85
9-20-78

12. 644

DOE/JPL/954877-3

STUDY PROGRAM TO DEVELOP AND EVALUATE DIE AND CONTAINER
MATERIALS FOR THE GROWTH OF SILICON RIBBONS

Quarterly Report No. 3

MASTER

MASTER

July 1978

Work Performed Under Contract No. NAS-7-100-954877

Miami Research Laboratories
Eagle-Picher Industries, Inc.
Miami, Oklahoma

U.S. Department of Energy

Solar Energy

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Paper Copy \$5.25

Microfiche \$3.00

STUDY PROGRAM TO DEVELOP AND EVALUATE DIE AND CONTAINER MATERIALS FOR THE GROWTH OF SILICON RIBBONS

Paul E. Grayson, Program Manager
Larry A. Addington, Project Engineer

Miami Research Laboratories
Eagle-Picher Industries, Inc.
Miami, Oklahoma 74354

QUARTERLY REPORT NO.3

JULY 1978

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.

Prepared Under Contract No. 954877 for
JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91103

EAGLE PICHER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ACKNOWLEDGEMENT

This report would not have been possible without the cooperation of Paul Grayson, Larry Addington, Dr. P. D. Ownby, Dr. J. J. Stiglich, Robert Holzl, and Bob Davis on developmental work and data reduction by Brian Zealer, Mike Barsoum, and John Koen. The assistance of Gene Cantwell in x-ray diffraction interpretation and A. L. Fluesmeier and George Alexander in other characterization efforts is also acknowledged.

The cheerful assistance of Ms. Billie Ginn and Ms. Mary Holland in typing the drafts and organizing the report is also deeply appreciated.

SUMMARY

Die and container material development efforts under the current program are shared among three organizations. Miami Research Laboratories (MRL) - ceramic process development and overall program management, University of Missouri - Rolla (UMR) - silicon sessile drop studies with characterization of reaction products and emphasis on atmospheric effects, Chemetal Corporation, Pacoima, California - special coatings to be applied to test coupons, die shapes and containers provided by MRL and tested/characterized by UMR.

Initial sessile drop experiments on SiC, Si₃N₄ and AlN have been conducted. Very promising results have been achieved on both SiC and Si₃N₄ where minimal penetration of these CNTD coatings by molten silicon was observed.

Efforts during the past quarter continued in the following areas. At MRL, a set of AlN and another set of Si₃N₄ substrates have been hot pressed. Hot pressing experiments have begun on crucible shapes. Characterization efforts have also begun on coatings and substrates. Chemetal delivered AlN coated substrates and began development efforts to produce Si-O-N coatings as predecessor to Si-O-Al-N coatings. UMR has succeeded in measuring the lowest oxygen partial pressures measured, to the knowledge of the investigators, with a solid electrolyte cell on a dynamic flowing gas buffer system. This was achieved with a yttria doped thoria oxygen sensor cell. Even lower pressures beyond this measurement capability have been achieved.

TABLE OF CONTENTS

Section	Page
ACKNOWLEDGEMENT	ii
SUMMARY	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	vi
LIST OF FIGURES	vii
1. INTRODUCTION	1
1.1 PROGRAM GOALS	1
1.2 MATERIALS UNDER INVESTIGATION	2
2. MIAMI RESEARCH LABORATORY EFFORTS	2
2.1 HOT PRESSING PROCEDURES FOR AlN AND Y ₂ O ₃ DOPED SUBSTRATE DISCS	3
2.2 DIE AND CRUCIBLE HOT PRESSING AND OPTICAL MICROSCOPY CHARACTERIZATION	3
2.3 X-RAY DIFFRACTION CHARACTERIZATION	7
2.3.1 SiC Coated SiC Substrates	11
2.3.2 Si ₃ N ₄ Coated Si ₃ N ₄ Substrates	12
3. CHEMETAL CORPORATION EFFORTS	13
4. UMR EFFORTS	14
4.1 INITIAL CHARACTERIZATION OF THE COATED SUB- STRATES	14
4.1.1 Physical Property Characterization of the Coat- ings	14
4.1.1.1 General Observations on the Physical Appearance of the Si ₃ N ₄ Specimens	14
4.1.1.2 Vickers Diamond Pyramid Hardness Measurements	17
4.1.2 Chemical Characterization of the Polished Coated Substrates by Auger Analysis	18

Table of Contents - continued

Section	Page
4.2	SESSILE DROP EXPERIMENTS 24
4.2.1	Characterization of the Coatings after Sessile Drop Runs 30
4.2.1.1	Auger Spectroscopy of Coatings Outside the Drop Area 30
4.2.1.2	Scanning Electron Microscopy of Fractured Surface Cross Sections of Test Specimens 30
5.	CONCLUSIONS 35
6.	PROJECTED ACTIVITIES FOR THE NEXT QUARTER 37
6.1	MIAMI RESEARCH LABORATORIES 37
6.2	UNIVERSITY OF MISSOURI - ROLLA 37
6.3	CHEMETAL 37

LIST OF TABLES

Table		Page
I	Substrate Materials and Characteristics (before coating)	A-1
II	Chemetal Observations and X-ray Diffraction Results, Silicon Carbide Coatings on Silicon Carbide Substrates	A-2
III	Chemetal Observations and X-ray Diffraction Results Si_3N_4 Coatings on "pure" Si_3N_4 (with 4 wt/o MgO) Sub- strates	A-4
IV	Chemetal Observations and X-ray Diffraction Results, Si_3N_4 Coatings on "impure" Si_3N_4 (with 4 wt/o MgO) Substrates	A-6
V	Summary of Sessile Drop Experimental Conditions and Results	A-8

