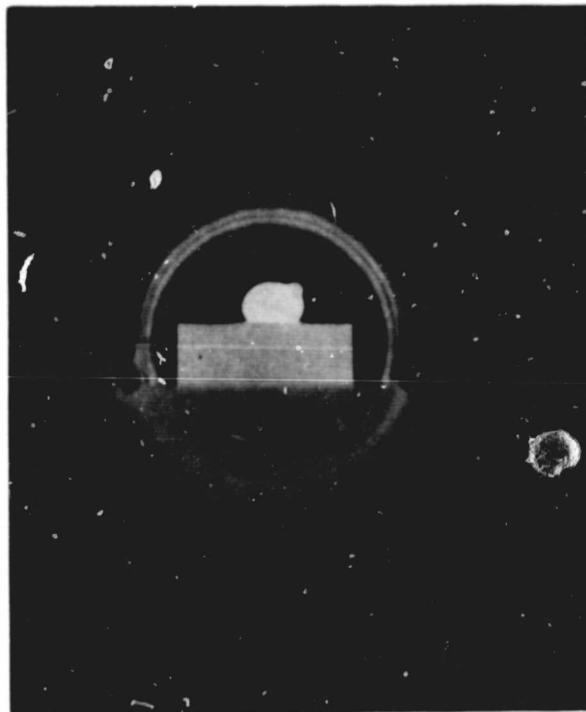
Figure 11: In situ photograph of silicon sessile drop experiment on Ω Sialon after cooling below melting point.
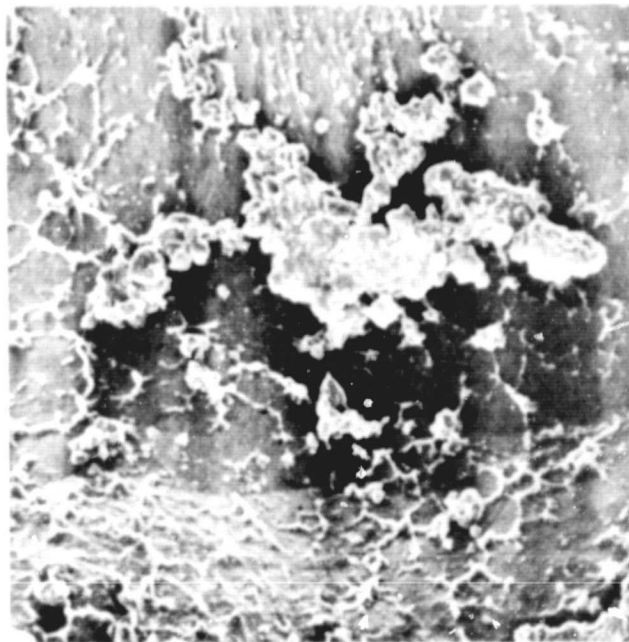
Figure 12: Scanning Electron Microscope phtomicrograph of silicon surface after sessile drop experiment on Ω Sialon.

