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DEVELOPMENT OF MULLITE SUBSTRATES AND CONTAINERS

Final Report, October 7, 1977—April 15, 1979

By
J. D. Sibold
D. G. Wirth

April 20, 1979

Work Performed Under Contract No. NAS-7-100-954878

Coors Porcelain Company
Golden, Colorado

U.S. Department of Energy

Solar Energy

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FINAL REPORT

(Covering the Period October 7, 1977 to April 15, 1979)

on

DEVELOPMENT OF MULLITE SUBSTRATES AND CONTAINERS

JPL Contract No. 954878
Silicon Sheet Task
Low-Cost Silicon Solar Array Project

to

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

April 20, 1979

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, by agreement between NASA and DOE

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

J. D. Sibold, Principal Investigator, and D. G. Wirth, Program Manager

COORS PORCELAIN COMPANY
GOLDEN, COLORADO 80401

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ABSTRACT

The objective of this program was to evaluate mullite in contact with molten silicon to be used as a substrate for Honeywell's Silicon-On-Ceramic process and as a container for melting solar grade silicon. A further requirement was to fabricate respective substrates and containers. To maintain solar grade silicon purity levels, the mullite must generally introduce less than 10^{15} atoms/cc of impurities.

To evaluate the mullite-molten silicon interaction, a series of bodies were made with variations in density, alumina-silica ratio and glass-crystalline ratio. These materials were tested in a sessile drop technique. None of the variations stood up to extended exposure to molten silicon sufficiently to be recommended as a container material. However, directional solidification experiments by Jet Propulsion Laboratory suggest that, under proper conditions, contamination of the silicon by mullite containers can be minimized.

To improve an already good thermal expansion match between mullite and silicon, compositional variations were studied. Altering of the alumina-silica ratio was determined to give a continuously varying thermal expansion. Thus, a composition can be selected to give the desired thermal expansion match with silicon.

Concurrent to this work, a standard mullite composition was selected to be used for fabrication development. The major fabrication development requirements were to make substrates 40 x 4 x .040 inches and slotted substrates. Fabrication of standard mullite composition substrates, nominally 40 x 4 x .040 inches, have been made and delivered to Honeywell. Slotted substrates of various configurations and various compositions are regularly being supplied to Honeywell.

INTRODUCTION

This study program started October 6, 1977. Its purpose was to develop and evaluate substrate and container materials for silicon. The alumino-silicate system was selected by Honeywell, Inc., to be used as a substrate to be coated with molten silicon to produce solar-cell quality sheet silicon. This system was also evaluated as a container material for melting solar grade silicon. These efforts were directed in support of the Jet Propulsion Laboratory (JPL) program to produce minimum cost solar cells with a terrestial conversion efficiency of 12 percent or greater.

Mullite is the only stable intermediate compound in the Al_2O_3-SiO_2 system. With a formula of $3AL_2O_3 \cdot 2SiO_2$, it is ideally 71.8% Al_2O_3 and 28.2 SiO_2. However, a range of solid solution is observed in this system. In practice, most commercial mullite bodies are made by combining kaolin clays with alumina to obtain compositions such as 58% Al_2O_3 and 40% SiO_2 with the remainder being mainly Fe_2O_3, TiO_2, K_2O, and Na_2O impurities. The result is a material composed of mullite crystals bonded by a high silica glass phase. The excess alumina is added to the clay to form more mullite which minimizes slumping at high use temperatures.

The property of initial interest was the coefficient of thermal expansion of the commercial mullite bodies which is approximately 5×10^{-6} in/in/°C. Since this approaches the coefficient of thermal expansion of silicon of 4.1×10^{-6} in/in/°C and mullite maintains good strength at 1450°C, commercial mullite met many of the requirements for substrates and containers in contact with molten silicon.

The mullite substrates are being used by Honeywell for their Silicon-On-Ceramic process. This process involves coating inexpensive ceramic substrates with solar quality sheet silicon. By coating one surface of the ceramic substrate with graphite, molten silicon wets the graphite coated side of the substrate. The molten silicon is presently applied by dipping the substrate in molten silicon. This technique requires good thermal shock resistance and mechanical stability at 1450°C in molten silicon. Additionally, because of the large temperature change upon cooling, the thermal expansion of the substrate must be near that of silicon to prevent breakage or bending of the composite.

The program included several subtasks. These included:

1. Evaluation of properties of several variations of a conventional mullite.
2. Development of mullite sheet for dip coating and continuous coating.
3. Development of slotted substrates for electrical contacting.
4. Manufacturing process.
5. Cost analysis for extended sheet.
6. Thermal expansion.
7. Container development.
8. Sessile drop experiments.

EVALUATION OF PROPERTIES OF SEVERAL VARIATIONS OF A CONVENTIONAL MULLITE

Initial material screening by Honeywell demonstrated that mullite was generally stable in molten silicon. Since substrates were desired and mullite substrates would initially be dry pressed, Coors' S-1-SI body was selected for initial trials. Substrates approximately 1.6 x 2.1 x .125 inches gave encouraging results in Honeywell's evaluation.

Since little was known about the optimum mullite composition, a series of eight variable compositions and firings based on Coors Standard S-1-SI mullite body were selected. Table 1 lists compositions, properties, and analyses of these bodies. Microstructures are shown in Figure 1A through H. These variables were selected to vary % mullite phase/% glass phase (A, B, C, G), the porosity (A, E, G), and the firing atmosphere (A, H). Approximately 50 substrates 1.6 x 2.1 x .125 inches were made for Honeywell from each composition. Dipping experiments by Honeywell eliminated only composition G, electrically fused mullite. The composition did not withstand the thermal shock. The other compositions were rated about equal.

		APPROXIMATE % OXIDE COMPOSITION									PROPERTIES				LAB ANALYSIS		
		Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	B_2O_2	Density	Porosity	Thickness Shrinkage	Length Shrinkage	% Mullite By X-ray	% Mullite By Photo Micrograph	Thermal Expansion Rm. Temp to 1000°C
1A Coor's Composition	STD S-1-SI	57.6	38.9	0.62	0.13	0.25	0.92	0.25	1.12	0.00	2.70	0.32	12.06	16.66	76.5	61.5	5.41×10^{-6}
1B High Mullite	982 HPM	67.2	31.4	0.45	0.02	0.01	0.16	0.18	0.54		2.86	.22	12.10	12.69	70.2	78.5	5.0×10^{-6}
1C High Silica	996 HPM	52.2	44.7	0.56	0.13	0.22	0.83	0.22	1.01	0.00	2.58		14.2	12.3	56.1	47.0	4.95×10^{-6}
1D Boric Acid	7 HPM	56.7	38.3	0.61	0.13	0.24	0.90	0.24	1.10	1.50	2.60	.19	11.72	13.72	66.8	74.0	5.52×10^{-6}
1E Open Porosity	STD S-1-SI	57.6	38.9	0.62	0.13	0.25	0.92	0.25	1.12	0.00	2.55	7.27	11.56	13.75	66.4	79.2	5.41×10^{-6}
1F High Purity	979 HPM	57.6	39.1	0.44	0.21	0.13	0.34	0.05	0.30	0.00	2.70	0.53	14.91	19.49	66.8	86.6	5.26×10^{-6}
1G Electrically fused	995 HPM	77.5	21.9	0.12	0.00	0.00	0.00	0.35	0.05	0.00	2.62	13.89	10.40	11.34	84.2	98.6	5.46×10^{-6}
1H Reducing Fire	S-1-SI	57.6	38.9	0.62	0.13	0.25	0.92	0.25	1.12	0.00	1)2.88 2)2.67	0.38 11.4	12.50	18.06	66.4	82.0	5.31×10^{-6}

1) All dark part
2) 50% dark part

COMMENTS

Table I

APPROXIMATE OXIDE COMPOSITION
AND
PROPERTIES OF FIRST EIGHT VARIATIONS OF S-1-SI

Figure 1a S1SI

Figure 1b High Mullite

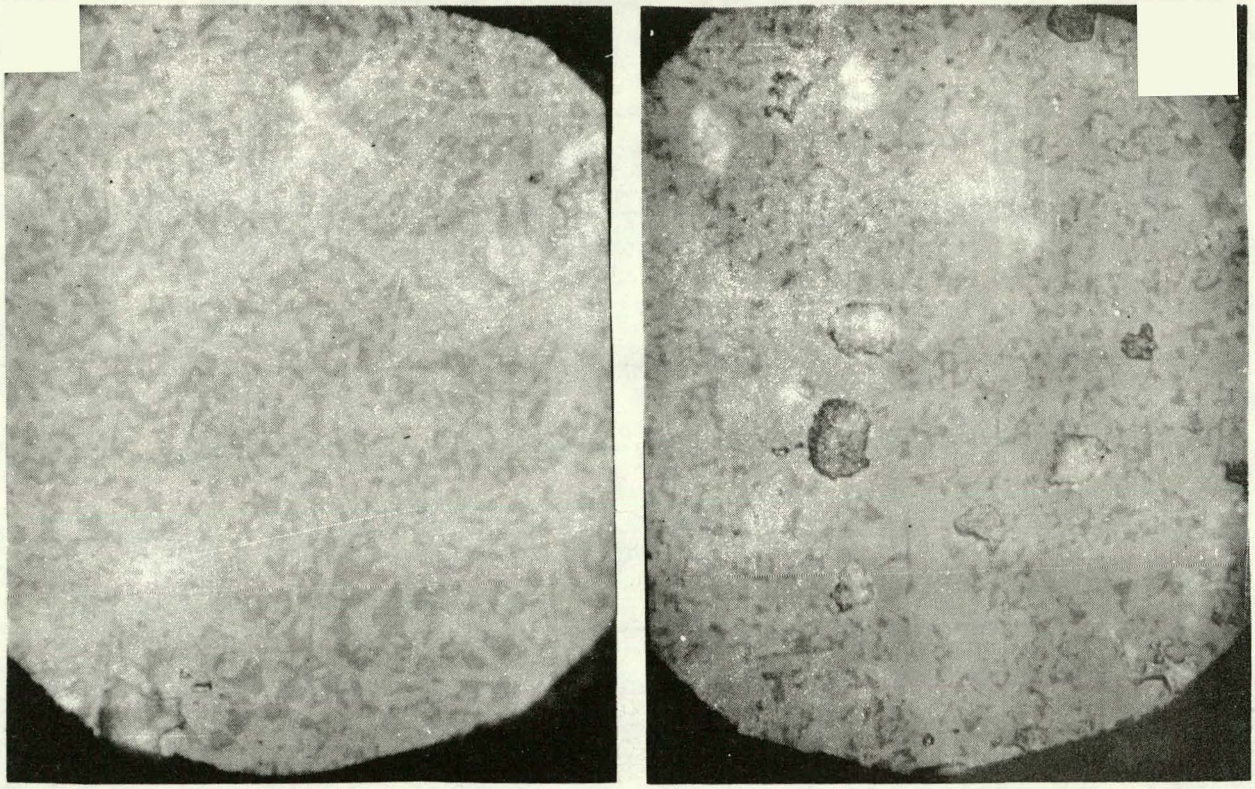
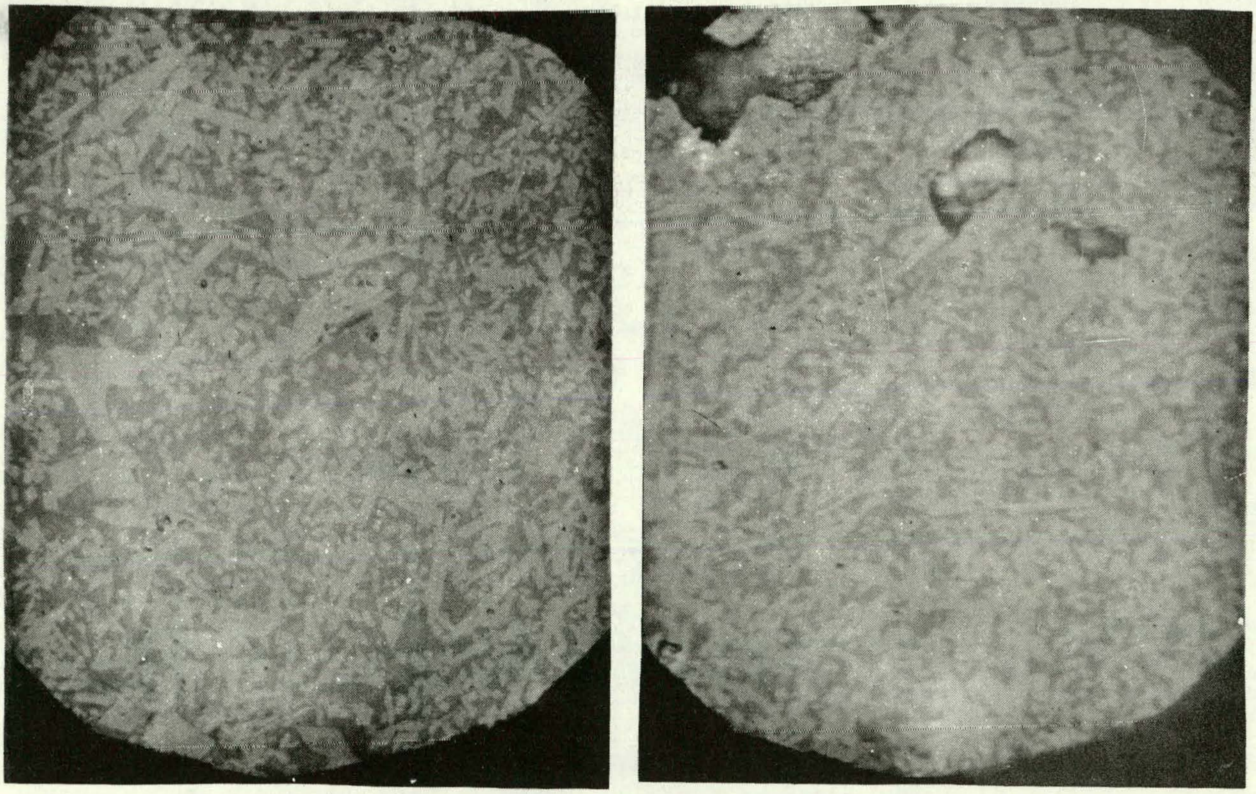