LIST OF FIGURES

Figures		Page
1.	Typical Hot Pressing Time/Temperature/Pressure Cycle	4
2.	CNTD SiC Coating at 52.5X (Lot PP-26, Part No. 7)	6
3.	CNTD Si ₃ N ₄ Coating on "Impure" Si ₃ N ₄ (with 4 wt/o MgO) at 2.44X (Lot PP-30, Part No. 14)	8
4.	CNTD Si ₃ N ₄ Coating on "Impure" Si ₃ N ₄ (with 4 wt/o MgO) at 52.5X. Before and After Polishing (Lot PP-30, Part No. 14) 4.A. As Deposited; Figure 4.B. After Polishing	9
5.	CNTD SiC Coating on Substrate Lot PP-26, Part No. 9 at 32.5X. Illustrates Grain Size of 0.0218 in. Thick Coating	15
6.	CNTD SiC Coating on Substrate Lot PP-26, Part No. 11 at 100X. Illustrates Grain Size of 0.0059 in. Thick Coating	15
7.	CNTD SiC Coating on Substrate Lot PP-26, Part No. 11 at 600X Illustrates Fine Grain Substructure	16
8.	Auger Electron Elemental Surface Analysis of Unspattered CNTD Si ₃ N ₄ Coating on "Pure" Si ₃ N ₄ (Lot PP-33, Part No. 3) Substrate	19
9.	Auger Electron Elemental Surface Analysis of Unspattered CNTD Si ₃ N ₄ Coating on "Impure" Si ₃ N ₄ (Lot PP-30, Part No. 2) Substrate	20
10.	Auger Electron Peak Height Variations with Time Under the Influence of the Electron Beam After 2 Minutes of Sputtering (Same Sample as Figure 8)	22
11.	Peak to Peak Amplitude Variation W/Time During Sputtering (40 Å Per Minute)	23
12.	White Deposit on Downstream Side After Sessile Drop Run Above Si + O ₂ = SiO ₂ Equilibrium PO ₂ (CNTD Si ₃ N ₄ on "Pure" Si ₃ N ₄ Substrate, PP-33, Part No. 13)	25
13.	Extreme Case of Oxide Formation and Subsequent Prevention of Drop Spreading (CNTD Si ₃ N ₄ Substrate, PP-33, Part No. 11)	25
14.	Time Dependence of Contact Angle for Silicon Sessile Drop Runs on CNTD Si ₃ N ₄ (PP-33) at 1450°C, P _{O2} ≤ 10 ⁻¹⁷	27

LIST OF FIGURES -continued

Figures		Page
15.	Time Dependence of Contact Angle for Silicon Sessile Drop Runs on CNTD SiC (PP-26) at 1450°C, $P_{O_2} \leq 10^{-18}$	28
16.	Silicon Sessile Drop on CNTD SiC (PP-26, Part No. 7) at 1450°C, $10^{-18} > P_{O_2} > 10^{-24}$, $\theta = 29^\circ$	29
17.	Fractured Section of Silicon Sessile Drop on CNTD SiC for Experimental Run Shown in Figure 16, 300X Magnification	31
18.	Fractured Section of Silicon Sessile Drop on CNTD SiC (same specimen as shown in Figures 16 & 17) 1000X Magnification	32
19.	Fractured Section of Silicon Sessile Drop on CNTD SiC (same specimen as shown in Figures 16, 17, & 18) 3000X Magnification	32
20.	Fractured Section of Silicon Sessile Drop on CNTD Si_3N_4 (PP-33, Part No. 14), 1450°C. One hr. at Temperature $10^{-17} > P_{O_2} > 10^{-24}$. 1000X Magnification	33
21.	Fractured Section of Silicon Sessile Drop on CNTD Si_3N_4 (same specimen, same area as Figure 20). 3000X Magnification	33

1. INTRODUCTION

The current program is a cooperative effort among three facilities to attack the die and container materials problems of the Low Cost Silicon Array Project. Miami Research Laboratories (MRL) will provide overall project management as well as die and container fabrication engineering and characterization. Chemetal Corporation (Pacoima, California) will apply ceramic coatings to substrates made by MRL for testing and later to die and container shapes using the proprietary "CNTD" (Controlled Nucleation by Thermochemical Decomposition) process. University of Missouri-Rolla (UMR) personnel will perform sessile drop experiments on coated substrates made by MRL and Chemetal. They will explore the effects of oxygen partial pressure and characterize the reactions using Auger-ESCA spectroscopy and other techniques.

1.1 PROGRAM GOALS

The goals of the present program are to develop successful die and container materials for handling liquid silicon while it is being formed into photovoltaic cell material. These goals will hopefully be accomplished by exploring various materials configurations for their reactivity with molten silicon. The combination of unique coating structures combined with control of oxygen partial pressures may yield a set of conditions which are useful for cost effective dies or containers for pulling ribbons from silicon melts. Successful experimental configurations will be scaled up into prototype dies and containers as appropriate during the third and fourth quarters of calendar 1978. Economics for large scale production of such prototypes will be defined as part of the program.

1.2 MATERIALS UNDER INVESTIGATION

The following material configurations have been fabricated by MRL and Chemetal to be tested for molten silicon contact angle and reactivity at UMR. CNTD SiC has been deposited on hot pressed SiC discs (dimensions 1.2" D. x 0.165" thick). CNTD Si_3N_4 has been deposited on two types of hot pressed Si_3N_4 discs - a "pure" and an "impure" grade. These materials were produced in March and April 1978. AlN discs were hot pressed at MRL and coated at Chemetal during April and May. Some SiC, Si_3N_4 and AlN polished coated specimens were furnished to UMR in June. Because of the apparent variations found from specimen to specimen, a detailed deposition description and x-ray characterization of each sample were supplied by Chemetal and MRL, respectively. These data appear in the Appendix. The Si-O-N and Si-O-Al-N coating processes were under development during June and should be completed in July.

2. MIAMI RESEARCH LABORATORY EFFORTS

During the third quarter, MRL completed hot pressing of discs for coating by Chemetal Corporation. The last two groups of substrate discs to be hot pressed were AlN without additive and Si_3N_4 with 10 wt/o Y_2O_3 to be used for deposition of AlN and Si-O-N/Si-Al-O-N coatings, respectively. Physical properties of these latter groups of hot pressed discs are shown in Table 1, Appendix. Hot pressing procedures are detailed in Section 2.1.

Characterization efforts at MRL include optical and SEM microscopy and x-ray diffraction. The optical and x-ray characterization are discussed in Sections 2.2 and 2.3 respectively. The SEM characterizations will be discussed in subsequent reports as efforts to resolve the ultimate grain size of the CNTD coatings are still underway.

2.1 HOT PRESSING PROCEDURES FOR AlN AND Y_2O_3 DOPED Si_3N_4 SUBSTRATE DISCS

AlN powder having a composition of Al+N = 97.5 wt/o, C = 0.01 wt/o and metallic impurities = 0.05 wt/o; particle size 3-10 micron was obtained from Electroschmelzwerk-Kempton (West Germany). No hot pressing additives were used. The major unreported impurity in AlN is normally oxygen, however, implying the presence of Al_2O_3 which may act as a pressing aid. Forty substrates 1.050" D. x 0.160" thick (nominal) were hot pressed in graphite tooling at 1890°C to 1905°C for an average time of 45 minutes (total). Time at temperature was typically 30 minutes. Maximum pressure was 6230 psi and was applied during the 30 minutes at maximum temperature for all parts.

Si_3N_4 powder was obtained from Kawecki Berylco (KBI) designated "controlled phase 85". Y_2O_3 (10 wt/o, Molycorp) was added to facilitate hot pressing. Thirty substrates 1.050" D. x 0.160" thick (nominal) were hot pressed in graphite tooling at 1850 to 1860°C for total times which ranged from 80 to 110 minutes. Maximum pressure was 6470 psi and was applied during the period of maximum temperature which ranged from 60 to 90 minutes.