Si   Fe Cu   Si   Ca Ti   Fe   Cu Zn
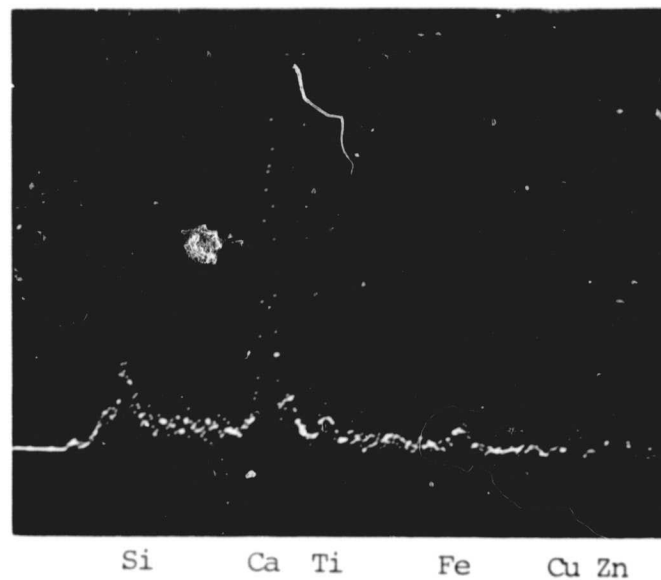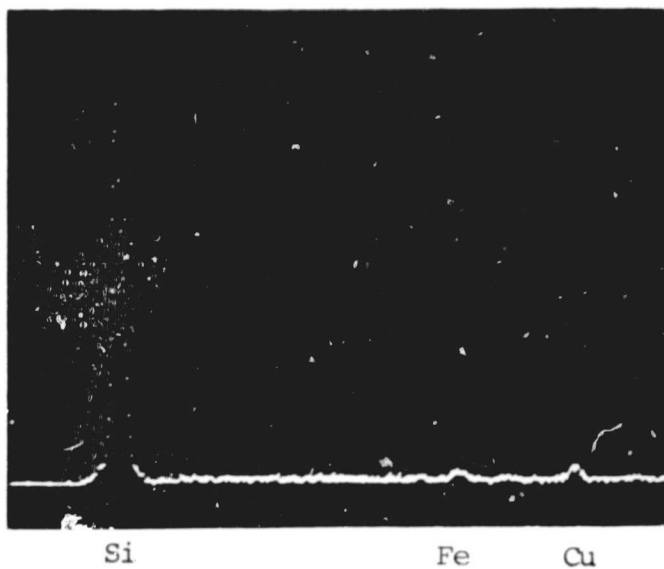
Figure 13: Non-dispersive x-ray analysis of silicon sample of Fig. 12 showing:

(a) Silicon in darker areas,   (b) Calcium in lighter areas.

SURFACE ENERGIES

The quantities which determine the way in which a liquid wets a solid, and thus the contact angle of a sessile drop, are the surface energies γ_{sv}, γ_{sl}, and γ_{lv}, where the subscripts refer to solid-vapor, solid-liquid, and liquid-vapor, respectively. If the sessile drop and the substrate are in an atmosphere containing molecules such as oxygen that will adsorb onto the solid substrate, then the surface energy, γ_{sv}, will be affected, decreasing as more molecules are adsorbed, while the other surface energies, γ_{sl} and γ_{lv}, will be relatively unaffected. By integrating the Gibbs' adsorption isotherm,

$$\left(\frac{d\gamma}{d\mu}\right)_T = - \Gamma$$

where: γ = interfacial free energy

μ = chemical potential of the adsorbed species

Γ = adsorbed species per unit area (coverage)

and assuming the adsorbed species to be oxygen, so that:

$$\mu = kT \ln pO_2 \quad ,$$

then combining this result with the Young equation:

$$\gamma_{sv} = \gamma_{ls} + \gamma_{lv} \cos \Theta \quad ,$$

where Θ is the contact angle of the sessile drop, we get:

$$\cos \Theta = - \left(\frac{kT\Gamma O_2}{\gamma_{lv}}\right) \ln pO_2 + \frac{\gamma_{ls}}{\gamma_{lv}} \ .$$

Since γ_{ls} and γ_{lv} are relatively insensitive to changes in pO_2, and assuming ΓO_2 varies much more slowly than $\cos \Theta$

with changes in pO_2, then by measuring the contact angles of sessile drops as a function of oxygen partial pressure, the value of ΓO_2, the number of oxygen molecules adsorbed per unit area, and γ_{sv}, the solid-vapor surface energy for the solid substrate can be obtained. This constitutes a new method for measuring the solid-vapor surface energy.

A more detailed derivation of the theoretical relationships between contact angle, oxygen partial pressure, surface coverage and energies can be found in reference 11 along with measured values of these quantities for CNTD silicon carbide, silicon nitride, and aluminum nitride.