Figure 1c High Silica

Figure 1d Boric Acid



MICROSTRUCTURES OF FIRST EIGHT VARIATIONS OF S-1-SI

Figure 1e Open Porosity

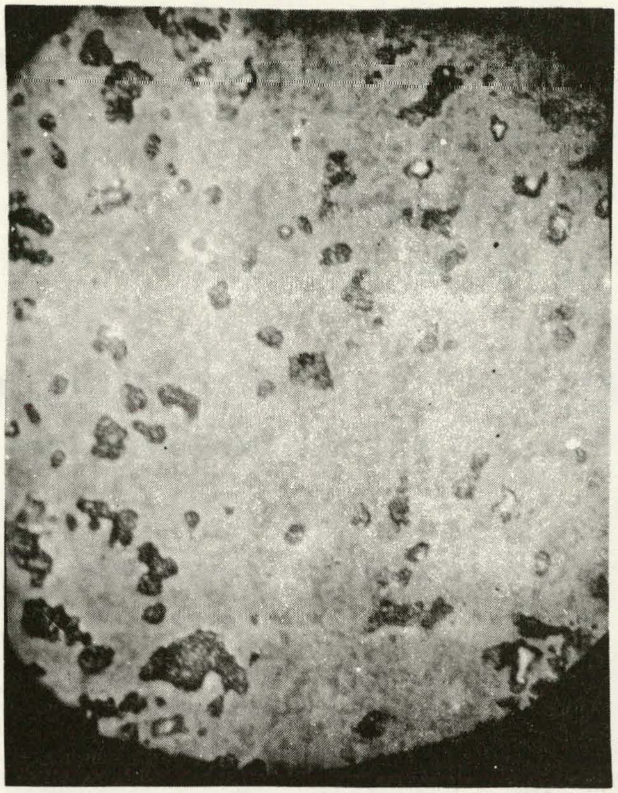


Figure 1f High Purity

Figure 1g Electrically Fused

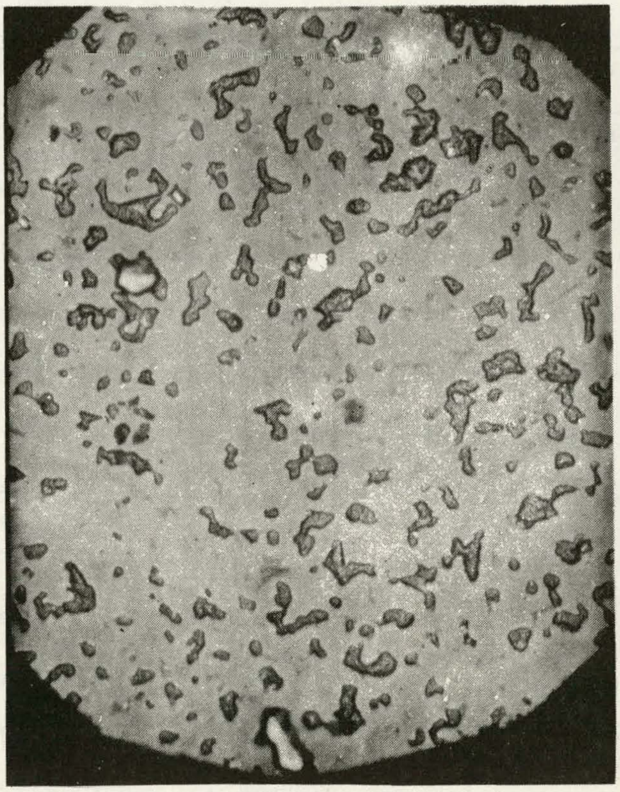
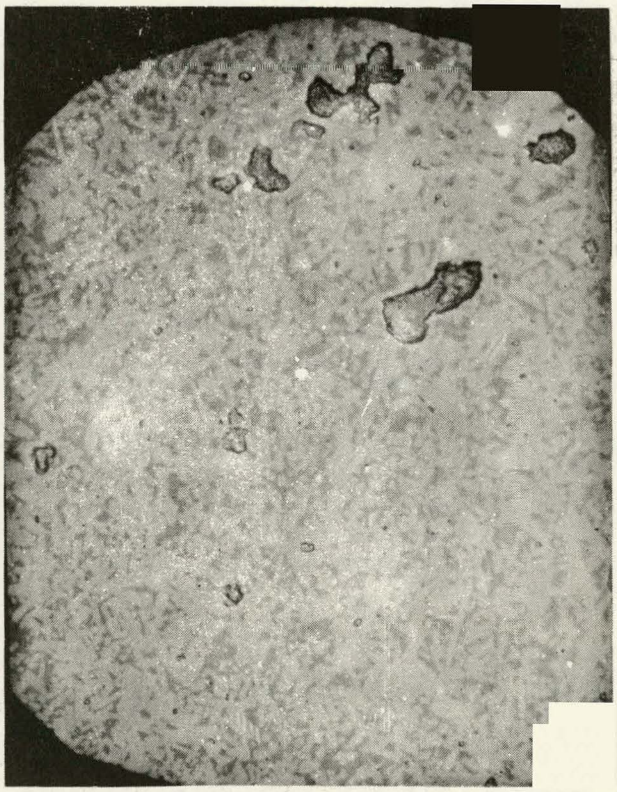


Figure 1h Reducing Fire



MICROSTRUCTURES OF FIRST EIGHT VARIATIONS OF S-1-SI

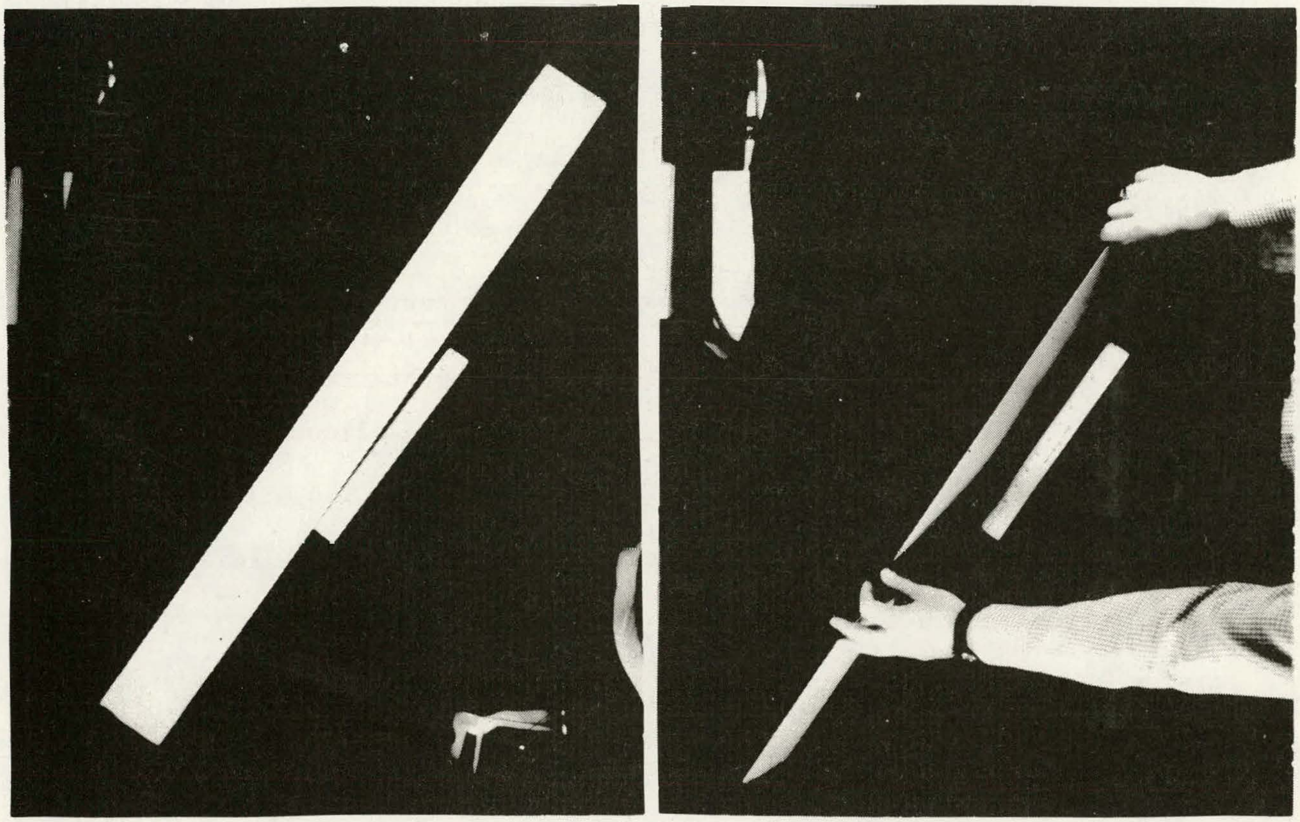
DEVELOPMENT OF MULLITE SHEET FOR DIP COATING AND CONTINUOUS COATING

Honeywell's Silicon-On-Ceramic process is predicated on growing a silicon film on an inexpensive substrate. The silicon film is applied by coating the substrate with molten silicon at approximately 1430°C. In cooling the substrate/silicon composite, thermal stresses develop due to thermal expansion/contraction mismatches. Therefore, to keep the silicon from spalling off the substrate during cooling, the substrate must have a thermal expansion close to that of silicon. Commercial mullite bodies made from kaolin clays and alumina are potentially inexpensive, have a thermal expansion fairly close to silicon, and are mechanically stable at the melting temperature of silicon.

Along with the compositional development, it was necessary to develop methods for making substrates in the shapes required by the Honeywell process. The initial requirement was for shapes 6.75 x 4.25 x 0.1 cm for dip coating and 100 x 10 x 0.1 cm for "scim" coating (scim-Silicon Coating by Inverse Miniscus). Scim coating coats one side of a moving substrate with silicon. To meet cost goals of $.50/watt in 1986, Silicon-On-Ceramic process requires extended sheets of ceramic to be coated with silicon. To make extended mullite sheets, a proprietary roll compaction process was selected. The goal was to make sheets 100 cm x 10 cm x 0.1 cm. Coors standard S-1-SI composition was selected for these extended sheets since this work was concurrent to the composition development. After 3 variations in proprietary binders, twelve sheets 100 cm x 10 cm x 0.1 cm were delivered to Honeywell. An example is shown in Figure 2. The sheets were quite flat, fairly smooth, and strong enough to be handled. Some early parts which were only .05 cm thick were very fragile and could be handled only with extreme care. No major difficulties were encountered in making these large substrates. Of course, no stringent tolerances or specifications have been required of these parts as yet. Such things as surface flaws and dimensional controls have not been evaluated.

Figure 2

PHOTOGRAPH OF 1 METER X 10 CENTIMETER X 1 MILLIMETER SUBSTRATE



DEVELOPMENT OF SLOTTED SUBSTRATES FOR ELECTRICAL CONTACTING

Since the mullite sheet is an electrical insulator, it was necessary to make both contacts on the front of an SOC solar cell. This, of course, reduced the total area efficiency of an SOC cell. Thus, to meet minimum acceptable efficiencies, it was necessary to develop a back contact technique. The most straight-forward method was to put holes or slots in the ceramic. A slot pattern, Figure 3, was designed by Honeywell to be used for the dipped substrates. This design has, in fact, improved the performance of the SOC cell. The hole at the top is for suspending the part in the silicon melt. The initial slotted substrates were made by sawing prefired hand dry pressed substrates. This was accomplished by using a small silicon carbide blade attached to a small high speed drill. The drill motor was attached to an indexing table. The results of these early efforts are shown in Figure 6. Of particular notice in these photographs is the irregular shape of the substrates and the tapered shape of the slots. The irregular shape of the substrate is due to the hand pressing. The slot shape is due to the sawing technique.

With the development of the roll compaction tape system, it became possible to punch the slots. All slots are simultaneously mechanically punched. Presently, this is done using plastic tooling which shears the tape in the prescribed pattern. The slots are then manually deshaded. This is an effective technique on quantities of less than 2000,. At higher quantities, hard metal tooling would be made with cycles over 30/minute. Punching the slots yields a much more uniform pattern as evidenced by Figure 5. During deshading, the edge of the slot at the back surface will shear away. The amount of this roughness varied with the flexibility of the tape. The more flexible, the less edge chipping.