A generalized MRL hot pressing cycle (time, temperature, and pressure) is shown in Figure 1 and with textual specifics it describes the pressing of all substrate materials to date.

2.2 DIE AND CRUCIBLE HOT PRESSING AND OPTICAL MICROSCOPY CHARACTERIZATION

Hot pressing experiments were performed during the current quarter to develop crucible shapes. Initial success was attained in hot pressing 1 1/4" deep x 3/4" I.D. crucibles using Si_3N_4 ("impure"), SiC, and AlN. The same powders were used for crucibles as were used for substrate discs

<u>MATERIAL</u>	<u>TMAX</u>	<u>PMAX</u>
Si_3N_4 ("IMPURE", 4 wt/o MgO)	1750-1785°C	5250 psi
Si_3N_4 ('PURE', 4 wt/o MgO)	1755°C	5600 psi
Si_3N_4 (<BI, 10 wt/o Y_2O_3)	1850-1860°C	6470 psi
AlN	1890-1905°C	6230 psi
SiC (1 wt/o B)	2200°C	6000 psi

Figure 1. Typical Hot Pressing Time/Temperature/Pressure Cycle.

coated by Chemetal. These prototype efforts were halted when it was clear that tooling designs were adequate and scale up to a larger crucible was possible (suitable for silicon melting and ribbon pulling). Crucibles having average densities of 90 percent to 95 percent of theoretical were made in the prototype efforts.

New tooling was designed and fabricated at the end of June to make crucibles having nominal inside dimensions of 2" deep x 2" I.D. The tooling was completed in early July, and preliminary results of hot pressing the large crucibles will be available in the July monthly report.

Tooling for hot pressed ribbon die blanks is also available, but no time has been spent fabricating die blanks. They are very simple rectangular solid shapes, and no problems are expected. A few experiments will be made on these shapes in July.

Characterization efforts received much emphasis at MRL during the third quarter. Optical photomicrographs have been taken on selected SiC coated substrates and all Si_3N_4 and AlN coated substrates at magnification factors from 2.44X to 52.5X both before and after polishing. The purpose of these low magnification micrographs was primarily to maintain an archive record of appearances of coatings prior to sessile drop experiments.

The CNTD SiC coatings were relatively consistent in appearance prior to polishing. An as deposited surface is shown in 52.5X in Figure 2. MRL observations of the SiC coatings are in agreement with those of UMR (see Section 4.1 and referenced figures). Photomicrographs of the polished SiC coatings were not obtained because of the mirror like, extremely high density, crack free surface. The only observable relief was due to polishing flaws.

Figure 2. CNTD SiC Coating at 52.5X
(Lot PP-26, Part No. 7)

The CNTD Si_3N_4 coatings (on both "pure" and "impure" Si_3N_4 with 4 wt/o MgO substrates) revealed certain visible effects. In general two types of Si_3N_4 were deposited, an "amorphous" structure and a "crystalline" structure. These structures will be discussed in greater detail in Section 2.3.2, but visually, the amorphous coatings were translucent yellow, green, or variegations thereof. The crystalline coatings were similarly colored, but were in general translucent, tending toward transparency. Of the twelve coatings on "impure" Si_3N_4 substrates, four were partially or totally amorphous (by x-ray diffraction), and of the twelve coatings on "pure" Si_3N_4 substrates, four were partially or totally amorphous (by x-ray diffraction).

The translucent coatings exhibited crack-like macrostructures suggesting coating/substrate thermal expansion mismatch, but nearly all of the systems ended within the coatings. Only a few appeared to come through to the free surface. A macrostructure typical of these observed in the CNTD Si_3N_4 coatings on Si_3N_4 (with 4 wt/o MgO) is shown at 2.44X in Figure 3. The crack-like system was not readily apparent prior to polishing as shown in Figure 4.A which is a 52.5X photomicrograph of the as deposited coating (same specimen as shown in Figure 3). Figure 4.B (after polishing) illustrates the above mentioned phenomenon of apparent cracks terminating below the surface. Polishing flaws at the surface are in sharp focus while the apparent cracks are below the depth of field of the microscope and are therefore out of focus. These details would have been in sharp focus had they propagated to the surface.

2.3 X-RAY DIFFRACTION CHARACTERIZATION

All substrate discs were characterized by obtaining x-ray diffraction patterns from both the coated and the uncoated (hot pressed)

Figure 3. CNTD Si_3N_4 Coating on "Impure" Si_3N_4
(with 4 wt/o MgO) at 2.44X (Lot PP-30,
Part No. 14)

Figure 4.A. As Deposited

Figure 4.B. After Polishing

Figure 4. CNTD Si_3N_4 Coating on "Impure" Si_3N_4 (with 4 wt/o MgO) at 52.5X. Before and After Polishing. (Lot PP-30, Part No.14) Same Part as Figure 3.

surfaces. The hot pressed surface had been ground flat using a 100 grit diamond wheel, and the coated surface was polished using a series of diamond pastes through the 15 micron grit size paste. Copper K α (Ni filter) radiation was used; the diffractometer was a Rigaku Denki instrument. Angular scanning speed was 2 $^{\circ}$ 2 θ per minute and tube power conditions were 35 KV, 15 ma. Various beam slit conditions were used depending on sample being investigated.

It was interesting to note that Chemetal observations on the crystalline or amorphous nature of their Si $_3$ N $_4$ coatings were verified in eight of a total of ten instances. In the two instances for which verification was not possible, both discs were identified as being "possibly" amorphous by Chemetal. The diffraction patterns for these discs, while not having the definite amorphous effects of the others, were still qualitatively different from the clearly crystalline deposits.

In general, the patterns made possible the identification of major and minor phases present in addition to providing evidence of preferred orientation, strain effects, small particle size effects, and the presence of partially or totally amorphous structures. These effects will be discussed in detail and related to the specific coating.