DEVITRIFICATION OF FUSED SILICA

When fused silica has been used as a substrate in silicon sessile drop experiments at UMR, devitrification has taken place in every case, effectively eliminating fused silica from further sessile drop experiments. Some attempt was made to determine if the furnace atmosphere had any effect on the devitrification. Although it was determined that the primary cause of devitrification was the slow heat-up (4 hours) and cool-down (8 hours) cycles of the UMR sessile drop furnace, the degree of devitrification was affected by the atmosphere, with nearly complete devitrification taking place in the CO/CO_2 atmosphere (60 parts CO to 1 part CO_2) and surface devitrification only on the silica heated in air and in helium.

OXYGEN PARTIAL PRESSURE MEASUREMENTS

AT OTHER FACILITIES

Mobil Tyco

The atmosphere in the Mobil-Tyco EFG ribbon pulling furnace consists of argon which flows into the system at a rate varying from 10 liters per minute to 2 liters per minute. Typically, commercially available argon contains oxygen as an impurity in about 1 to 100 parts per million, corresponding to 10^{-6} to 10^{-4} atm. oxygen partial pressure at 1 atm. total pressure. The furnace contains large amounts of graphite as crucibles, heaters, die and die holder, etc., all of which serve to reduce the amount of free oxygen in the system and thus lower the pO_2.

Prior to actual measurements of the oxygen partial pressure of the furnace atmosphere, the performance of the oxygen cell was first checked by measuring the pO_2 of forming gas (95% N_2, 5% H_2). The value of 10^{-19} atm. at $1000^{O}C$ obtained was consistent with previous measurements made with the cell at UMR.

The argon purge gas did not have a specific gas exit port from the furnace, but instead was allowed to escape through the silicon ribbon exit slot and various other openings to the atmosphere. Since there was not sufficient pressure under these conditions to force the argon through the oxygen cell, it was found necessary to sample the furnace gas oxygen partial pressure by inserting a quartz tube through one of the openings to the furnace and drawing gas into the

oxygen sensor with a mechanical pump hooked to the oxygen cell exhaust line. Since the cell had not initially been designed to operate under a negative pressure, there existed a possibility that oxygen may have been drawn into the cell (in small quantities) from the air. The seals have subsequently been improved and checked under negative pressures comparable to those existing in the above measurements. Another visit to the Mobil Tyco facility is planned to verify the initial measurements.

JPL

The oxygen cell was transported to the JPL facility at Pasadena, California, where the oxygen partial pressure of the atmosphere in their silicon sessile drop furnace was measured. The gas used in this furnace was helium from standard cylinders, which typically have oxygen impurity levels of about 10^{-5} atm. pO_2 at one atmosphere total pressure. The flow rates used varied between 16 and 22 SCFH, or from 5 to 10 ℓ/min. In this case, the furnace was sealed so the intake and exhaust gas could be sampled at the required flow rate without the use of a pumping system. There was graphite present in the furnace, as in the case of the Mobil Tyco furnace, which would reduce the oxygen content of the atmosphere by forming CO and CO_2.

Results and Discussion

When an inert carrier gas, such as argon or helium, having an oxygen impurity level of between 1 ppm and 100 ppm (corresponding to oxygen partial pressure between 10^{-6} atm.

and 10^{-4} atm.), comes in contact with graphite at 1700K, the following reaction occurs: $2C + O_2 \rightarrow 2CO$. If the gas flow is sufficiently slow and all the gas comes in intimate contact with 1700K graphite such that an equilibrium is established, all but a very small fraction of the oxygen would combine with carbon to form CO, resulting in a pO_2 of 9.5×10^{-17} atm. in the exit gases at 1700K. However, if the flow rate were too high and/or the gas did not all contact 1700K graphite, then equilibrium would not be established, and significant amounts of oxygen would remain unreacted, resulting in a higher pO_2 and a lower pCO.

This non-equilibrium behavior is in qualitative agreement with the CO measurements made on the Mobil Tyco furnace gas by the Kitagawa cell method simultaneously with the oxygen partial pressure measurements. With a high (10 ℓ/min.) argon purge rate, the CO concentration was less than 30 ppm, but this increased to over 100 ppm when the purge rate was dropped to 2 ℓ/min. as would be expected nearer equilibrium conditions.