Figure 3

SLOT PATTERN FOR SLOTTED SUBSTRATES

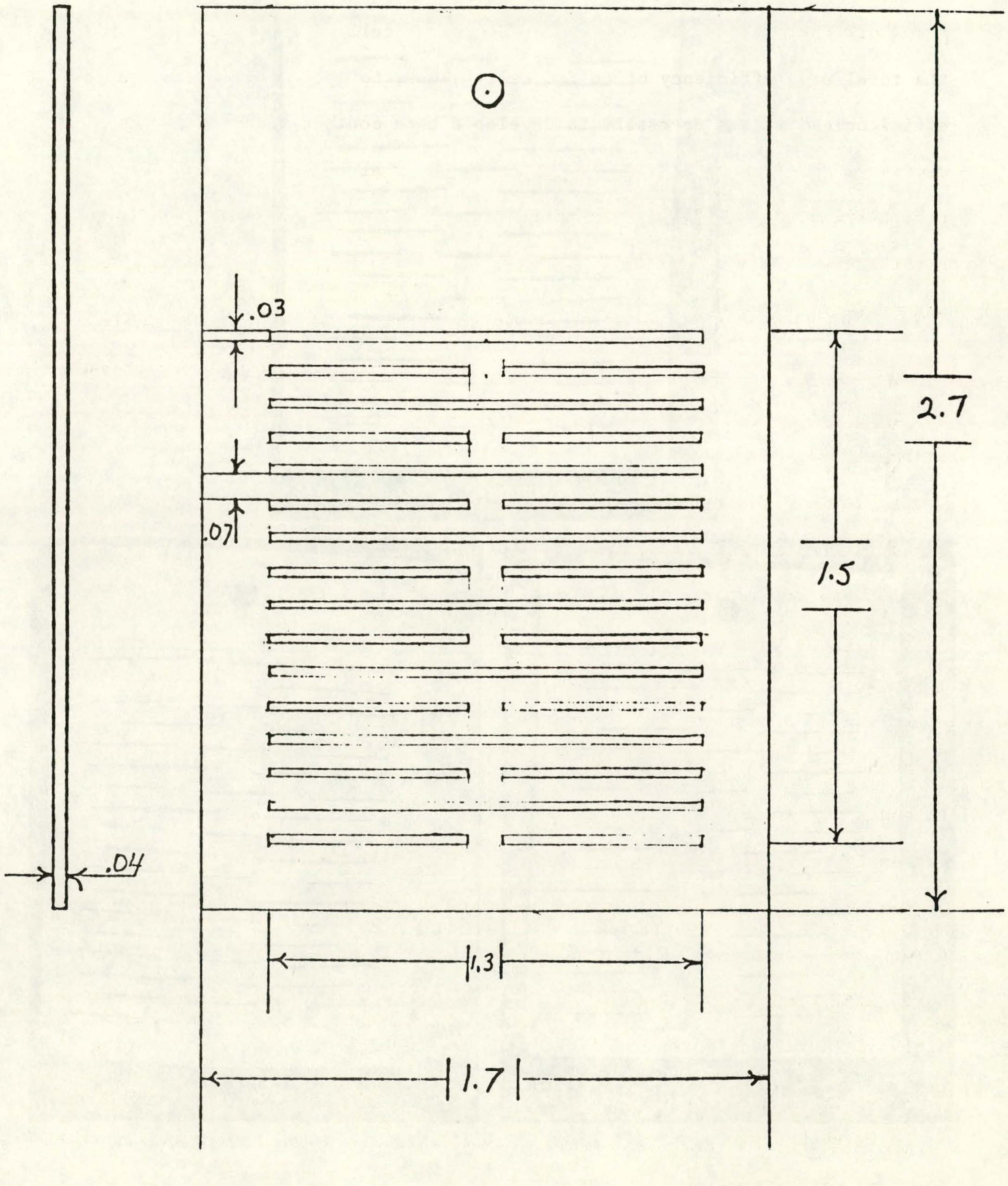


Figure 4

PHOTOGRAPH OF SAWN SUBSTRATE

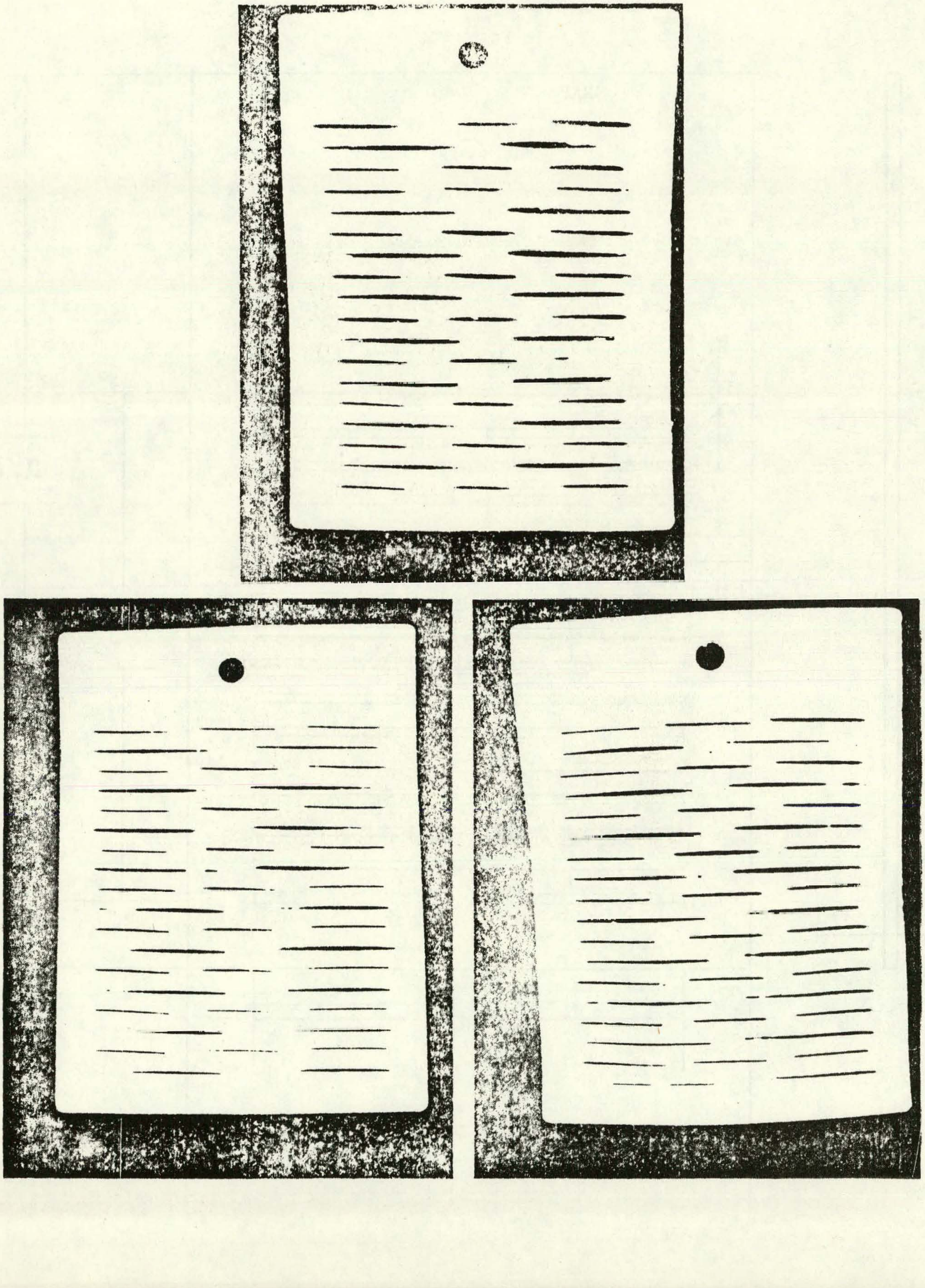
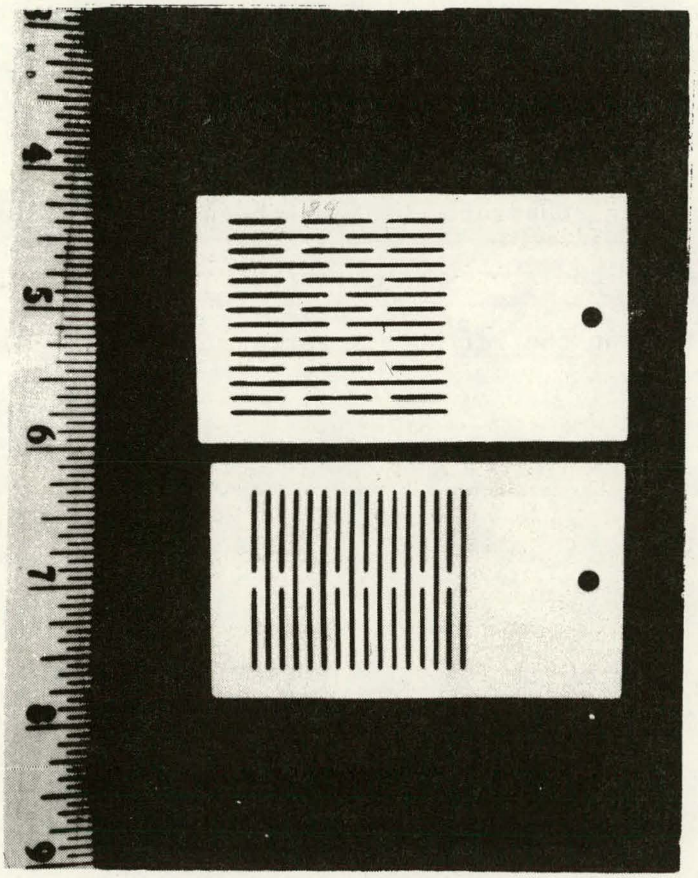


Figure 5

PHOTOGRAPH OF PUNCHED SUBSTRATE

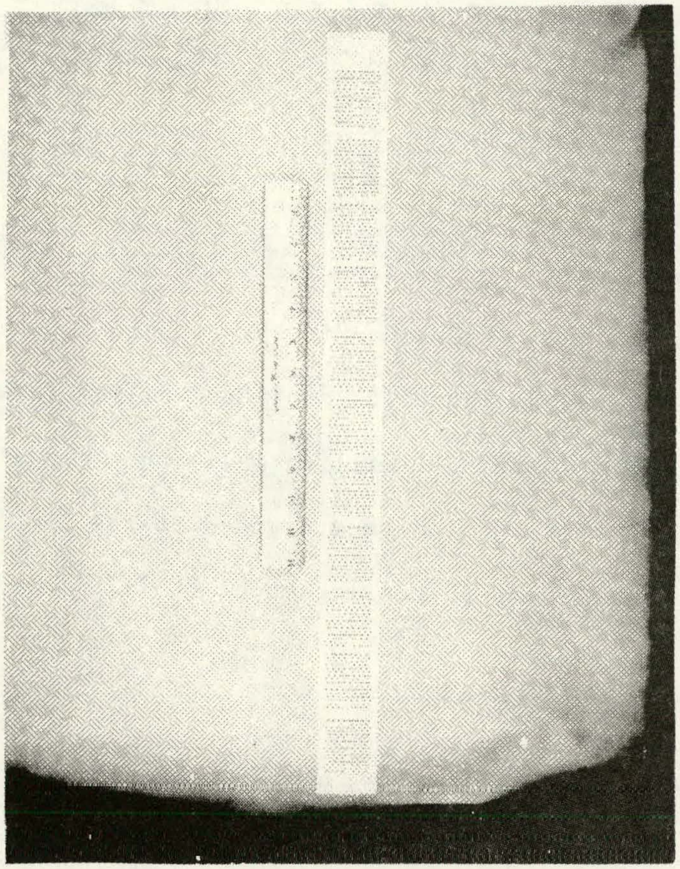


Another irregularity which is noticed in Figure 5 is the widening of the long slot. This is due to the drag of the shrinking part on its setter during firing. This can probably only be remedied by using a shorter slot. In discussions with Honeywell, this would probably be an acceptable solution to them.

Figure 6 shows a long substrate which has been punched repeatedly. In firing these longer pieces, the slot width becomes more of a problem because the end slots must drag on the refractory setter for longer distances.

Figure 6

PHOTOGRAPH OF LONG PUNCHED SUBSTRATE



MANUFACTURING PROCESS

Currently "K" modification substrates are being regularly manufactured for Honeywell. The process consists of blending Coors S-1-SI body with amorphous silica, wet ball milling, spray drying, roll compacting, cutting and/or punching and firing. Presently, Coors is manufacturing slotted and unslotted substrates nominally 75 x 45 x 1 mm and also 560 x 50 x 1 mm.

S-1-SI is a Coors composition that is used for pressing mullite ceramics. Its approximate oxide composition is listed as "A" in Table II. The amorphous silica used is Sil-Co-Sil, a product of Ottawa Silica. A formulation of 72.5% S-1-SI and 27.5% amorphous silica is weighed out and wet ball milled using Coors AB-9 milling media in a ceramic lined ball mill. The appropriate proprietary binders are added to the slurry. The slurry is then spray dried in a Bowen Engineering model BE 717 nozzle type spray dryer.

(Since S-1-SI is a proprietary Coors formulation, a formulation developed under this contract is presented in Figure 7. The same manufacturing process as described above is used with this formulation. This formulation produced substrates with a thermal expansion the same as the K modification. This result further supports the Al_2O_3/SiO_2 ratio relationship to thermal expansion in the mullite system.)

Figure 7

MULLITE FORMULATION

Batch 227 RCM N Modification Mullite

Material	Weight Per cent	Supplier
Mulcoa Mulgrain 45, 35F	89.74	C.E. Minerals
Silcosil	10.26	Ottawa Silica Co.

Calculated Oxide Composition

Al_2O_3	41.0%
SiO_2	56.5
Fe_2O_3	0.89
TiO_2	1.56
CaO	0.02
MgO	0.04
K_2O	0.02
NO_2O	0.03

The spray dried body is then roll compacted into a continuous flexible tape approximately 1 mm thick. The roll compaction process is a proprietary Coors process for making alumina substrates. The process has been adapted to making these mullite substrates.

The roll compacted tape is cut or punched to the final shape. The 560 x 50 x 1 mm unslotted substrates are simply cut with a razor blade to their unfired lateral dimensions. The 75 x 45 x 1 mm slotted and unslotted substrates are punched using plastic tooling which punch the outline and the slot pattern into the green tape. These parts must then be hand deshaded. If the quantity increases to above 2000 pieces, it becomes economical to buy a steel or carbide punch tool. With this hardened tooling, punching rates of 1500 to 2000 pieces per hour could be expected.

The punched parts are then fired on mullite bonded alumina refractory setters. The flatter and smoother the setters, the flatter and smoother the substrates are. The "K" modification is fired to cone 28 (approximately 1525°C for 2 hours). The resulting substrates are impervious. The parts are dye checked with a penetrating dye and visually examined for cracks, surface irregularities, and excessive camber.

COST ANALYSIS FOR EXTENDED SHEET

A cost analysis was made on producing 5 x $10^6 m^2$/year of substrates 1 meter x 10 centimeters x 1 millimeter. The analysis was based on realistic present day rates. The results of this analysis are shown in Figure 8. Obviously, the firing is the major cost step in the process. Proprietary techniques have demonstrated 10 to 20 times improvement in firing efficiency in related products. This would lower cost projections to $\$3.19/_{m}2$ to $\$3.61/m^2$. Also apparent is that changes in composition and in thickness can sufficiently affect raw material cost. Slotting of the substrates would also lower raw material cost since less raw material would be used. However, the addition of a punching step for the slots would at least offset the savings. The cost analysis does not reflect losses in yield due to specifications that are unknown at this time. These specifications could greatly affect the cost depending on how they affected the yield and what processing changes would be necessitated by these specifications.

Figure 8

COST ANALYSIS - UNSLOTTED MULLITE SUBSTRATES

Quantity - 5 x 10^6 m^2/year.

Size - 1 m x 10 cm x 1 mm

Breakdown	$/$m^2$ at 1 mm thk.
Raw Material	$ 1.21
Body Preparation	$ 0.02
Roll Compaction	$ 1.25
Forming	$ 0.25
Firing	$ 7.21
Refractory	$ 1.25
	$11.19

Above costs based upon:

80% process yield

For other compositions raw material cost is as follows:

Raw Material Cost	
B. High Mullite	$1.238
C. High Glass	$1.078
D. Glass Property Modification	$1.666
E. Open Porosity	$1.145
F. High Purity Clays	$0.878
G. Electrically Fused	$3.095
H. Reducing Fire	$1.243

Sensitivity on above factors:

1. **Thickness - Will directly effect raw material cost and body preparation only.**
2. **Firing - Improved firing efficiency by the following factors would reduce cost as follows:**

	FIRING COST	TOTAL COST
Standard Condition	$ 8.46	$ 11.19
10X Improvement	.845	3.61
20X Improvement	.423	3.19

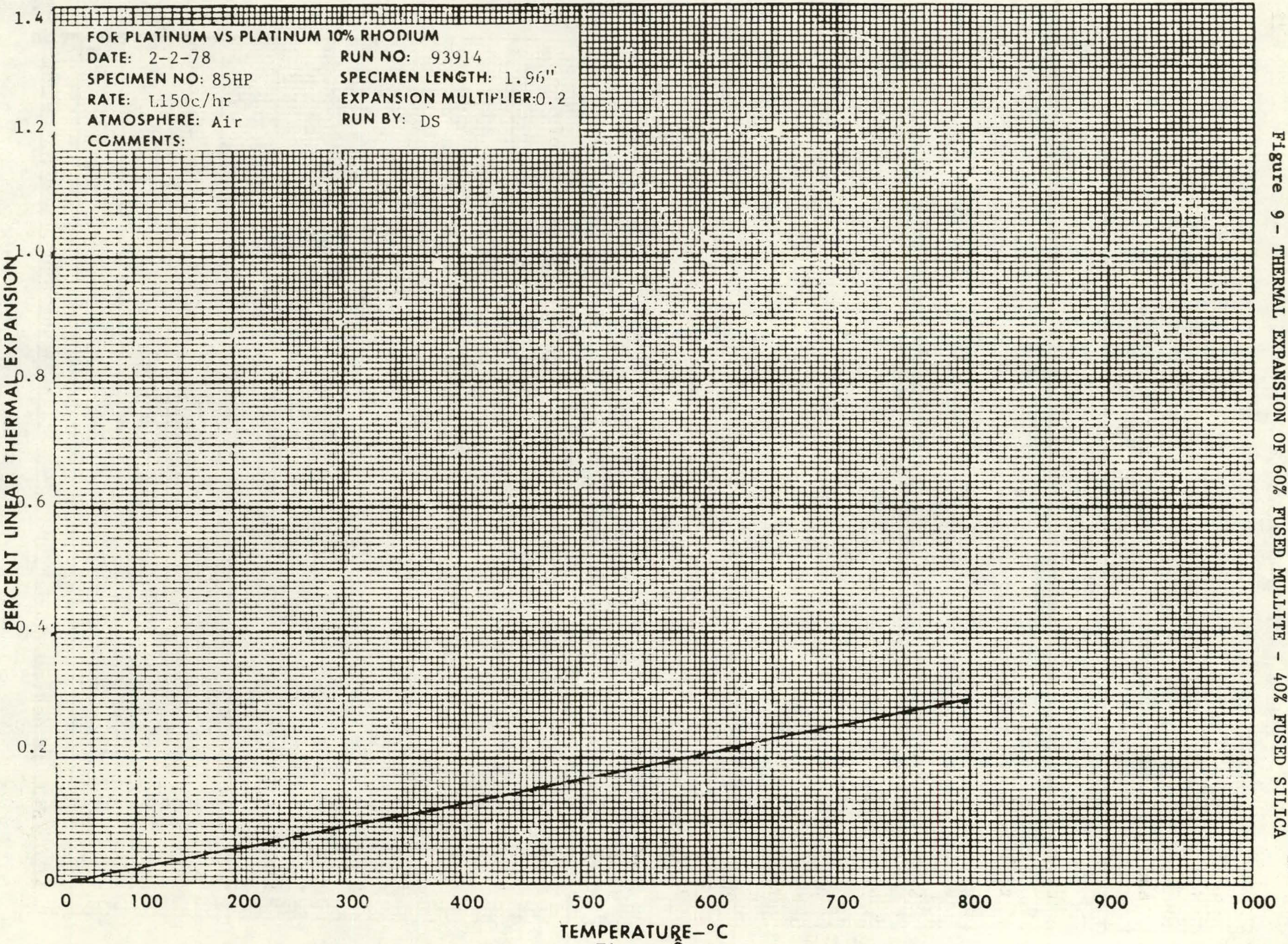
THERMAL EXPANSION

As Honeywell began dip coating S-1-SI pressed substrates, it became apparent that the thermal expansion mismatch of the substrates and the silicon would have to be minimized. As long as the S-1-SI substrates were thick enough (.125 inches) no fractures would occur. However, as we made .040 inch thick substrates with slots, fractures began occurring in the silicon after solidification, during further processing, and some would just break after a few days of storage.