Powder patterns were also obtained on the starting powder mixtures from which the substrate discs were hot pressed. There were no anomalous or atypical effects in any of these patterns and all five patterns qualitatively verified the presence of the materials from which the mixtures were formed. Although no quantitative phase analysis was attempted, the diffraction patterns for the "pure" and "impure" Si $_3$ N $_4$

(obtained from Cerac) and for the KBI Si_3N_4 generally agreed with the manufacturer's phase analysis for α and β phases. Hot pressing these materials resulted in the expected (small) increase in β phase peak intensities. Since hot pressing times were minimized and high strengths (as in gas turbine components) are not required for dies and crucibles, there was very little conversion of α to β - Si_3N_4 . AlN powder yielded a standard AlN pattern. The large number of α -SiC polytypes made the SiC powder pattern difficult to interpret. The presence of β -SiC cannot be definitely established. Although there was one strong, unambiguous β peak, all of the other strong β peaks coincided with various α polytype peaks. The presence of α -I, α -II, and α -III polytypes was firmly established by comparison with ASTM powder diffraction file data. The α -V and α -VI forms were probably present, and the α -IV form was doubtfully present. The pure boron additive (1 wt/o) was not identified nor would it be expected to contribute a pattern due to its low atomic weight and the small quantity present.

2.3.1 SiC Coated SiC Substrates

The SiC coatings yielded generally consistent diffraction patterns.^(*) A low intensity diffuse peak occurred between approximately 20 to $30^\circ 2\theta$. This peak then blended into an extremely large β SiC (111) peak at about $35.5^\circ 2\theta$ after revealing an isolated unknown peak at approximately $32^\circ 2\theta$. A small β -SiC (200) peak blended into the (111) peak at approximately $41^\circ 2\theta$ but its position was obscured by a very pronounced asymmetry on the high angle side of the (111) peak. In addition, both peaks (the (111) and (200)) showed broadening probably due to fine particle

(*) See Table II, Appendix

size effects. The next peak was the β (220) at approximately $60^{\circ}2\theta$; particle size broadening was also present in the (220), but asymmetry might also be present. The β (311) and (222) were next at approximately 71.5° and $75.0^{\circ}2\theta$ respectively. The (311) showed some broadening while the (222) was extremely intense, tending to confirm the presence of a preferred orientation. The pronounced asymmetry of the (111) was not repeated in the (222).

The substrates exhibited a well defined α -SiC pattern qualitatively similar to the starting powder pattern. Again, there were no effects associated with the boron added as a hot pressing aid. It would be expected to form SiB_6 or possibly to go into solid solution in the SiC lattice, but there were no SiB_6 peaks present nor were there identifiable solid solution effects.

2.3.2 Si_3N_4 Coated Si_3N_4 Substrates

Both types of Si_3N_4 ("pure" and "impure" with 4 wt/o MgO) substrates will be discussed in a single presentation because the coatings applied to each were chemically similar. Tables III & IV, Appendix, contain a tabulation of visual observations made by Chemetal on the quality, color, degree of crystallinity, and thickness of the coating.

The substrate (uncoated side) characteristics will be discussed briefly. The presence of a set of barely noticeable peaks (typically 3 to 6) was established in all of the substrate diffraction patterns. They are not β - Si_3N_4 but seem to be related to MgO and/or magnesium silicates. MgO may be present due to some of the shorter times at temperature and possibly due to inhomogeneous mixing of the starting powders. Magnesium silicates are to be expected because of the reaction of MgO and Si_3N_4 at elevated temperatures to form the liquid silicates which support the densification/compaction process. There were not sufficient unknown peaks to unequivocally identify the material which they represent.

The x-ray diffraction results on the coatings are best presented in tabular form. Refer to Table III and IV of the Appendix. The coatings were, as mentioned in Section 2.3, of two basic types, crystalline and amorphous. The crystalline coating diffraction patterns indicate essentially α phase with some doubtful β . The relative intensity ratios varied from pattern to pattern indicating possible orientation effects.

3. CHEMETAL CORPORATION EFFORTS

Chemetal activities during the third quarter were directed toward depositing AlN coatings on AlN discs and toward developing a Si-O-N and a Si-Al-O-N coating.

AlN coatings were produced and furnished to MRL at the end of May. Si_3N_4 (10 wt/o Y_2O_3) discs were sent to Chemetal during the first three weeks of June, and development of Si-O-N and Si-Al-O-N coatings begun in that order. These coatings were completed at the end of June and the beginning of July and returned to MRL for characterization. Results of this characterization should be available in the August monthly report. Chemetal obligations for the five sets of coated samples to be supplied under the initial scope of work are thus satisfied.

4. UMR EFFORTS

4.1 INITIAL CHARACTERIZATION OF THE COATED SUBSTRATES

Silicon carbide coated substrates were received and characterized by scanning electron microscopy with respect to surface flatness. Typical photo micrographs are shown in Figures 5 and 6. The nodules in the surface were found to vary in size, increasing with coating thickness as shown in the figures. Higher magnifications reveal however that the nodule size does not represent the ultimate grain size but that the nodules themselves have a very fine grain sub-structure (Figure 7). At the edges, the nodules are larger and elongated because of the very small radius of curvature in the transition from the top surface to the edge of the substrate discs. The roughness of the edges are roughly the same as the top surfaces on a given disc.

Meaningful sessile drop experiments require flat parallel surfaces in order to level the disc in the furnace and to be able to measure the contact angle at temperature. A smooth surface is required to prevent localized contact angle variations. Therefore, before any sessile drop experiments could be conducted on these samples they were ground flat and diamond polished at MRL.

4.1.1 Physical Property Characterization of the Coatings

Because some of the properties of the CNTD material are considered to be somewhat unique, attempts to measure them on the discs before doing sessile drop experiments appeared to be in order.

4.1.1.1 General Observations on the Physical Appearance of the Si_3N_4 Specimens

The color of the polished coatings varied from specimen to specimen and in most cases from point to point on each

Figure 5. CNTD SiC Coating on Substrate Lot PP-26, Part No. 9 at 32.5X. Illustrates Grain Size of 0.0218 in. Thick Coating

Figure 6. CNTD SiC Coating on Substrate Lot PP-26, Part No. 11 at 100X. Illustrates Grain Size of 0.0059 in. Thick Coating

Figure 7. CNTD SiC Coating on Substrate
Lot PP-26, Part No. 11 at 600X
Illustrates Fine Grain Sub-
structure

individual specimen itself. Some specimens appeared to be more opaque while others looked quite translucent and even somewhat transparent. Networks of crack-like macrostructure are commonly seen in the specimen but the shape and form of the networks differ widely from specimen to specimen. In some samples they seem to be under the polished surface entirely while on others they appear to intersect the surface. Some samples display both types. A characterization of each specimen by Chemetal and MRL are found in the Appendix, and these observations are in agreement.

The variation of physical properties displayed by the specimens is confirmed by these data. An understanding of these variations suggest a change in the sessile drop experimental plan is indicated for future experiments in order to obviate the problem of changing more than one variable in a given experiment.

4.1.1.2 Vicker's Diamond Pyramid Hardness Measurements

Two different instruments were used to measure hardness. A Reihle Model AKB hardness testing machine by Ametek was capable of applying loads up to 100 gram maximum and a Reichert instrument was used for the heavier loads. The data was obtained from a randomly selected single specimen from each type and may not be representative.