The oxygen partial pressure of the purge gas after passing through the furnace was measured at 1273K by the oxygen cell to be $10^{-12.1}$ atm. for the Mobil Tyco system and $10^{-13.4}$ atm. for the JPL system, indicating that in both cases, roughly half of the original oxygen impurity was converted to CO.

The figure of one-half can be rationalized by considering the following scenario: Consider one million units of "inert"

gas containing 100 units O_2 as an impurity entering a molten sili-
con furnace at 1700K. (1) Use x parts O_2 to form 2x parts CO,
leaving 100-x parts O_2 unreacted. This non-equilibrated mixture
of gases consisting of nearly one million parts inert gas, 2x
parts CO, and 100-x parts oxygen, then leaves the silicon furnace
and enters the oxygen cell where it equilibrates at 1273K. If x
is less than 50, then (2) 2x parts CO combine with x parts O_2 to
form 2x parts CO_2 and leaving 100-2x parts O_2 still unreacted.
This constitutes a pO_2 of $(100-2x) \times 10^{-6}$ atm. If x is greater
than 50, then (3) most of the O_2 leaving the silicon furnace,
that is, 100-x parts O_2 combine with $2x-\delta$ parts CO (leaving δ
parts unreacted) to form $2x-\delta$ parts CO_2 according to the reaction:

$$(2x-\delta) CO + (100-x) O_2 = (2x-\delta) CO_2$$
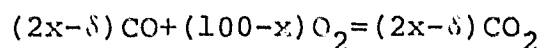
For this to balance, then $2x-\delta = 2(100-x)$, or $\delta = 4x-200$, and the
resulting CO/CO_2 ratio is:

$$\left(\frac{pCO}{pCO_2}\right) = R = \frac{\delta}{2x-\delta} = \frac{2x-100}{100-x} .$$

The amount of oxygen used in the first reaction, x, can be found
from the pO_2 measured in the oxygen cell by solving the mass
action equation for x; using the above CO/CO_2 ratio:

$$pO_2 = \left(\frac{pCO_2}{pCO}\right)^2 \exp \frac{\Delta G}{RT}$$

$$x = 100 \left(\frac{1 + \left(\frac{pO_2}{\exp \Delta G/RT}\right)^{1/2}}{1 + 2\left(\frac{pO_2}{\exp \Delta G/RT}\right)^{1/2}} \right)$$

The results of plotting Log pO_2 vs. 100-x is shown on Figure
14, where it can be seen that if half the impurity O_2 reacts

Figure 14: Graph of Log pO$_2$ of equilibrated gas at 1273K versus parts O$_2$ unreacted at 1700K. Based on 100 parts oxygen impurity per million parts purge gas.