In reviewing our first eight compositional variations listed in Table I, variations of the glass phase were felt to be a likely approach to lower the expansion. Low expansion borosilicate glass compositions were selected since the boron might be tolerated as a dopant. To facilitate testing and since the boric acid addition did not lower expansion, a series of bodies were made by dry milling Pyrex and fused mullite to 75% less than 20 microns. The fired results gave high expansions and slumped at about 700°C. This slumping is obviously unsatisfactory for contact with molten silicon at 1425°C. At the same time, a series of bodies were made with fused silica and fused mullite. These compositions were dry milled to 75% less than 10 microns. Firing of these bodies provided a dense, white, translucent ceramic. One composition, 60% fused mullite and 40% fused silica, had a thermal expansion lower than recorded for silicon. See Figures 9 and 10. It was expected that the fused silica would devitrify either during initial firing or in subsequent heat treatment. However, no change in thermal expansion was recorded on heat-up and cool-down or after refiring to 1450°C for 4 hours.

Since these fused mullite/fused silica bodies would be impractical, efforts in changing S-1-SI's thermal expansion were explored by varying the Al_2O_3/SiO_2 ratio. This proved very fruitful as evidenced by Table II. As the Al_2O_3/SiO_2 ratio decreases, the thermal expansion at 800°C also decreases. This is also shown in Figure 11 which is a plot of percent thermal expansion at 800°C versus Al_2O_3/SiO_2 ratio. Figure 12 shows the phase diagram for the alumina-silica system. Since these bodies are being fired above 1600°C, the equilibrium field of interest is the mullite solid solution plus liquid phase field. Because of the high viscosity of the liquid phase upon cooling, no silica crystalline phase such as cristobalite is formed, only a silica rich glass phase. X-ray diffraction analysis detected only mullite and an amorphous phase. In Figure 12 in the mullite solid solution plus liquid phase field, a dotted line has been drawn at 1650°C and compositions A, K, L, and M have been denoted. In decreasing the Al_2O_3/SiO_2 ratio from A (1.48) to M (.67) ideally the glass phase has increased from 29% (A) to 57% (M). However, this is not an equilibrium situation and in examining Table II, we can see a large amount of impurities which will affect the liquidus temperatures. Nevertheless, microscopic studies do indicate an increasing amount of glass phase formed as the Al_2O_3/SiO_2 is decreased.

*60% Fused Mullite 40% Fused Silica


FOR PLATINUM VS PLATINUM 10% RHODIUM

DATE: 2-2-78

RUN NO: 93914

SPECIMEN NO: 85HP

SPECIMEN LENGTH: 1.96"

RATE: L150c/hr

EXPANSION MULTIPLIER: 0.2

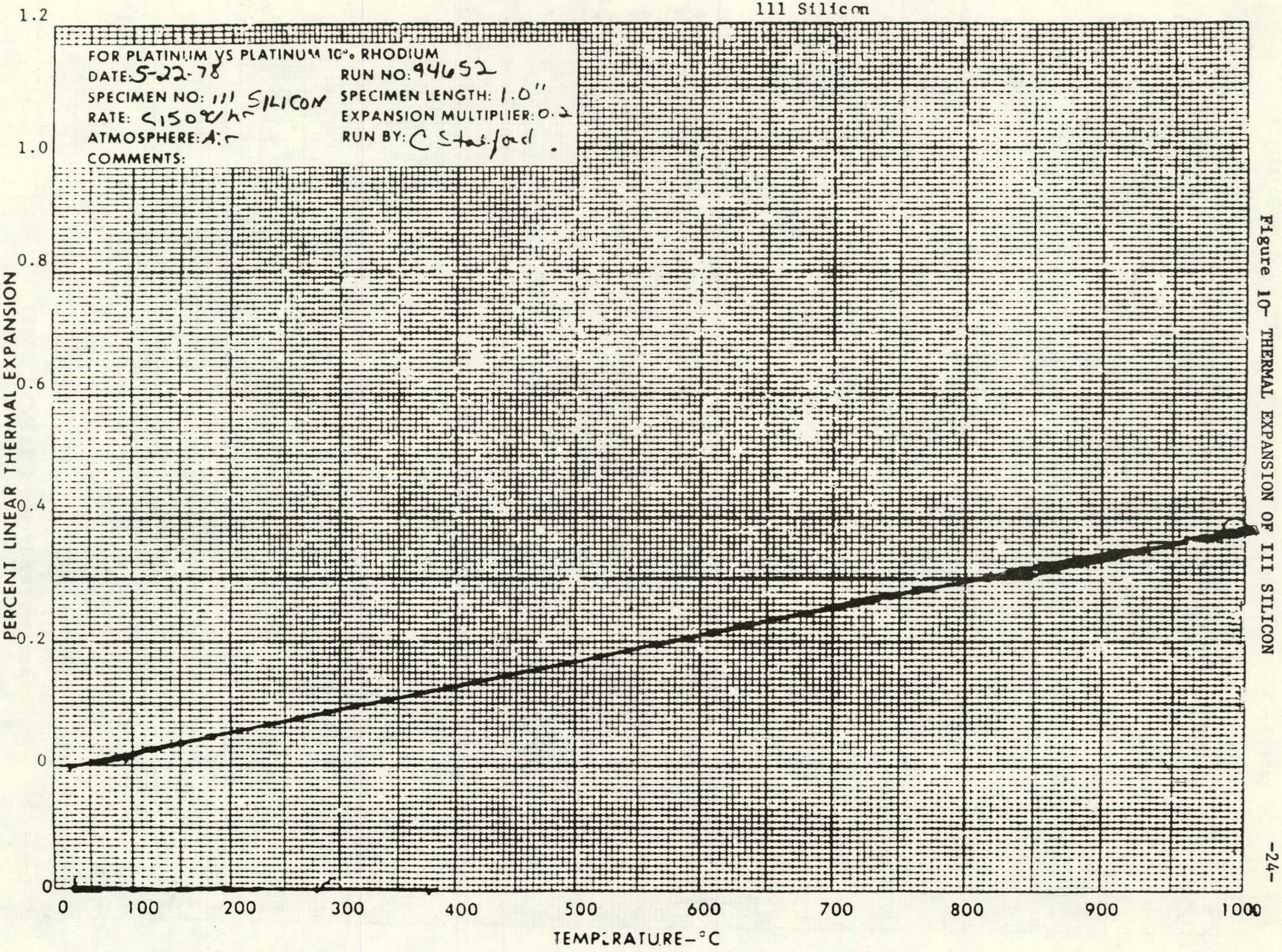
ATMOSPHERE: Air

RUN BY: DS

COMMENTS:

Figure 9

Figure 9 - THERMAL EXPANSION OF 60% FUSED MULLITE - 40% FUSED SILICA



FOR PLATINUM VS PLATINUM 10% RHODIUM
DATE: 5-22-78
RUN NO: 94652
SPECIMEN NO: 111 SILICON
SPECIMEN LENGTH: 1.0"
RATE: <150°C/hr
EXPANSION MULTIPLIER: 0.2
ATMOSPHERE: Air
RUN BY: C Stanford.
COMMENTS:

Figure 10- THERMAL EXPANSION OF III SILICON

TABLE II

APPROXIMATE OXIDE COMPOSITION, Al_2O_3/SiO_2 RATIO & THERMAL EXPANSION AT 800°C FOR SiO_2 ADDITIONS TO S-1-SI

TASK	BODY	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	K_2O	NaO_2	TiO_2	Al_2O_3/SiO_2	Th.Ex. 800°C
A	Std S-1-SI Coors' Composition	57.6	38.9	0.62	0.13	0.25	0.92	0.25	1.12	1.48	0.375
	996 HPM High Silica	52.2	44.7	0.56	0.13	0.22	0.83	0.22	1.01	1.17	0.35
	117 HPM S-1-SI + 10% SiO_2	52.3	44.7	0.56	0.14	0.23	0.83	0.22	1.02	1.17	0.37
	118 HPM S-1-SI + 12.5% SiO_2	51.1	46.0	0.55	0.14	0.22	0.81	0.22	0.99	1.11	0.36
	119 HPM S-1-SI + 15% SiO_2	49.9	47.2	0.54	0.14	0.22	0.80	0.21	0.97	1.07	0.38
1ST J	120 HPM S-1-SI + 17.5% SiO_2	48.8	48.3	0.53	0.14	0.21	0.78	0.21	0.85	1.01	0.37
	121 HPM S-1-SI + 20% SiO_2	47.8	49.4	0.52	0.14	0.21	0.76	0.20	0.93	0.97	0.33
1st K	134 HPM S-1-SI + 27.2% SiO_2	45.0	52.4	0.49	0.14	0.20	0.72	0.19	0.87	0.86	0.32
2nd J	183 HPM 80% S-1-SI + 20% SiO_2	45.8	51.5	0.50	0.14	0.20	0.73	0.19	0.89	0.89	
2nd K	184 HPM 72.5% S-1-SI + 27.5% SiO_2	41.4	56.2	0.45	0.14	0.18	0.66	0.18	0.81	0.74	0.292
L	71.43% S-1-SI 28.57% SiO_2	40.7	56.9	0.45	0.14	0.18	0.66	0.18	0.79	0.715	0.287
M	69% S-1-SI 218 HPM 31% SiO_2	39.2	58.4	0.43	0.14	0.17	0.64	0.17	0.77	0.67	0.315
M_A	By Chem Lab Analysis	44.6	54.2	NA	NA	NA	NA	NA	NA	0.82	0.315
M_R	69% S-1-SI 304 HPM 31% SiO_2	39.2	58.4	0.43	0.14	0.17	0.64	0.17	0.77	0.67	0.290
	66.8% S-1-SI 307M 33.2% SiO_2	38.1	59.7	0.42	0.14	0.17	0.61	0.16	0.74	0.64	0.285
	63.65% S-1-SI 308M 36.35% SiO_2	36.2	61.6	0.40	0.14	0.16	0.58	0.15	0.76	0.59	0.277
	56.7% S-1-SI 43.3% SiO_2	32.2	65.9	0.36	0.14	0.14	0.51	0.14	0.63	0.49	0.330