The following summarizes the data taken at 500 gram loads.

<u>CNTD Coating</u>	<u>DPN</u>
Si_3N_4	2090 $\pm$ 208
AlN	942 $\pm$ 86
SiC	2113 $\pm$ 186
<u>Hot Press Substrates (uncoated face)</u>	
Si_3N_4 (PP-33)	1430 $\pm$ 100
AlN	977 $\pm$ 100

CNTD SiC was measured at various loads as follows:

<u>Load (gms)</u>	<u>D.P.N.</u>
1100	2533 $\pm$ 200
1000	2434 $\pm$ 200
500	2133 $\pm$ 186
100	2353 $\pm$ 200
50	1822 $\pm$ 179

4.1.2 Chemical Characterization of the Polished Coated Substrates by Auger Analysis

Silicon Nitride coated substrates were characterized using Auger spectroscopy. A continuous Auger multiplex analysis of the relative peak-to-peak heights of four elements was attempted but was not possible because of sample charging. The same result was accomplished by a series of discrete analyses between sputtering intervals. Figures 8 and 9 show the Auger analysis of the surface of two different samples in the as-received and unsputter condition.

The difference between these two samples is that the hot pressed substrate under the coating of the sample in Figure 8 was of the "pure" type (sample #3) and that of Figure 9 was of the "impure" type (sample #2).

The dominant carbon peak is typical of unsputtered surfaces due to adsorbed carbon containing species. Chlorine and oxygen are also present on the unsputtered surface in addition to silicon and nitrogen. The difference in peak heights from Figure 8 to Figure 9 is due to the difference in the primary beam current; the relative peak heights are about the same.

Figure 10 shows the same spot on the sample of Figure 8, after a two minute sputter. The dots below the bottom of the carbon peak and also above the bottom of the silicon peak represent the changing peak heights with time while the electron beam was left on. That is, under the influence of the electron beam, the carbon signal increased at the expense of the silicon signal. However, with the electron beam off between analyses both peaks remain constant with time. This appears to indicate that carbon may be diffusing to the surface under the influence of localized heating by the electron beam, increasing the carbon concentration and decreasing the silicon concentration at the surface. Figure 11 shows the multiplex run for the same spot on the same sample as in Figure 8 and 10. After the initial removal of adsorbed species, the concentration of each of the four elements, Si, N, C and O reach and maintain a relatively constant value through 1800⁰Å in from the surface, indicating a fairly constant coating composition in this range. No metallic impurities are detected at any level within this range. After sputtering, the influence of the electron beam remaining on after sputtering ceased, is again seen at this depth as on the original surface the carbon concentration increases at the expense of silicon initially with time. It appears however, that a new C/Si ratio is established after about 10 minutes.

It was also noted that during sputtering, all of the Si₃N₄ coatings outgassed, increasing the system pressure above 5×10^{-5} torr after a few minutes sputtering.

Additional Auger data are given in a later section of this report on a substrate surface after going through a sessile drop run.

Figure 10. Auger Electron Peak Height Variations with Time Under the Influence of the Electron Beam After 2 Minutes of Sputtering (Same Sample as Figure 8).

$\frac{dN}{dE}$

22

SPECIMEN

Silicon Nitride

Element			Etching
1	Silicon	o	1 Gun 2
2	Nitrogen	•	Ep
3	Carbon	+	le
4	Oxygen	<	
5			
6			Rate:

Figure 11. Peak to Peak Amplitude Variation W/Time During Sputtering (40 Å Per Minute)
Same part as Figures 8 & 10

Ep= 2 Kv

Ip= 1.3 ma

Vmod= 2

RC= 0.003

Vmult.= 850

SENS= 40X

4.2 SESSILE DROP EXPERIMENTS

Sessile drop experiments on the CNTD coated substrates were initiated. Seven or eight mm cubes of nominal 100 ohm cm, semiconductor grade Eagle-Picher silicon were used to form the sessile drops. The plan of attack was to conduct a series of runs on each coating type beginning with the higher oxygen partial pressure above the Si-SiO₂ equilibrium oxygen pressure and then on subsequent runs, lowering the oxygen pressure through and below the equilibrium value. Experiments on Si₃N₄ coated substrates at 10⁻¹⁶ atmospheres (above the equilibrium value) produced a powder-like white (SiO₂) deposit around the silicon drop downstream from gas flow (see Figure 12). This occurs prior to melting as the silicon cube is being heated on the substrate. During heat-up, prior to attaining the run temperature of 1450°C the equilibrium oxygen pressure is lower than the value at 1450°C. Therefore when making runs close to or above the equilibrium value a SiO₂ deposit forms around the silicon cube which acts as a fence around the melting drop, preventing the drop from spreading and attaining equilibrium wetting. An extreme case of this is shown on Figure 13.

Subsequent sessile drop experiments were then made on coated substrates only at oxygen partial pressures below the equilibrium value. Contact angles have been measured on both SiC and Si₃N₄ coated substrates as a function of time at 1450°C at constant P_{O₂} values.

Characterization of the coatings outside the silicon drop area and the sessile drop - coating interfaces have begun. Oxygen partial pressures down to the order 10⁻²⁵ atmospheres at 1000°C have been successfully measured using a solid electrolyte yttria doped thoria sensor cell. To our knowledge, this is the lowest oxygen partial pressure ever measured in a flowing gas

Figure 12. White Deposit on Downstream Side After Sessile Drop Run Above $\text{Si} + \text{O}_2 = \text{SiO}_2$ Equilibrium P_{O_2} (CNTD Si_3N_4 on "Pure" Si_3N_4 Substrate, PP-33, Part No. 13).

Figure 13. Extreme Case of Oxide Formation and Subsequent Prevention of Drop Spreading (CNTD Si_3N_4 Substrate, PP-33, Part No. 11)

buffer system using such an oxygen concentration cell. The flowing gas then passes into the sessile drop furnace where it is heated to 1450°C. A new higher equilibrium oxygen pressure is then established by the buffer reaction $2H_2 + O_2 = H_2O$ as it shifts to the left establishing a new equilibrium down to the order of 10^{-19} atmospheres. Oxygen partial pressures below this value, down to that fixed by the Ti-TiO₂ equilibrium or the Al - Al₂O₃ equilibrium of the furnace tube and hardware itself (of the order at 10^{-24} atmospheres) have not been precisely defined or directly measured as yet, since they are below the present measuring capability of the thoria cell. Attempts will be made to extend the measurement capability of the cell below 10^{-19} atmospheres by using a reference gas with an oxygen pressure much closer to that value so that the oxygen pressure difference from one side of the cell to the other will be much smaller.