Parts O$_2$ Unreacted

(ppm, or x10^{-6} to get PO$_2$ in silicon furnace)
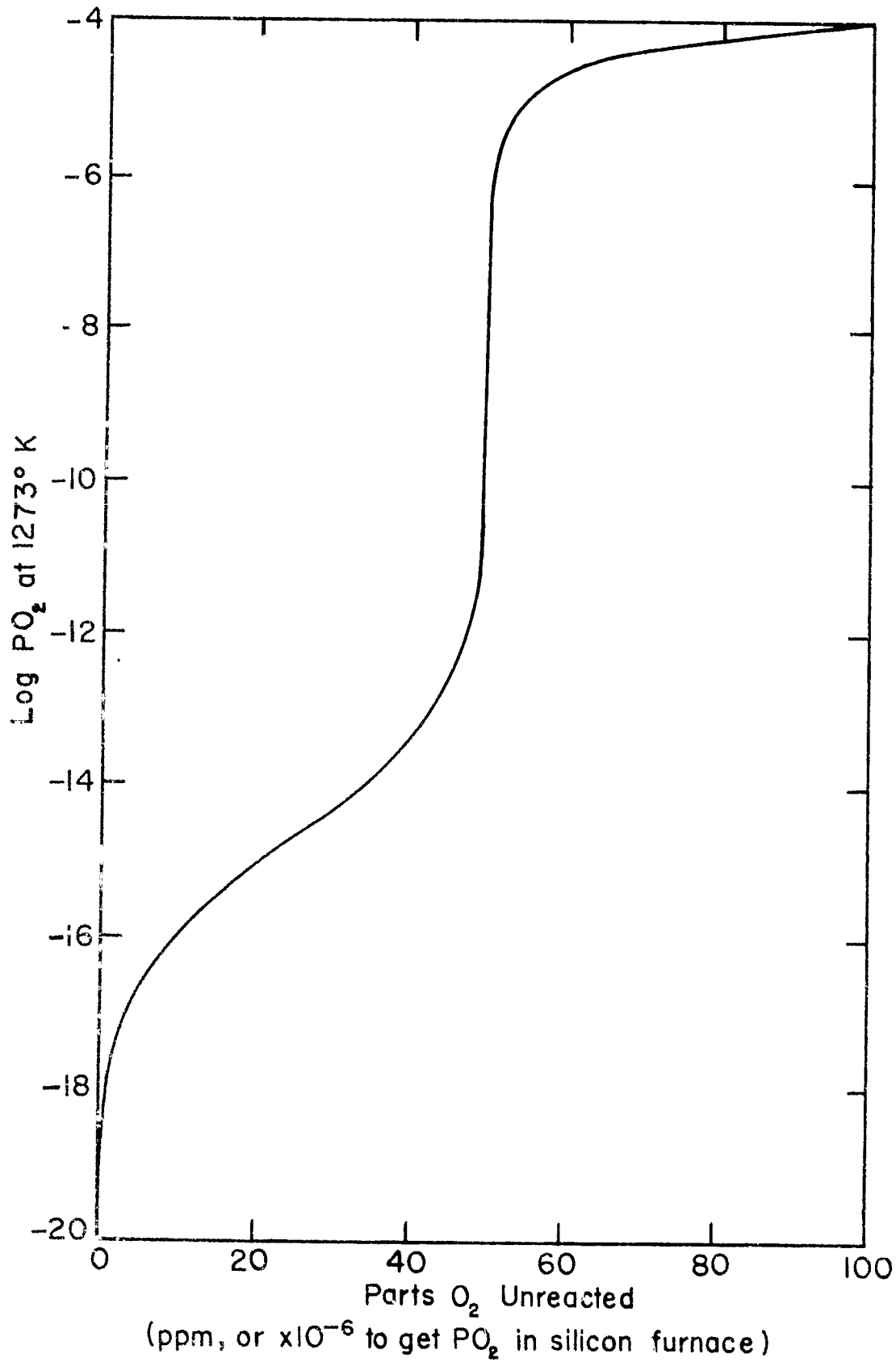
with carbon in the silicon furnace, the oxygen partial pressures in the range between 10^{-5} and 10^{-13} atm. should be measured with the oxygen cell.

SUMMARY & CONCLUSIONS

All sessile drop experiments were conducted at one atmosphere total pressure and oxygen partial pressures less than 1×10^{-19} atmospheres. The materials investigated for potential die and container applications in the present study fall into two categories; Those upon which silicon melts, forming a sessile drop with an equilibrium contact angle, and those upon which a contact angle representing equilibrium between clean liquid silicon, the substrate candidate material, and the gaseous environment, is not obtained.

In the first category are two varieties of hot pressed silicon nitride (from Kawecki-Berylco (KBI) and AVCO) and CNTD silicon nitride coated on hot pressed silicon nitride. The silicon - CNTD silicon nitride contact angle data obtained in this study agree very well with previous measurements made on the same material, and therefore provided a control for reproducibility verification. Although the final contact angle (after 8 hours) of molten silicon on the AVCO hot pressed silicon nitride is higher than for the KBI material, the latter appears to react more strongly with molton silicon, as evidenced by photomicrographs and the continued decrease in contact angle after 8 hours.

Ultracarbon silicon carbide coated graphite and Battelle Ω'
Sialon fell into the category of materials on which silicon did
not form a true sessile drop. In the formal material, the SiC
coating proved to not be a completely integral surface, so molten
silicon could seep through the coating to the underlying graphite,
which is very porous and subject to impregnation by the molten
silicon. For the limited size silicon sample used in the sessile
drop experiments, all of the silicon penetrated the SiC coating,
saturating the graphite under the coating and precluding the
formation and measurement of an equilibrium contact angle on this
material.