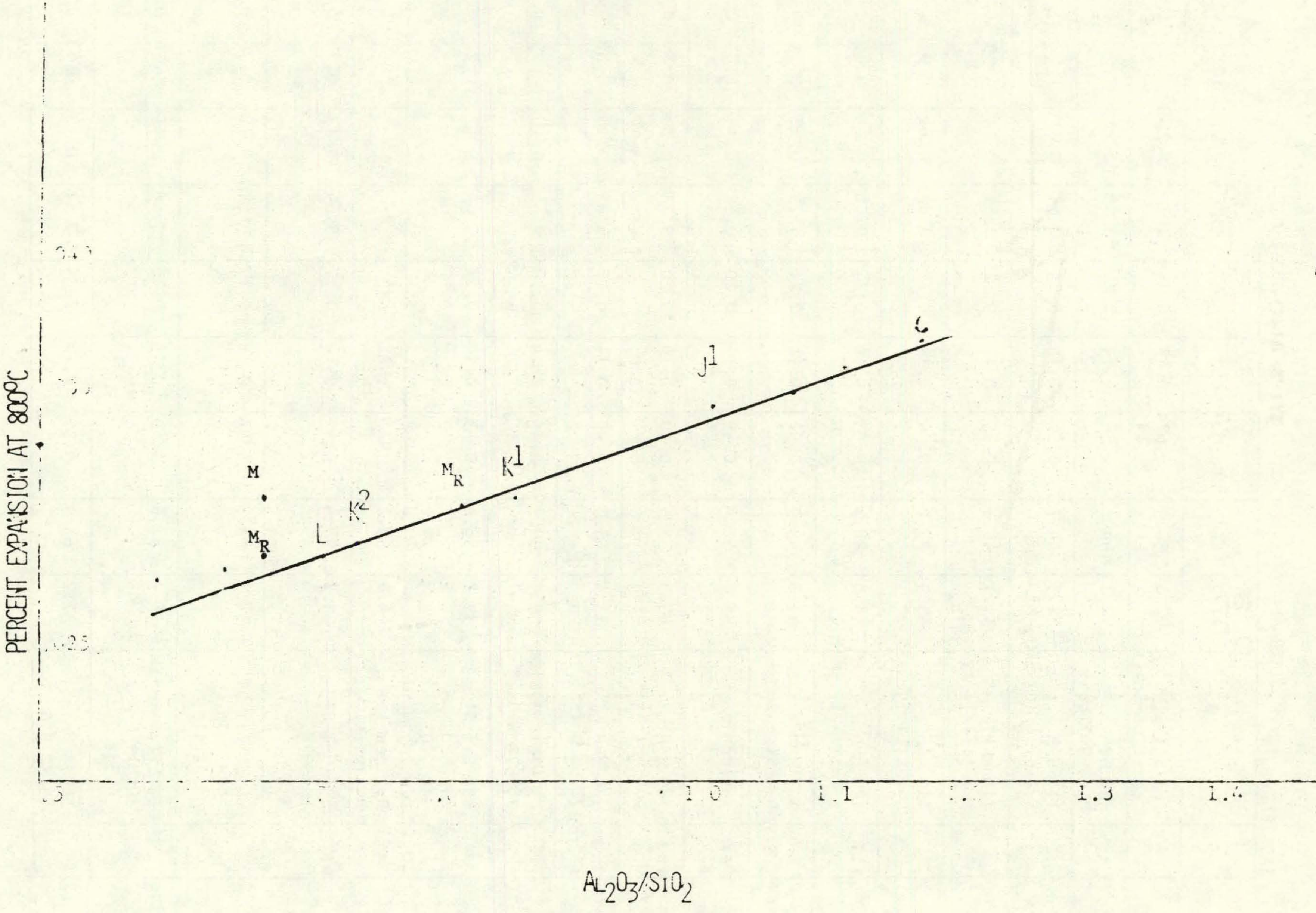
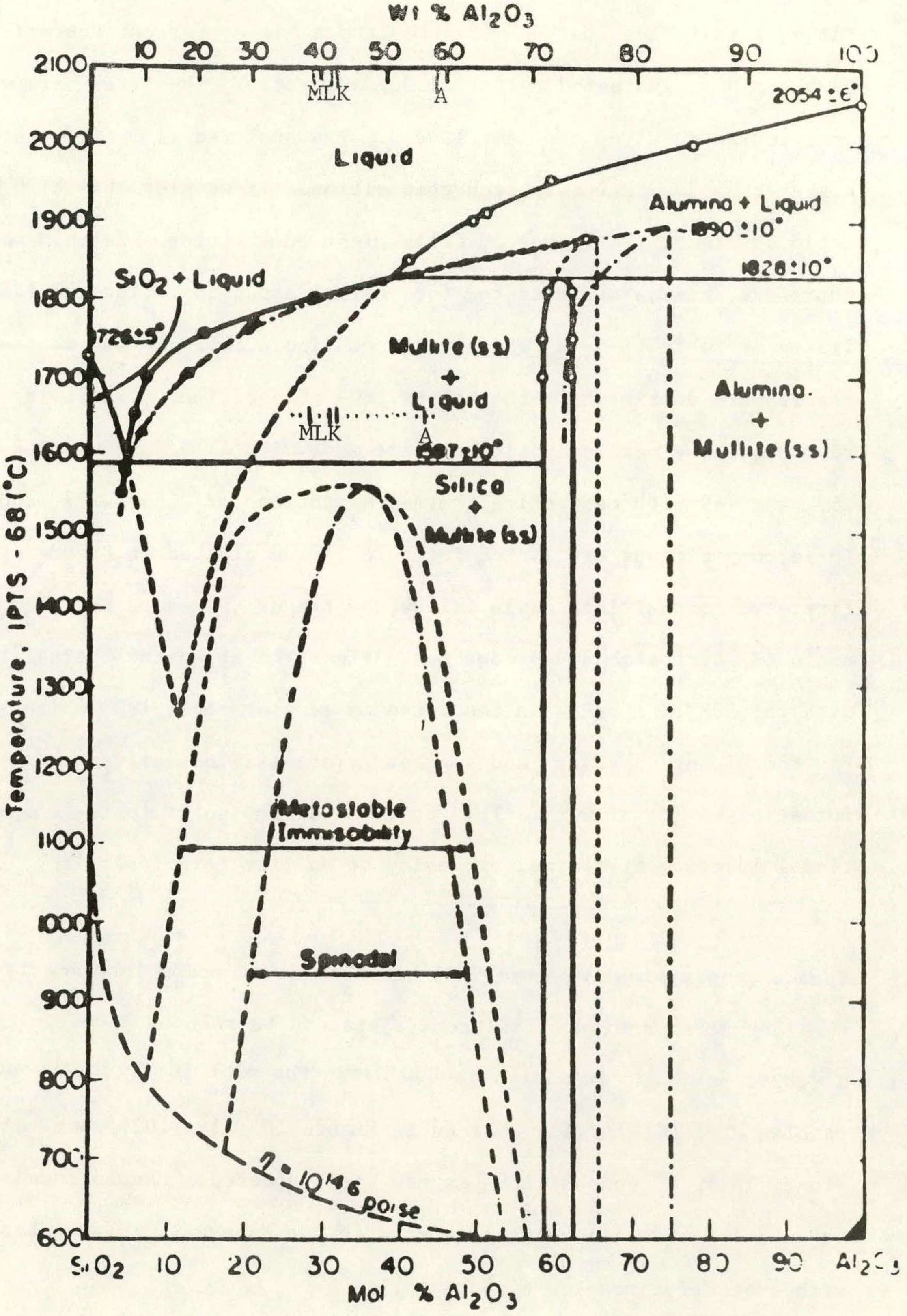


Figure 11
PER CENT THERMAL EXPANSION AT 800°C VERSUS Al_2O_3/SiO_2 RATIO

Figure 12

PHASE DIAGRAM OF Al_2O_3-SiO_2 SYSTEM

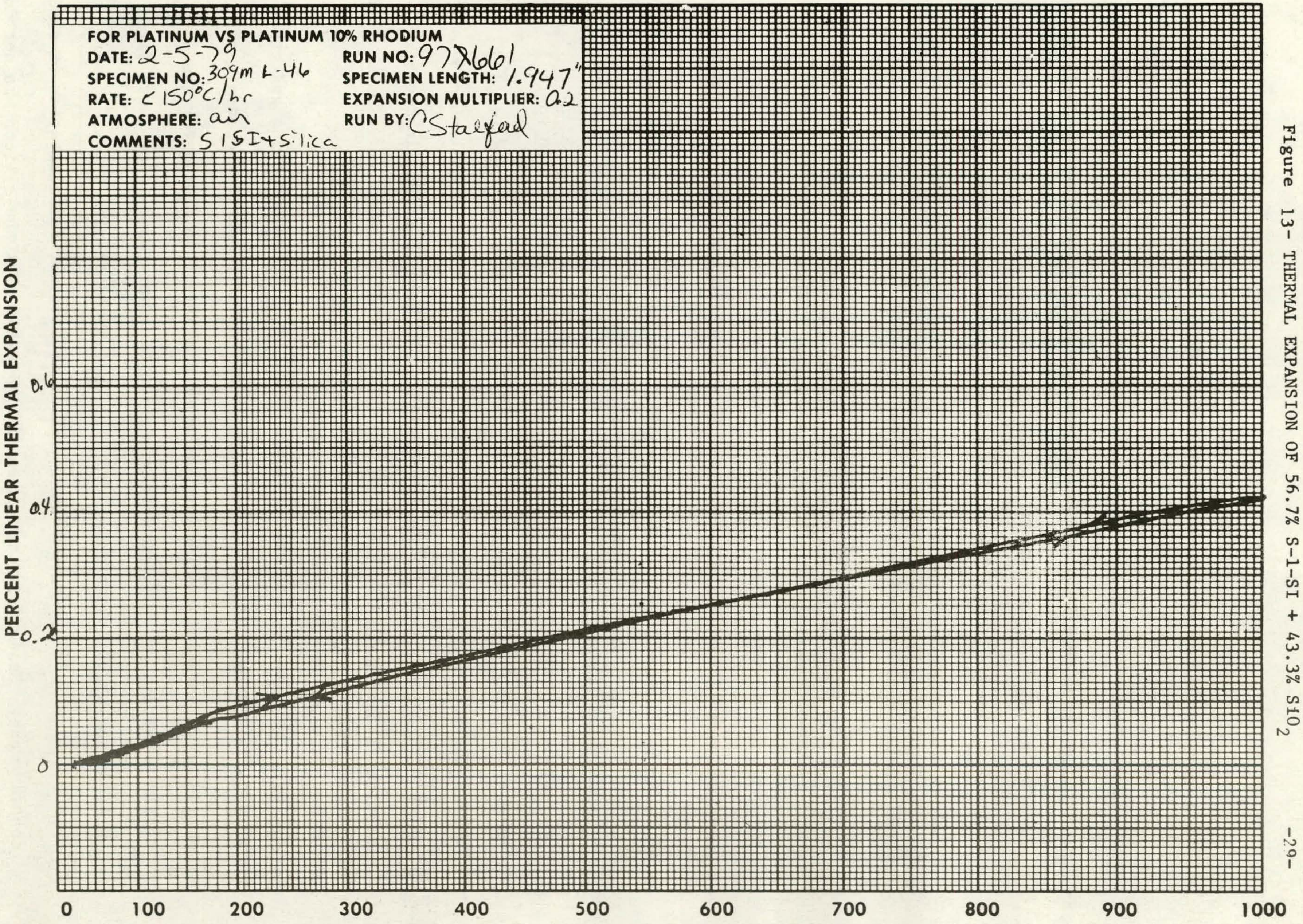


Ref.: S.H.Risbud, J.A. Pask, J.Mats,Sci. 13(1978) 2449-2454

Table II indicates that "M" (218HPM) had a higher percent thermal expansion than would be indicated by the Al_2O_3/SiO_2 ratio. The fired part was analyzed as shown on the next line M. The analyzed Al_2O_3/SiO_2 ratio is higher than the intended batch composition. If we plot this Al_2O_3/SiO_2 ratio on Figure 11, we see it falls right on the plot. Batch M was, therefore, remade and retested for thermal expansion. The results are listed in Table II as M_R and plotted on Figure 11 as M_R and we see the results are consistent with the previous compositions. Following these results, three more compositions were made with Al_2O_3/SiO_2 ratios of .64, .59, and .49 with respective thermal expansions of .285, .277, and .330. These compositions are listed in Table II and plotted on Figure 11. The first two compositions again follow the trend. However, the Al_2O_3/SiO_2 ratio of .49 (batch 309M) does not. Figure 13 shows the thermal expansion data for 309M. A break in the curve is seen at about 180° which accounts for the higher expansion and suggests a crystalline silica phase transformation may be at work. This suggests an end point to the compositional lowering of thermal expansion of mullite ceramics.

Thus a composition, denoted "K", has been developed which exactly matches the thermal expansion of silicon. This can be seen by comparing the point K^2(.0295 per cent expansion at 800°C) on the plot in Figure 11 and the expansion at 800°C for III silicon in Figure 10 (also .0295 per cent expansion). This "K" composition has now been repeatedly manufactured into both dip coating and scim coating substrates for Honeywell in a number of batches with successful results by Honeywell.

56.7% S-1-SI + 43.3% SiO_2



FOR PLATINUM VS PLATINUM 10% RHODIUM

DATE: 2-5-79
RUN NO: 97X661
SPECIMEN NO: 309m L-46
SPECIMEN LENGTH: 1.947"
RATE: < 150°C/hr
EXPANSION MULTIPLIER: 0.2
ATMOSPHERE: air
RUN BY: C Stafford
COMMENTS: S1SI+Silica

Figure 12

Figure 13- THERMAL EXPANSION OF 56.7% S-1-SI + 43.3% SiO_2

CONTAINER DEVELOPMENT

Another part of this program has been to make mullite containers for melting silicon. Most all processes for making solar grade silicon require melting of silicon in a container. This is true for Czochralski growth as well as most of the sheet technologies. Silicon is frequently melted in a fused silica container. Since fused silica devitrifies at the temperature of molten silica, it has a limited life. Furthermore, since fused silica has a thermal expansion coefficient an order of magnitude lower than silicon, it fractures on cooling and cannot be used. Mullite does not devitrify and is structurally stable at 1450°C. The thermal expansion coefficient of mullite, as aforementioned, is close to that of silicon. Thus, mullite appears to fulfill some requirements for a container material for molten silicon.

The mullite container development included evaluating mullite in contact with silicon and delivering sample crucibles for evaluation by JPL. The evaluation of mullite in contact with molten silicon was accomplished by using a series of sessile drop experiments. This is described in the next section of this report.

Mullite crucibles 60 x 40 mm were made from S-1-SI by iso-pressing and green forming on a lathe. These parts would likely be slip cast for economic reasons, but it was felt unnecessary to develop a slip cast system for these initial evaluations. Approximately 15 crucibles were made. Some were fired to full density while the remainder were underfired to give about 7.5 percent porosity. In a single test by JPL, a directional solidification of silicon was made. Resistivity measurements indicated that the silicon was not doped by the mullite crucible too badly. No quantitative analysis has been reported.

Based on these results, three additional crucibles were made from "K" modification material. Since this composition matches the thermal expansion of silicon, the crucible should survive the cool-down and, therefore, could be reused. Since the "K" modification is also higher in silica content, it is suspected that less impurity pickup might be observed. This expectation is based on the observation that the silicon dissolves the mullite crystal much more quickly than the glass phase. Thus, the "K" modification, with its higher silica content, would have more glass phase and, possibly, the phase will have higher silica content. No results of any experiments with these crucibles have been obtained.

SESSILE DROP EXPERIMENTS

A sessile drop technique was used to study various mullite compositions in contact with molten silicon. Silicon sessile drop experiments have been performed on mullite of eight composition and firing variations. The variations are listed below:

A. S-1-SI - Coors standard mullite ISO press body.

B. High mullite content - Kyanite substituted for clay.

C. High glass S-1-SI - Excess SiO_2 added to S-1-SI.

D. Glass property modification - Attempt to add B_2O_3 to glass phase of S-1-SI.

E. Open porosity S-1-SI - S-1-SI fired to approximately 10% porosity.

F. High purity S-1-SI - E. P. Kaolin substituted for ball clay on S-1-SI.

G. Electrically fused mullite - Electrically fused mullite grain sintered approximately 20% porosity.

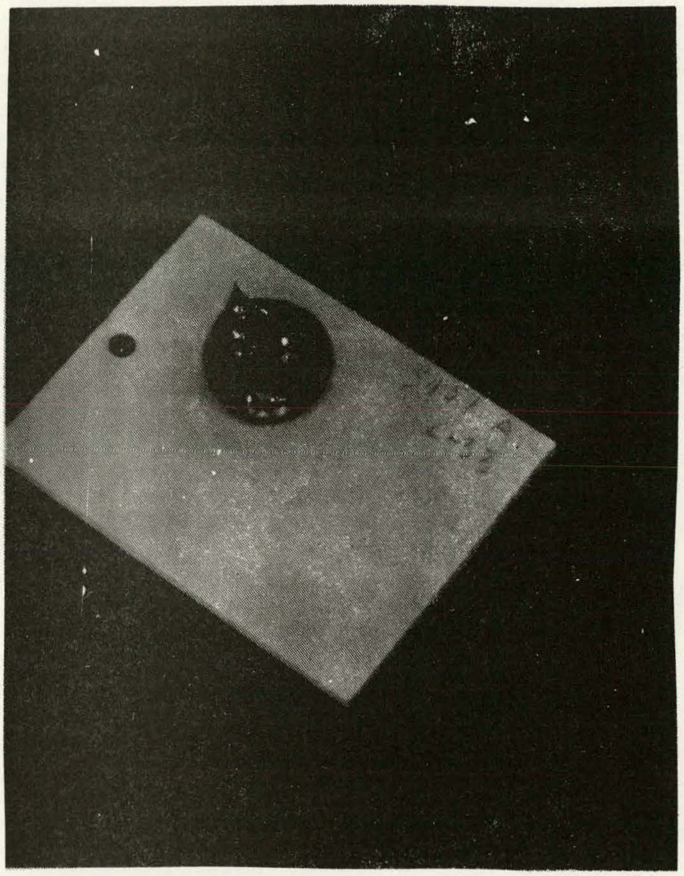
H. Reducing fire S-1-SI - Hydrogen atmosphere firing.