The contact angle measurements made to date on Si₃N₄ and SiC are shown on Figures 14 and 15 respectively. In all of these runs the contact angles have decreased from the initial value upon melting down to a relatively constant angle after about 40 minutes. For Si₃N₄, initial contact angles range from about 90° to 65° and finally settle between 60° and 50° with time. For SiC an initial range between 45° and 50° becomes from 27 - 30° with time. Figure 16 shows a photograph of a silicon sessile drop on a SiC substrate (#7) taken during the run. The contact angles observed in these runs on these coatings were about 10° smaller than previously reported in the literature for SiC. These runs together with an AlN run are summarized on Table V**. It appears that there may be a relationship between the contact angle and the oxygen partial pressure for both of those silicon/coating sets over the range investigated. These data suggest that the contact angle may decrease with a decreased oxygen partial pressure in the sessile drop environment.

Figure 14. Time Dependence of Contact Angle for Silicon Sessile Drop Runs on CNTD Si_3N_4 (PP-33) at 1450°C , $P_{\text{O}_2} \leq 10^{-17}$

Figure 15. Time Dependence of Contact Angle for Silicon Sessile Drop Runs on CNTD SiC (PP-26) at 1450°C, $P_{O_2} \leq 10^{-18}$

Figure 16. Silicon Sessile Drop on CNTD SiC
(PP-26, Part No. 7) at 1450°C,
 $10^{-18} > p_{O_2} > 10^{-24}$ $\theta = 29^\circ$

4.2.1 Characterization of the Coatings after Sessile Drop Runs

4.2.1.1 Auger Spectroscopy of Coatings Outside the Drop Area

It is of interest to determine if the nature of the CNTD coated surface was changed during the sessile drop run regime. The coatings are therefore being analyzed outside the drop area by Auger spectroscopy to determine if the surface chemistry is altered in the run. The same elements were detected in the Si_3N_4 coating i.e., silicon, nitrogen, carbon and oxygen. A detectable decrease in the nitrogen content of the surface was found suggesting that some nitrogen loss may be occurring from the coating surface during the sessile drop runs.

4.2.1.2 Scanning Electron Microscopy of Fractured Surface Cross Sections of Test Specimens

The photomicrographs of the molten silicon/CNTD SiC and CNTD Si_3N_4 interfaces taken to date supports the general macroscopic observation that corrosive penetration of the coatings by molten silicon is minimal under the conditions of these experiments. Figures 17, 18 and 19 show the Si/SiC interface & Figures 20 and 21 show the Si/ Si_3N_4 interface on two samples in the previously described runs. The hot pressed SiC substrate can be seen in Figure 17 at 300X at the bottom of the photograph with the CNTD coating in the middle and the silicon drop on top. The interface between the silicon drop and the coating appears straight and thin. The Si/CNTD SiC interface also appears clean, straight and thin in Figure 18, at 1000X and Figure 19 at 3000X.

The residual stress present in the silicon/CNTD Si_3N_4 coating interface resulted in a more pronounced relief difference between the two phases making a clear delineation of the fractured surface interface more difficult. Figures 20 and 21, however, once again show only a minimal interfacial zone. A detailed characterization of those interfaces is

← ← Silicon Sessile Drop

← ← ← CNTD SiC

← ← Hot Pressed SiC
(with 1 wt/o B, PP-26)

Figure 17. Fractured Section of Silicon Sessile Drop on CNTD SiC for Experimental Run Shown in Figure 16, 300X Magnification

Silicon Sessile
← ← ← Drop → → →

CNTD
SiC → → →

Figure 18. Fractured Section of Silicon Sessile Drop on CNTD SiC (same specimen as shown in Figures 15 & 17) 1000X Magnification

Figure 19. Fractured Section of Silicon Sessile Drop on CNTD SiC (same specimen as shown in Figures 16, 17, & 18) 3000X Magnification

Silicon Sessile
← ← ← Drop → → →

CNTD
← ← ← Si_3N_4 → → →

Figure 20. Fractured Section of Silicon Sessile Drop on CNTD Si_3N_4 (PP-33, Part No. 14), 1450°C. One hr. at Temperature, $10^{-17} > \text{P}_{\text{O}_2} > 10^{-24}$. 1000X Magnification

Figure 21. Fractured Section of Silicon Sessile Drop on CNTD Si_3N_4 (same specimen, same area as Figure 20). 3000X Magnification

proceeding. The data to date indicates that the CNTD SiC and Si₃N₄ coatings may be much more resistant to chemical and microstructural attack by molten silicon than other SiC and Si₃N₄ materials reported in the literature.

5. CONCLUSIONS

The silicon sessile drop experiments and the subsequent characterization thereof performed establish the viability of both CNTD SiC and CNTD Si₃N₄ as candidate materials for coating die and crucible configurations. The interfacial surface is free of gross reaction evidence, however, more experimentation and characterization is in order.

The need for polishing the specimens in order to obtain meaningful sessile drop data was not anticipated and has contributed to program delays. The impact of this realization is now under control and polishing of the CNTD coatings should be a requirement for sessile drop experiments only.

The extension of the measurement range of the yttria doped thoria electrolyte sensor cell to below 10^{-19} atmospheres oxygen partial pressure is necessary before the systematic study of oxygen partial pressure effects can be completed. This does not, however, prevent sessile drop screening tests of candidate coatings at a single, controlled oxygen partial pressure below the Si + O₂ equilibrium. The effects of oxygen partial pressure seem to obtain to contact angle more than to reactivity. The study program can in this way move forward to the die and crucible hot pressing and coating activities as required by the program plan. Two viable candidates have been established to date.

The polished CNTD SiC substrates were black, shiny, and uniform in appearance and the x-ray diffraction indicated very uniform phase content. These coated specimens are suitable for the oxygen partial pressure studies without division into sublots.

While the visual examination of the coated and polished substrates indicated significant variations existed, the x-ray diffraction patterns showed the CNTD Si_3N_4 coatings to be reasonably uniform with respect to crystalline phases present, however, some coatings were totally or partially amorphous. This indicates two sublots should be formed for the oxygen partial pressure studies, however, the data to date indicates similar behavior of crystalline and amorphous coatings.

The program, in summary, can be kept near schedule in hardware delivery by virtue of the materials screening tests while careful characterization of the material and reaction products proceeds at an urgent but not program limiting rate.

6. PROJECTED ACTIVITIES FOR THE NEXT QUARTER

6.1 MIAMI RESEARCH LABORATORIES

SiC and Si_3N_4 crucibles and die blanks will be hot pressed. A decision will be made in August as to which will be first delivered to Chemetal. This decision will be based upon consideration of relative ease of fabrication and the latest available characterization and sessile drop data. Crucibles of one of these materials, suitable for CNTD coating will be delivered during the third week in September with dies to follow as soon as machining can be completed.