A pseudo-sessile drop formed on the Battelle Ω' Sialon be-
cause a semi-rigid, skinlike coating having a high concentration
of calcium formed on the surface of the liquid silicon drop pre-
venting attainment of equilibrium. The thickness of this coating,
and thus its rigidity, depended on the length of time the sample
was held just below the silicon melting temperature prior to the
melt plus the time after melting. For short pre-melt hold times,
the silicon appeared to form a high-contact angle drop, but sub-
sequent cooling showed evidence of the thin coating on the silicon
surface. The Ultracarbon SiC on graphite and the Battelle Ω'
Sialon materials are, therefore, not recommended for use as die
or container materials for containment of molten silicon.

Analysis of the oxygen content of the purge gases in the
Mobil Tyco silicon ribbon pulling furnace and the JPL silicon
sessile drop furnace shows the presence of relatively high

quantities of oxygen - of the order of 1 to 100 parts per million - which is far higher than the $Si-O_2$ equilibrium partial pressure of 10^{-19} atm. The fact that oxide does not form to the extent expected under equilibrium conditions such as those established in the UMR sessile drop experiments indicates that these equilibrium conditions are not achieved in the Mobil Tyco and JPL furnaces. Possible reasons for this include the high purge gas flow rates, large amounts of hot graphite which removes oxygen from the gas preferentially near the molten silicon, and reaction rates that are slow compared to experimental hold and thermal cycle times in the case of the JPL sessile drop furnace.

REFERENCES

1. Eagle Picher Final Report to JPL on contract #DOE/JPL-954877-78/3.

2. P.J. Jorgensen and J.H. Westbrook, "Role of Solute Segregation at Grain Boundaries During Final-Stage Sintering of Alumina," J. Am. Cer. Soc., 47(7), 332-38, (1964).

3. S.S.C. Tong and J.P. Williams, "Chemical Analysis of Grain Boundary Impurities in Polycrystalline Ceramic Materials by Spark Source Mass Spectrometry," ibid., 53(1), 58-59, (1970).

4. H.L. Marcus and M.E. Fine, "Grain-Boundary Segregation in MgO-Doped Al_2O_3," ibid., 55(11), 568-70, (1972).

5. W.C. Johnson and D.F. Stein, "Additive and Impurity Distributions at Grain Boundaries in Sintered Alumina," ibid., 58(11-12), 485-88, (1975).

6. R.I. Taylor, J.P. Coad, and R.J. Brook, "Grain-Boundary Segregation in Al_2O_3," ibid., 57(12), 539-40, (1974).

7. R.I. Taylor, J.P. Coad, and A.E. Hughes, "Grain-Boundary Segregation in MgO-Doped Al_2O_3," ibid., 59(7-8), 374-75, (1976).

8. A.W. Funkenbusch and D.W. Smith, "Influence of Calcium on the Fracture Strength of Polycrystalline Alumina," Metall. Trans., A6(12), 2299-2301, (1975).

9. W.C. Johnson, "Mg Distributions at Grain Boundaries in Sintered Alumina Containing $MgAl_2O_3$ Precipitates," J. Amer. Cer. Soc., 61(5-6), 234-37, (1978).

10. D.R. Clarke, "Grain-Boundary Segregation in an MgO-Doped Al_2O_3," J. Amer. Cer. Soc., 63, 339, (1980).

11. M.W. Barsoum and P.D. Ownby, "Effect of Oxygen Partial Pressure on Wetting of SiC, AlN, and Si_3N_4 by Si, and a Method for Calculating Surface Energies Involved," Proceedings of 7th LBL/MMRD International Materials Symposium, 17th University Conference on Ceramics, University of California, Berkeley, California, July 28-August 1, 1980 and M.W. Barsoum, M.S. Thesis, University of Missouri-Rolla, (1980).