The sessile drop experiments were carried out in a graphite resistance heated vacuum furnace with a heating zone of 6" x 6" x 15". The sample mullite substrates were pretreated at 1200°C in air to clean the surfaces. The various samples were then loaded into the vacuum furnace and a silicon nugget about 1/2" was placed upon the sample. The furnace was raised to 1450°C in a vacuum of about 10^{-4} Torr. Timing exposure began as soon as liquid droplets of silicon could be seen. After the prescribed exposure time was reached, the furnace was shut off and allowed to cool. Solidification of the silicon droplet took place in 5 to 10 minutes. Selected samples were evaluated materiallographically as shown in Figures 14 to 21. Figure 14 shows composition A (dense S-1-SI) with a 5 minute soak at 1450°C.

Figure 14a shows the substrate and crystallized sessile drop. The slight shadowing on the substrate results from the sessile drop moving around while molten. It is thought that gas evolution at the interface (SiO) causes thi motion. Figure 14b and 14c are polished sections of the interface at 50x and 200x, respectively. The dark areas in the mullite (on the left) are pores. In Figure 14c mullite crystals in the continuous glassy phase can be seen. Figure 15 is the same series of photographs of the same composition with a 10 hour (600 minute) soak. In Figure 15a the sessile drop was much more mobile. The drop can also be seen to conform to the edge of the substrate. Figure 15b shows apparent cracks in the silicon with also a large amount of debris in the silicon. It is also apparent that silicon is now filling some voids in the mullite close to the interface. Closer inspection in 14c shows a reaction layer of different reflectivity at the interface and in the voids of the mullite body. There is also a reaction zone visible in the mullite, some of which is seen in the silicon. No chemical or phase analysis has been made of these reaction areas.

Figure 14

SESSILE DROP OF DENSE S-1-SI 1450°C - 5 MINUTES



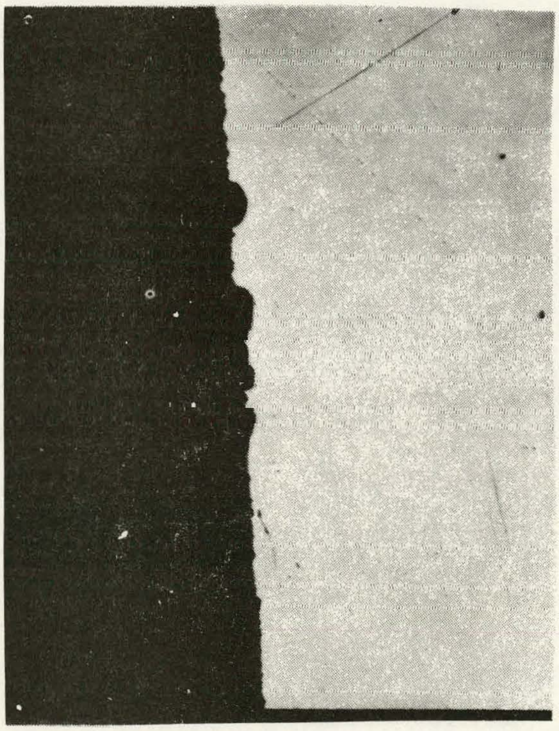
Composition A - Dense S-1-SI
5 minute soak.

14-a Substrate and sessile drop.

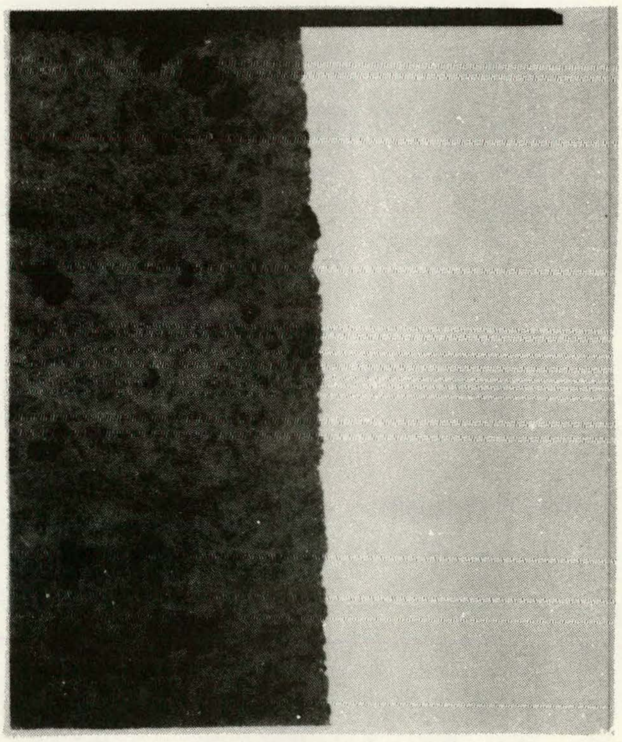
14-b Polish section 50x.
Mullite left. Silicon right.

14-c Polish section 200K.
Mullite left. Silicon right.

14-a

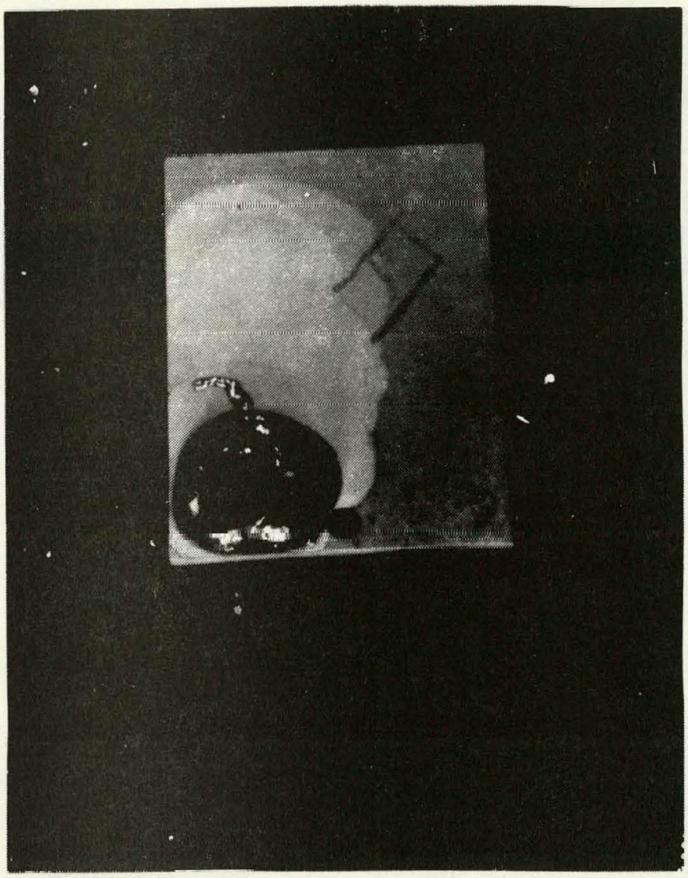


14-b



14-c

Figure 15
SESSILE DROP OF DENSE S-1-SI 1450°C - 600 MINUTES



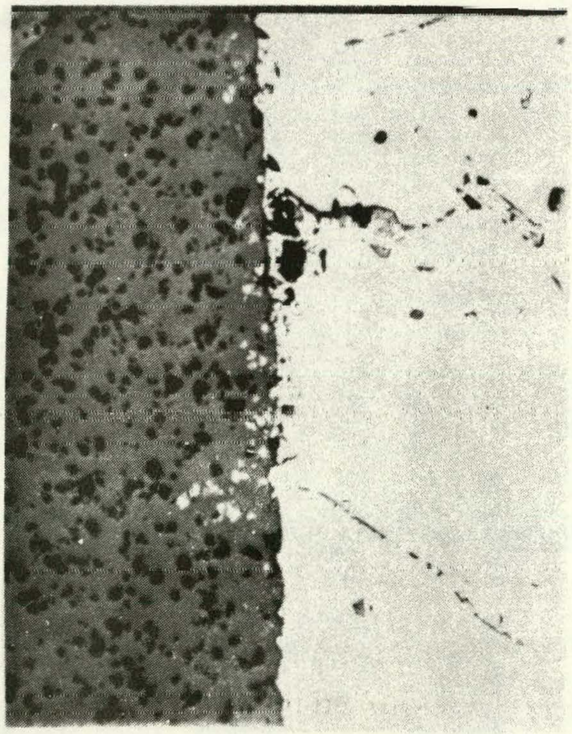
15-a

Composition A - Dense S-1-SI
10 hour (600 min.) soak.

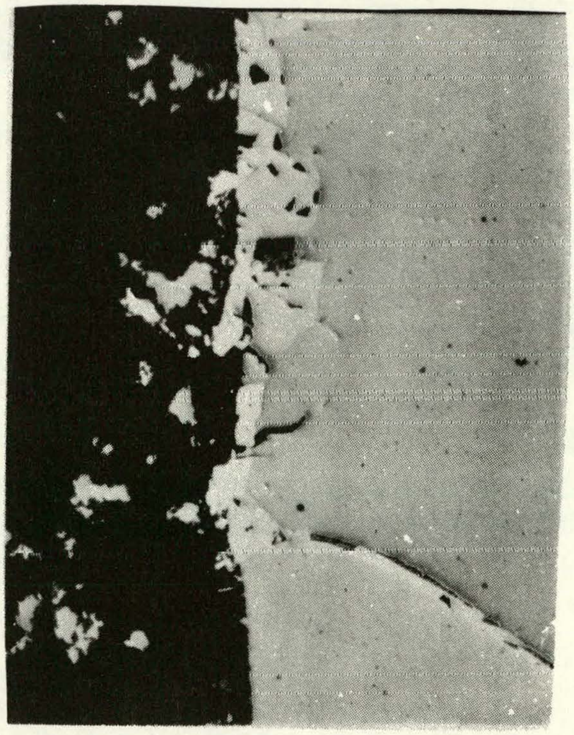
15-a Substrate and sessile drop.

15-b Polish section 50x.
Mullite left. Silicon right.

15-c Polish section 200x.
Mullite left. Silicon right.



15-b



15-c

Figure 16 is composition E (open porosity S-1-SI) with 5 minute soak at 1450°C. At this length of time the only noted difference between composition A and composition E is the penetration of silicon into the open porosity of E. However, composition E after 10 hours (600 minutes) of soak time is shown in Figure 17 to have severe reaction. The substrate appears to be completely eroded and corroded away. (The smooth material in 17b and 17c is the potting material for the mount.) The sections 17b and 17c indicate the reacted substrate to be mainly composed of the same two reactants observed in Figure 15, the long soak time dense S-1-SI. It is assumed that the increased surface area of the porous substrate, coupled with the lower firing temperature, contributed to its poor showing in this test.

Composition F, (high purity S-1-SI) soaked at 1450°C for 5 minutes, is shown in Figure 18. At this exposure time, F appears similar to the dense S-1-SI in Figure 14. In Figure 19, the 10 hour soak again shows the same reaction areas as Figure 15. Figure 19c is a 200x photo of an area away from the interface in the silicon containing the reaction phases. There seems to be no change in reaction due to the increased purity of composition F versus composition A.

Figures 20 and 21 show the electrically fused mullite, composition G. This composition has the highest purity, no apparent glass phase, and approximately 20% porosity. In Figure 20 infiltration can be seen in the surface pores after 5 minute duration. Also, a crack extends from the mullite through the interface into the silicon. This crack is also observed in other compositions as well as in Figure 20. The increased reaction with longer time is apparent although this reaction is not as severe as the porous S-1-SI composition. In Figure 21c, an area in the silicon away from the interface is observed to have the bright reaction product. In this photograph, the reaction material appars to be crystallizing from a nucleation point.

Figure 16

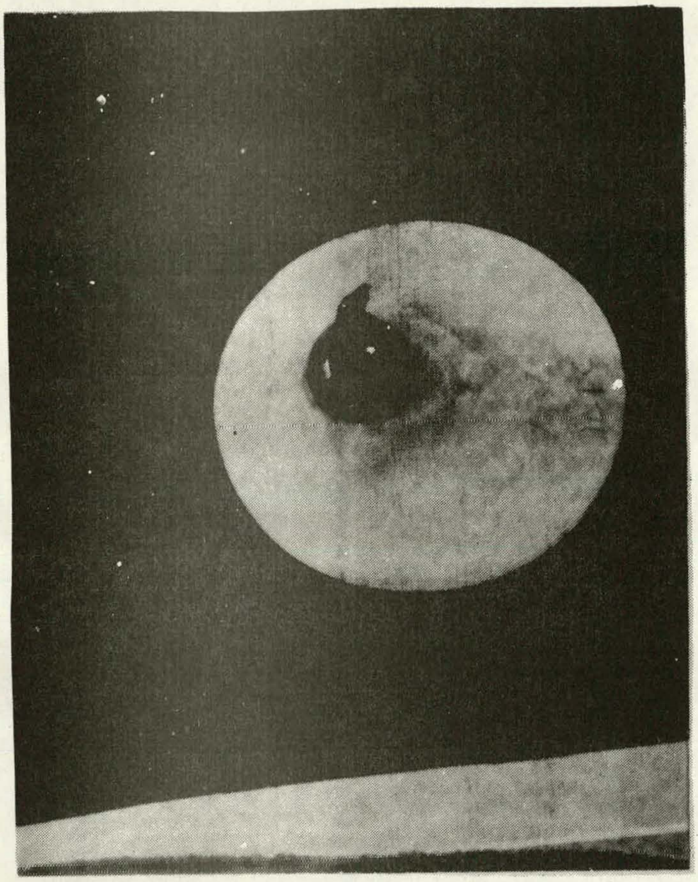
SESSILE DROP OF 10% POROUS S-1-SI 1450°C - 5 MINUTES

Composition E - Open porosity S-1-SI
5 minute soak.

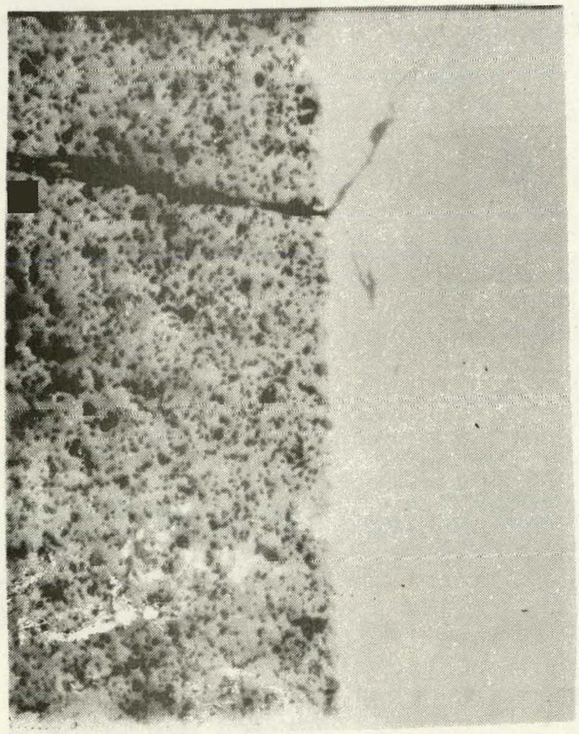
16-a Substrate and sessile drop.