Characterization studies will be directed toward evaluation of AlN x-ray diffraction patterns, obtaining and evaluating patterns on Si-O-N and Si-Al-O-N, and elucidating the ultimate grain structure of all materials.

6.2 UNIVERSITY OF MISSOURI - ROLLA

Sessile drop experiments will continue in screening candidate materials at a reproducible, low oxygen partial pressure. Concurrent efforts will be directed toward extending the measurement range of the yttria doped thoria electrolyte cell below 10^{-17} atmospheres oxygen partial pressure.

UMR characterization efforts will continue with SEM and chemical analysis profiles of the silicon/coating interface. The latter will be obtained using Auger spectroscopy, electron microprobe, and EDX analyses.

6.3 CHEMETAL

Chemetal activities will be directed first toward applying CNTD SiC and CNTD Si_3N_4 to shapes machined from the appropriate grades of graphite, based on consideration of coefficients of thermal expansion. This is advisable because of the lower cost of these substrates. The coating processes will then be extrapolated to the ceramic substrates.

APPENDIX

- TABLE I. Substrate Materials and Characteristics (before coating)
- TABLE II. Chemetal Observations and X-Ray Diffraction Results, Silicon Carbide Coatings on Silicon Carbide Substrates
- TABLE III. Chemetal Observations and X-Ray Diffraction Results, Si_3N_4 Coatings on "pure" Si_3N_4 (with 4 wt/o MgO) Substrates
- TABLE IV. Chemetal Observations and X-Ray Diffraction Results, Si_3N_4 Coatings on "impure" Si_3N_4 (with 4 wt/o MgO) Substrates
- TABLE V. Summary of Sessile Drop Experimental Conditions and Results

TABLE I

Substrate Materials and Characteristics (before coating)

<u>Material</u>	<u>Additive</u>	<u>T.D.</u>	<u>Mean</u>	<u>Density Range</u>
Si ₃ N ₄ (KBI "controlled phase 85")	10 wt/o Y ₂ O ₃ (MOLYCORP)	3.30 gm/cm ³	95.8 % T.D. (39 substrates)	2.99 to 3.31 gm/cm ³ (39 substrates)
AlN, Elektro- schmelzwerk- Kempen lot number 312872	None (Al ₂ O ₃ possibly present in as-received powder)	3.26 gm/cm ³	95.7 % T.D. (40 substrates)	3.02 to 3.22 gm/cm ³ (40 substrates)

TABLE II

Chemetal Observations and X-Ray Diffraction Results, Silicon Carbide Coatings on Silicon Carbide Substrates
(P-26, substrate lot #)

<u>Chemetal Designation</u>	<u>MRL Designation</u>	<u>COATING THICKNESS</u>	<u>Chemetal Observations</u>	<u>Chemetal Stoichiometry</u>	<u>MRL X-Ray Diffrac. Results Morphology/phases present</u>
1-4304-28-098	Part #5	.0060	very fine crystals, slightly green tint, good deposit	Correct	Strong crystalline β -SiC plus an unknown peak possibly represent a minor crystalline phase or super structure and a low angle, low intensity diffuse peak
-29	#6	.0069	rough surface, smoother than R28. deposit had a bluish-black color (shiny).	"	" " "
-30	#7	.0069	smoother surface, deposit is a dull bluish-black color	"	" " "
-31	#8	.0130	smooth, shiny, reflective surface but still a little bumpy	"	Except no diffuse peak
-32	#9	.0218	shiny, rough surface with a darker deposit on the outer radius	"	" " "
-33	#10	.0033	very smooth surface but a little dull	C-rich	Except no diffuse peak
-34	#11	.0059	smooth surface and slightly reflective surface	C-rich	" " "
-35	#12	.0036	very bumpy surface, not a good deposit, extremely uneven deposit, dark & dull on appearance	C-rich	" " "
-36	#13	.0130	" " "	C-rich	" " "
-37	#14	.0153	Smooth, dark and reflective surface, good deposit	C-rich	" " "

TABLE II -continued

<u>Chemetal Designation</u>	<u>MRL Designation</u>	<u>COATING THICKNESS</u>	<u>Chemetal Observations</u>	<u>Chemetal Stoichiometry</u>	<u>MRL X-Ray Diffrac. Results Morphology/phases present</u>		
1-4304-39-098	Part #16	.0070	slightly rough deposit, had a dull surface	Si-rich	"	"	"
-40	#17	.0083	rather smooth surface, slightly reflective	"	"	"	"
-41	#18	.0176	appearance same Run #40	"	"	"	"
-42	#19	.0072	smooth, dark, reflective deposit	"	"	"	"
-43	#20	.0096	smooth, shiny, slightly reflec- tive deposit, light bluish- black color	"	"	"	"

TABLE III

Chemetal Observations and X Ray Diffraction Results, Si_3N_4 Coatings on "pure" Si_3N_4 (with 4 wt/o MgO) Substrates
(PP-33, substrate lot #)

<u>Chemetal Designation</u>	<u>MRL Designation</u>	<u>COATING THICKNESS</u>	<u>Chemetal Observations</u>	<u>MRL X Ray Diffract. Results Morphology/phases present</u>
1-4305-22-098	PART #3	0.0057"	very fine crystals, slightly green tint, good deposit	crystalline/strong $\alpha\text{-Si}_3\text{N}_4$, weak $\beta\text{-Si}_3\text{N}_4$
-23	#4	0.0052"	very fine crystals same as #22 (PART #3)	crystalline/strong $\alpha\text{-Si}_3\text{N}_4$, possible $\beta\text{-Si}_3\text{N}_4$
-24	#5	0.0053"	large crystals, deposit very uneven	crystalline/strong $\alpha\text{-Si}_3\text{N}_4$, very weak $\beta\text{-Si}_3\text{N}_4$
-25	#6	0.0044"	small crystals, deposit very uneven	amorphous/devitrifying to $\alpha\text{-Si}_3\text{N}_4$, possible presence of β as well.
-26	#7	0.0055"	large crystals, even deposit, good deposit	crystalline/strong $\alpha\text{-Si}_3\text{N}_4$, possible $\beta\text{-Si}_3\text{N}_4$
-27	#8	0.0047"	small crystals, even deposit	→ to JPL
-28	#9	0.0079	larger crystals than #27 (PART #8), even deposit	→ to JPL
-29	#10	0.0088	semi amorphous/semi crystalline, small crystals	anomalous pattern-possibly amorphous/uninterpretable must be rerun.
-30	#11	0.0049	clear deposit, non crystalline, smooth, cracks visible	amorphous/devitrification just starting no identification of phase (s)
-32	#13	0.0107	medium size crystals with some cracks visible	amorphous/anomalous pattern
-33	#14	0.0059	small crystals, cracks visible.	crystalline/strong $\alpha\text{-Si}_3\text{N}_4$, possible $\beta\text{-Si}_3\text{N}_4$.