16-b Polish section 50K.
Mullite left. Silicon right.

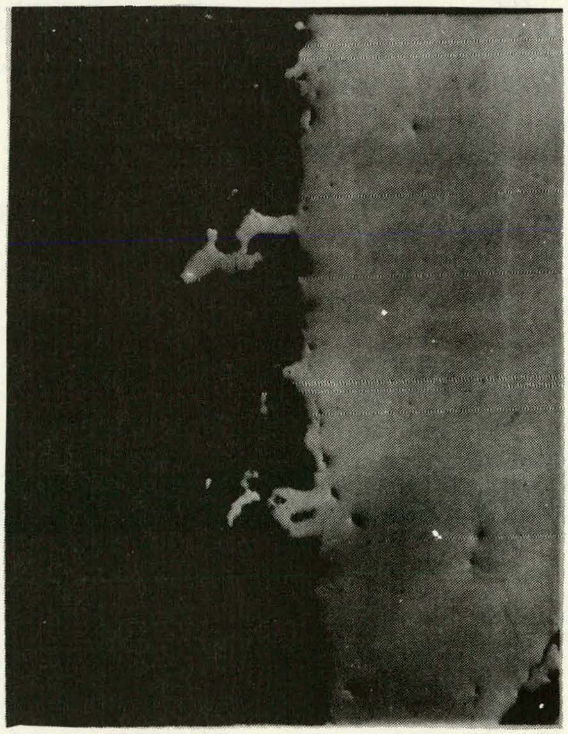
16-c Polish section 200x.
Mullite left. Silicon right.



16-a



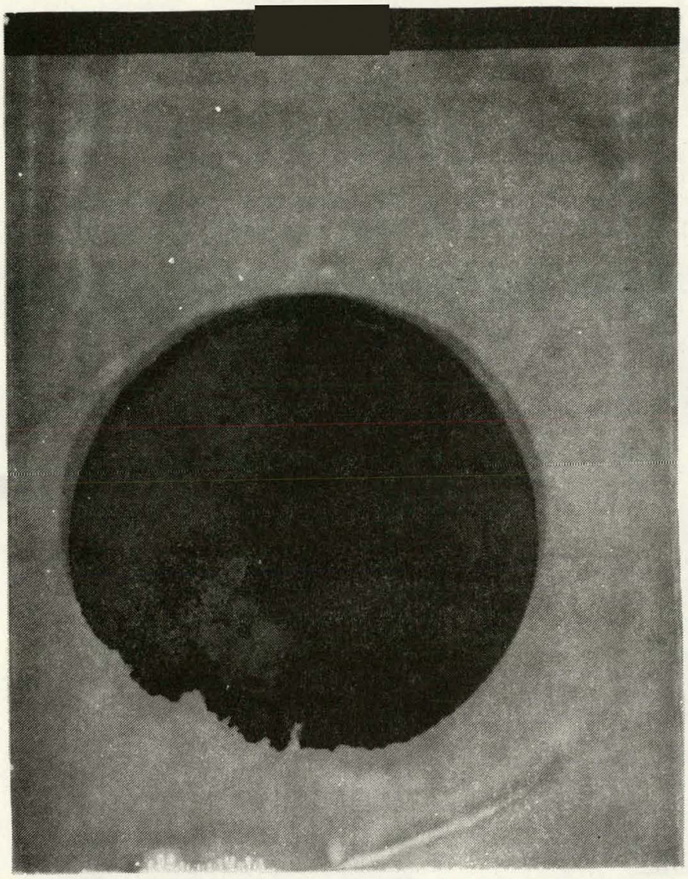
16-b



16-c

Figure 17

SESSILE DROP OF 10% POROUS S-1-SI 1450°C - 600 MINUTES


[redacted]

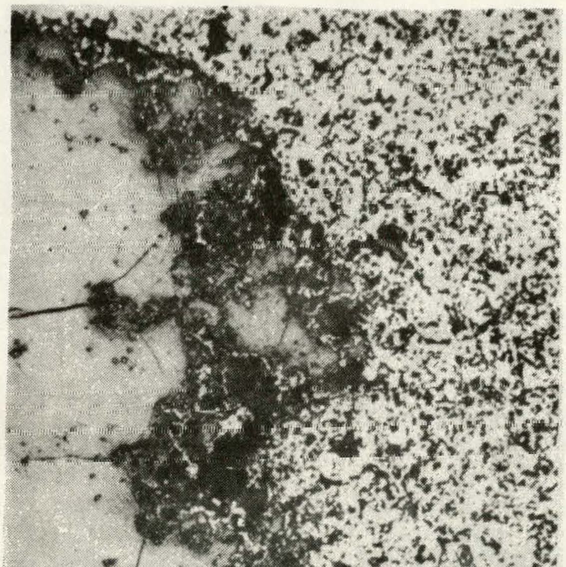
Composition E - Open porosity S-1-SI 10 hour (600 min.) soak.

17-a Substrate with reacted area.

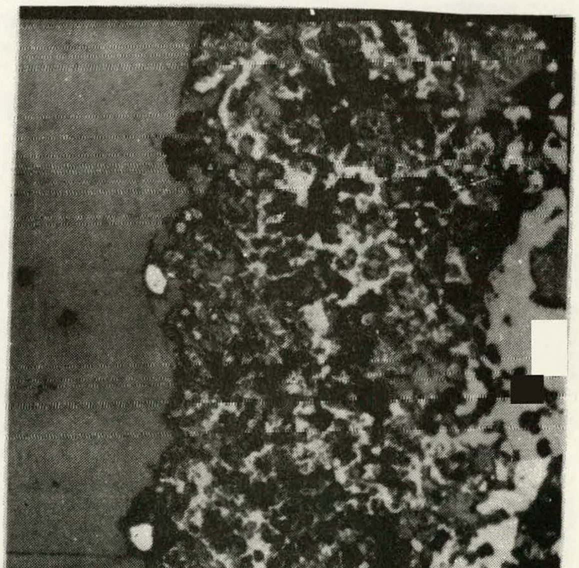
17-b Polish section 50x - Substrate reacted area right, potting material left.

17-c Polish section 200x - Substrate reacted area right, potting material left.

17-a



17-b



17-c

Figure 18

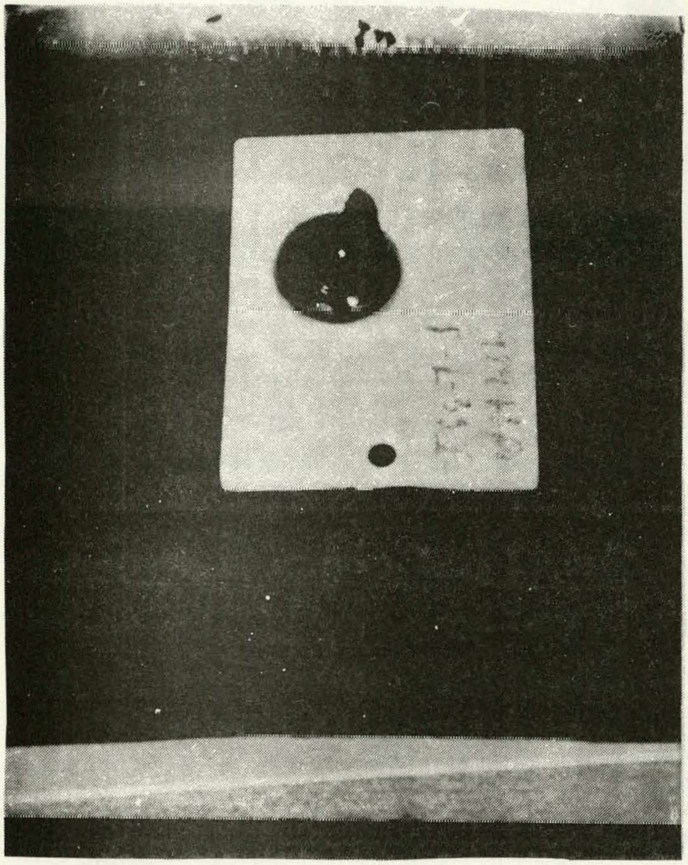
SESSILE DROP OF HIGH PURITY S-1-SI 1450°C - 5 MINUTES

Composition F - High purity S-1-SI
5 minute soak.

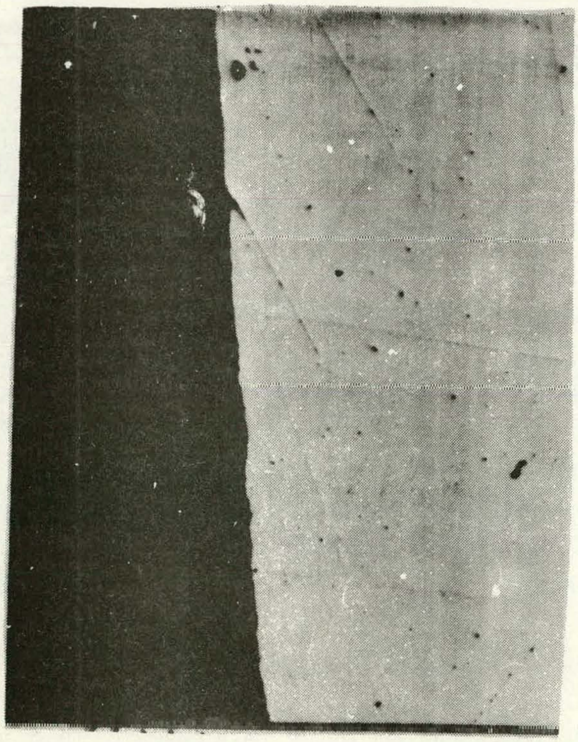
18-a Substrate and sessile drop.

18-b Polish section 50x.
Mullite left. Silicon right.

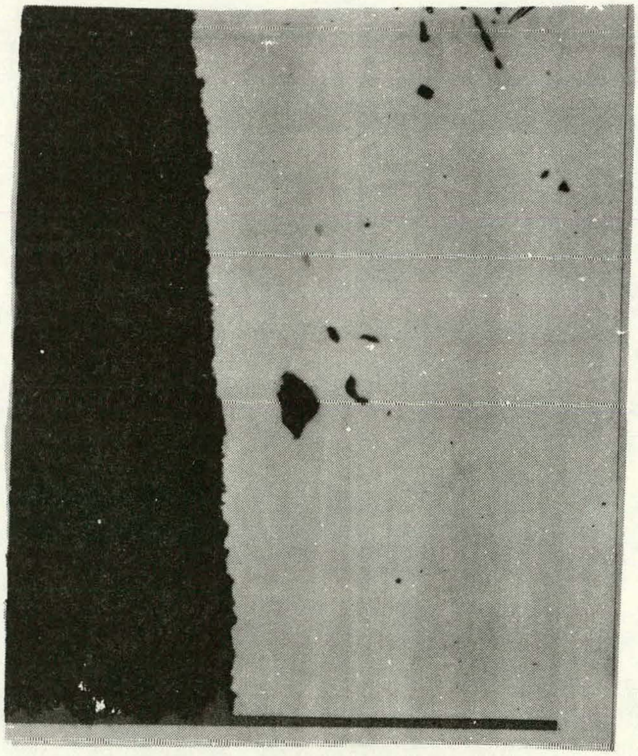
18-c Polish section 200x.
Mullite left. Silicon right.



18-a



18-b



18-c

Figure 19

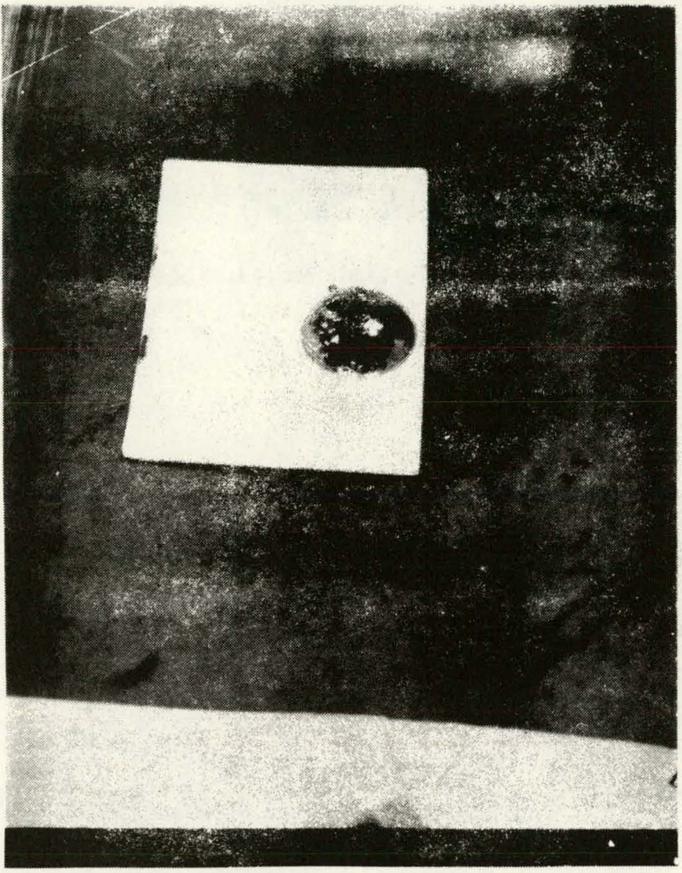
SESSILE DROP OF HIGH PURITY S-1-SI 1450°C - 600 MINUTES

Composition F - High purity S-1-SI
10 hour (600 min.) soak.

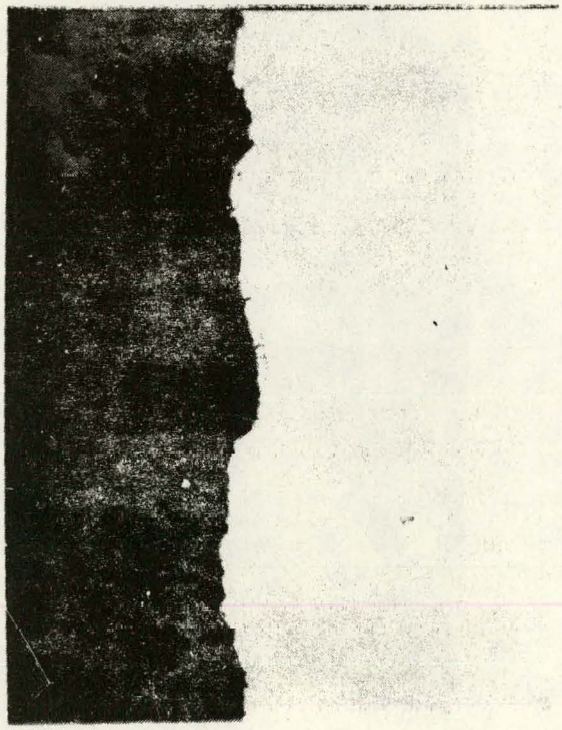
19-a Substrate and sessile drop.