TABLE III -continued

<u>Chemetal Designation</u>	<u>MRL Designation</u>	<u>COATING THICKNESS</u>	<u>Chemetal Observations</u>	<u>MRL X Ray Diffrac. Results Morphology/phases present</u>
1-4305-34-098	PART #15	0.0059"	small crystals, even deposit (no cracking visible)	crystalline/strong α - Si_3N_4 , possible β - Si_3N_4
-35	#16	0.0096"	medium size crystals, translucent deposit	crystalline/strong α - Si_3N_4 , no β - Si_3N_4 noticeable
-36	#17	0.0094"	large crystals, very translucent deposit	crystalline/strong α - Si_3N_4 , no β - Si_3N_4 noticeable
-37	#18	0.0106"	large crystals, slightly green color, good deposit	→ to JPL

TABLE IV

Chemetal Observations and X-Ray Diffraction Results, Si_3N_4 Coatings on 'impure' Si_3N_4 (with 4 wt/o MgO) Substrates
PP-30, substrate lot #1)

<u>Chemetal Designation</u>	<u>MRL Designation</u>	<u>COATING THICKNESS</u>	<u>Chemetal Observations</u>	<u>MRL X-Ray Diffrac. Results Morphology/phases present</u>
8-4306-264-021	PART #1	0.011"	glassy amorphous, slightly bumpy, yellowish brown color	amorphous/no crystalline peaks visible
-265	#2		coating did not bond see run #270 below	→ see remarks below
-266	#3	0.011"	full crystalline deposit	anomalous crystalline pattern
-267	#4	0.005"	crystalline deposit, clear yellow in center, darker on edges	crystalline/strong $\alpha\text{-Si}_3\text{N}_4$ possible $\beta\text{-Si}_3\text{N}_4$
-268	#5	0.010"	smooth amorphous with some crystalline regions	amorphous/devitrifying to $\alpha\text{-Si}_3\text{N}_4$
-269	#6		full crystalline deposit	→ to JPL
-270	RERUN OF PART #2		full crystalline deposit	crystalline/very strong $\alpha\text{-Si}_3\text{N}_4$, possible $\beta\text{-Si}_3\text{N}_4$
-271	#7	0.0086"	crystalline surface changing to amorphous near substrate	crystalline/strong $\alpha\text{-Si}_3\text{N}_4$, possible $\beta\text{-Si}_3\text{N}_4$
-272	#3	0.014"	amorphous-glassy, bumpy deposit	amorphous/no crystalline peaks visible
-273	#9	0.0165"	crystalline deposit yellow- ish color in center	crystalline/strong $\alpha\text{-Si}_3\text{N}_4$, possi- ble $\beta\text{-Si}_3\text{N}_4$
-274	#10	0.0087"	crystalline deposit, smaller grains than previous runs	crystalline/strong $\alpha\text{-Si}_3\text{N}_4$, possi- ble $\beta\text{-Si}_3\text{N}_4$

TABLE IV -continued

<u>Chemetal Designation</u>	<u>MRL Designation</u>	<u>COATING THICKNESS</u>	<u>Chemetal Observations</u>	<u>MRL X-Ray Diffrac. Results Morphology/phases present</u>
8-4306-275-021	PART #11	0.011"	small grains, crystalline translucent, smooth deposit	crystalline/strong α -Si ₃ N ₄ , possible β -Si ₃ N ₄
-276	#12		small grains, smooth translucent deposit	→ to JPL
-277	#13	0.016"	amorphous/crystalline mixture	amorphous/mostly devitrified to α -Si ₃ N ₄
-278	#14	0.017"	crystalline deposit, possibly cracked	mostly crystalline pattern/ α -Si ₃ N ₄ present almost total devitrification
-279	#15	0.0106"	small grains, smooth deposit	crystalline/ α -Si ₃ N ₄ + unknown pattern
-280	#16		small grained deposit, crystalline facets visible	→ to JPL

TABLE V

Summary of Sessile Drop Experimental Conditions and Results

Coated Substrate Designation	Experimental Atmosphere	P_{O_2} (atm.)	Contact Angle After 40 Min	Oxidation of Silicon	Comments (2)
CNTD Si_3N_4 ⁽¹⁾ Part No. 10	(3)	$> 10^{-17}$	Not measurable	Yes	Sessile drop off edge
CNTD Si_3N_4 ⁽¹⁾ Part No. 11	"	"	132° Apparent ⁽⁴⁾	"	Silicon oxidized & prevented drop from spreading, system leak
CNTD Si_3N_4 ⁽¹⁾ Part No. 6	"	$\geq 10^{-16}$	Not measurable	"	Same as immediately above
CNTD Si_3N_4 ⁽¹⁾ Part No. 13	"	$\sim 10^{-17}$	58°	Slight	This pressure was near or slightly above the equilibrium P_{O_2} for $Si + O_2 = SiO_2$
CNTD Si_3N_4 ⁽¹⁾ Part No. 5	(5)	10^{-17} $+ 10^{-24}$	56°	No	See Figure 14, Contact Angle Vrs. Time
CNTD Si_3N_4 ⁽¹⁾ Part No. 14	(6)	"	52°	"	Same as immediately above

(1) Coating on "Pure" Si_3N_4 (with 4 wt/o MgO), Substrate Lot PP-33

(2) All experiments performed at 1450°C, 1 hr at temperature

(3) As received hydrogen (cylinder)

(4) Value unreliable due to SiO_2 "fence"

(5) Hydrogen over titanium at 870°C

(6) Hydrogen over titanium at 870°C then through liquid nitrogen cold trap

TABLE V -continued

<u>Coated Substrate Designation</u>	<u>Experimental Atmosphere</u>	<u>P_{O₂} (atm)</u>	<u>Contact Angle After 40 Min</u>	<u>Oxidation of Silicon</u>	<u>Comments (2)</u>
CNTD SiC (7) Part No. 7	(3)	10^{-18} → 10^{-24}	29°	No	See Figure 15, Contact Angle Vrs. Time
CNTD SiC (7) Part No. 19	(8)	"	27°	"	Same as immediately above
AlN (9), Part No. 1	(3)	$\sim 10^{-17}$	72°	"	

(7) Coating on SiC (with 1 wt/o B), Substrate Lot PP-26

(8) Hydrogen over titanium at 1000°C

(9) Coating on AlN pressed w/o additive