19-b Polish section 200x.
Mullite left. Silicon right.

19-c Polish section 200x.
Reaction zone in silicon.



19-a

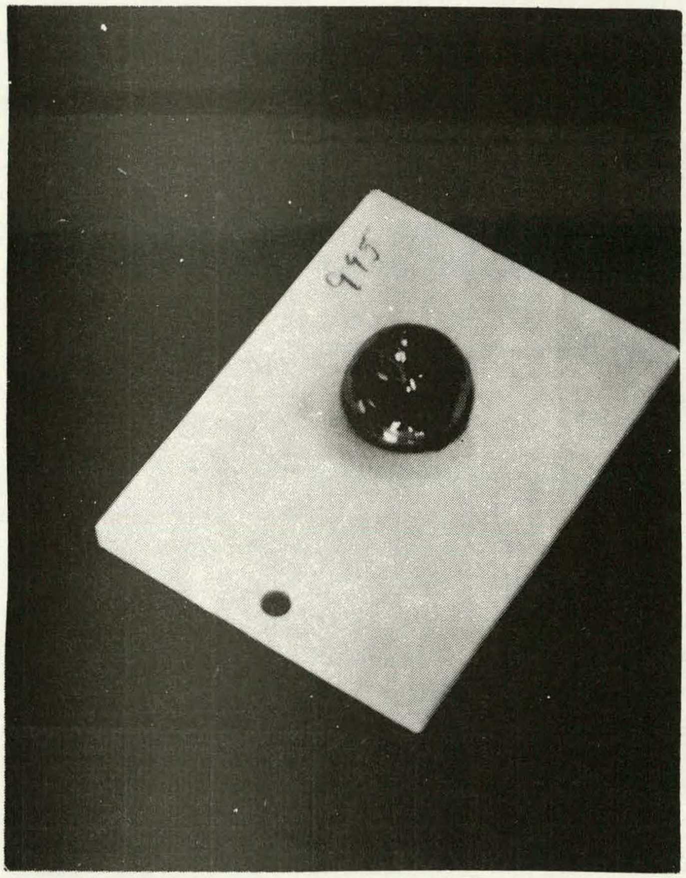


19-b

19-c

Figure 20

SESSILE DROP OF FUSED MULLITE 1450°C - 5 MINUTES



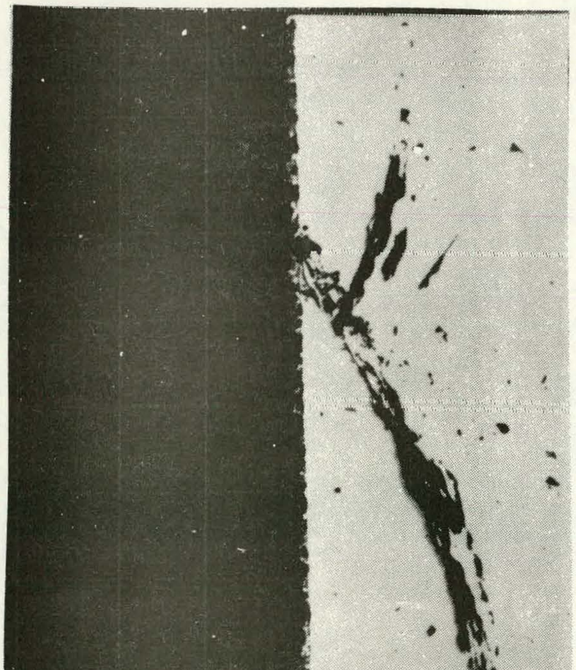
Composition G - Electrically Fused Mullite 5 minute soak.

20-a Substrate and sessile drop.

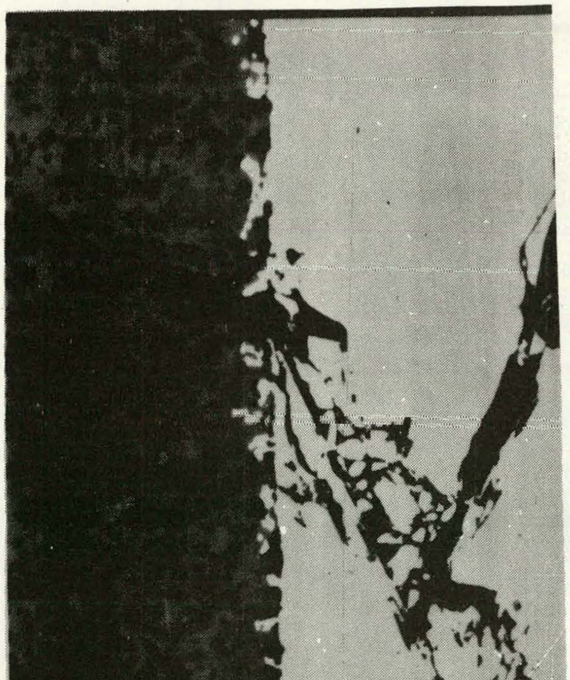
20-b Polish section 50x.
Mullite left. Silicon right.

20-c Polish section 200x.
Mullite left. Silicon right.

20-a



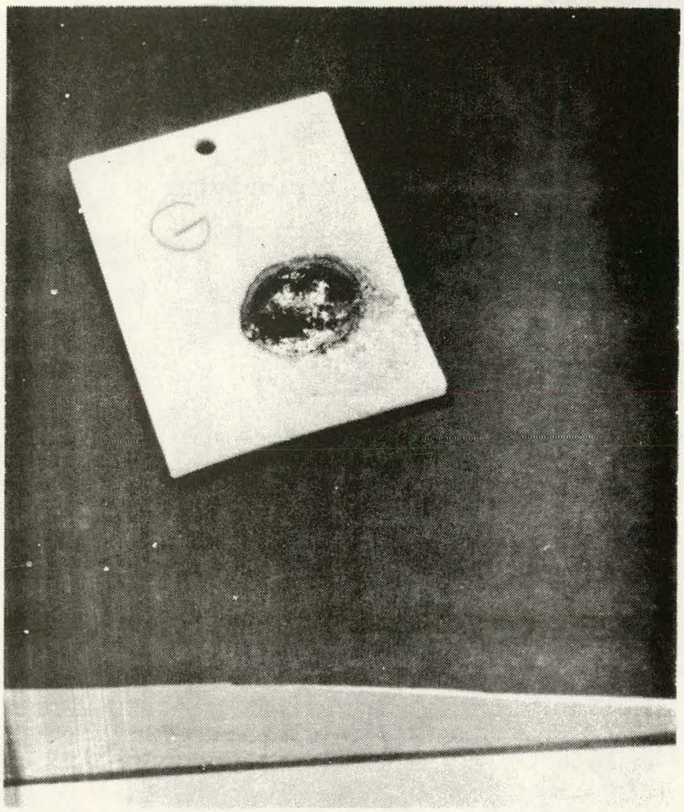
20-b



20-c

Figure 21

SESSILE DROP OF FUSED MULLITE 1450°C - 600 MINUTES



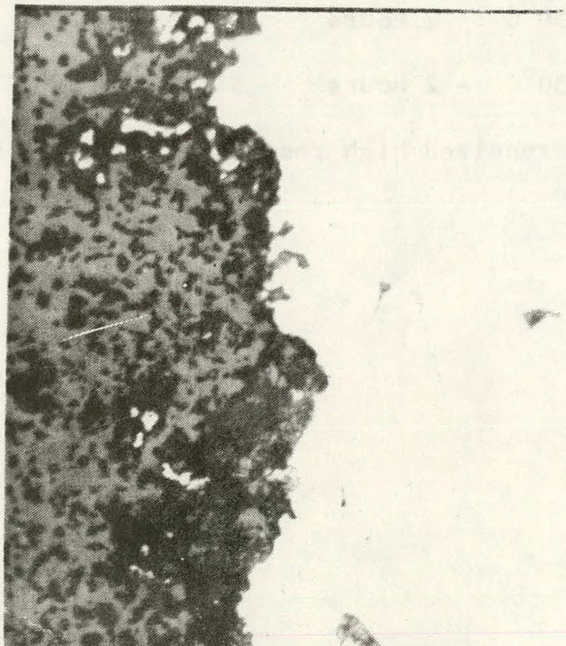
Composition G - Electrically fused Mullite 10 hour (600 min.) soak.

21-a Substrate and sessile drop.

21-b Polish section 200x.
Mullite left. Silicon right.

21-c Polish section 200x.
Silicon reaction zone.

21-a



21-b

21-c

Table III

FOUR PROBE RESISTIVITY

NOTE: Because of varying geometry of specimens the resistivity data is useable only as relative values.

SPECIMEN	APPARENT RESISTIVITY (Ω -CM)	SPECIMEN DESCRIPTION	
A-3	0.092	1450°C - 5 min.	S-1-SI
A-4	0.008	1450°C - 10 hours	S-1-SI
E-3	0.190	1450°C - 5 min.	S-1-SI Porous
F-3	0.074	1450°C - 5 min.	High Purity
F-4	0.007	1450°C - 10 hours	High Purity
G-3	0.040	1450°C - 5 min.	Electrically fused
G-4	0.004	1450°C - 10 hours	Electrically fused
A-6	0.028	1450°C - 2 hours	S-1-SI
E-6	0.011	1450°C - 2 hours	S-1-SI Porous
Silicon	3.8×10^6	As received high resistivity Silicon Nugget	

Analysis of the sessile drop tests shows a large reduction in resistivity and increase in aluminum content. Four point resistivity results are shown in Table III. The analysis shows a tremendous drop in resistivity when silicon is melted in contact with all mullite compositions studied to date. This resistivity drop is observed whether the time of exposure is 5 minute or 10 hours. The 10-hour exposure is an order of magnitude worse than 5 minutes. An attempt was made to evaluate the silicon in contact with fused quartz, but the silicon fractured too badly to be tested. The composition evaluation of mullite content and purity did not show any appreciable change in resistivity from the S-1-SI.

Copies of the Emission Spectroscopy semi-quantitative chemical analysis are shown in Figures 22 and 23. The analysis of silicon melted on S-1-SI is nearly identical to the analysis of silicon on fused quartz. Either the analysis is too insensitive or vapor transport of impurities is being observed. This level of contamination would appear to preclude the use of mullite in direct contact with silicon. However, the aforementioned directional solidification test by JPL indicates a much lower level of contamination. It is felt that this discrepancy can be explained by the difference in the kinetics of the two tests. The sessile drops were observed to move around on the substrate while at temperature. This would bring the silicon into contact with fresh surface instead of generating a reaction boundary layer as would likely occur in the crucible test. Thus, it appears that the directional solidification in the crucible should be further explored.

Figure 22

ANALYSIS OF SILICON SESSILE DROP ON FUSED SILICA

CHEMICAL ANALYSIS CHART
CI-1401-A

			DATE RECEIVED
LABORATORY NUMBER 95474	DATE COMPLETED 7-24	ANALYST B	SAMPLE NUMBER Quartz

ELEMENT	%	ELEMENT	%	ELEMENT	%	ELEMENT	%
ALUMINUM Al	.2	GALLIUM Ga	< .005	SILICON Si	> 10	RUBIDIUM Rb	
ANTIMONY Sb	< .003	GERMANIUM Ge	↓	SILVER Ag	< .001		
ARSENIC As	< .01	INDIUM In		STRONTIUM Sr	< .08		
BARIUM Ba		IRON Fe	.01	TIN Sn	< .003		
BERYLLIUM Be	< .001	LEAD Pb	< .008	TITANIUM Ti	< .001		
BISMUTH Bi	< .005	MAGNESIUM Mg	.001	VANADIUM V	< .005		
BORON B	< .003	MANGANESE Mn	< .001	ZINC Zn	< .08		
CADMIUM Cd	< .05	MERCURY Hg		ZIRCONIUM Zr	< .01		
CALCIUM Ca	< .03	MOLYBDENUM Mo	< .01	SODIUM Na	.05		
CHROMIUM Cr	< .003	NICKEL Ni		CESIUM Cs			
COBALT Co	< .01	NIOBIUM Nb		LITHIUM Li	< .1		
COPPER Cu	.004	PHOSPHORUS P	< .3	POTASSIUM K			

☒ Results based on sample as received.

☐ Results based on ______________

☐ Qualitative

☒ Semi-Quantitative (± 50%)

☐ Quantitative (as indicated)

☐ Atomic Absorption

☒ Optical Emission

☐ Wet Chemistry

☐ X-Ray

<= Less Than

>= Greater Than

Figure 23

ANALYSIS OF SILICON SESSILE DROP ON S-1-SI

CHEMICAL ANALYSIS CHART
CI-1401-A

						DATE RECEIVED	
LABORATORY NUMBER 95474		DATE COMPLETED 7-24		ANALYST B		SAMPLE NUMBER A	
ELEMENT	%	ELEMENT	%	ELEMENT	%	ELEMENT	%
ALUMINUM Al	.2	GALLIUM Ga	<.005	SILICON Si	> 10	RUBIDIUM Rb	
ANTIMONY Sb	< .003	GERMANIUM Ge	↓	SILVER Ag	< .001		
ARSENIC As	< .01	INDIUM In		STRONTIUM Sr	< .08		
BARIUM Ba		IRON Fe	.01	TIN Sn	< .003		
BERYLLIUM Be	< .001	LEAD Pb	< .008	TITANIUM Ti	< .001		
BISMUTH Bi	< .005	MAGNESIUM Mg	.001	VANADIUM V	< .005		
BORON B	< .003	MANGANESE Mn	< .001	ZINC Zn	< .08		
CADMIUM Cd	< .05	MERCURY Hg		ZIRCONIUM Zr	< .01		
CALCIUM Ca	< .03	MOLYBDENUM Mo	< .01	SODIUM Na	.05		
CHROMIUM Cr	< .003	NICKEL Ni	↓	CESIUM Cs			
COBALT Co	< .01	NIOBIUM Nb		LITHIUM Li	< .1		
COPPER Cu	.006	PHOSPHORUS P	.3	POTASSIUM K			

☒ Results based on sample as received.

☐ Results based on ____________

☐ Qualitative

☒ Semi-Quantitative (± 50%)

☐ Quantitative (as indicated)

☐ Atomic Absorption

☒ Optical Emission

☐ Wet Chemistry

☐ X-Ray

= Less Than

= Greater Than

CONCLUSIONS:

The following conclusions have been drawn as a result of this study program:

1. A mullite composition has been developed that matches the thermal expansion of silicon.
2. This composition is made of low cost clay and silica sand raw materials.
3. Substrates up to 1 meter x 10 cm x 1 mm have been fabricated.
4. The substrates can be slotted to allow back contacts to be made in the SOC process.
5. Mullite in contact with molten silicon has been studied. Mullite is mechanically stable. Contamination of silicon by mullite was found to be kinetically controlled and, therefore, design and use of a mullite container would be critical.

RECOMMENDATIONS:

1. As the Honeywell Silicon-On-Cermic process progresses towards meeting their goals, larger quantities of ceramic substrates will be required. While prototype quantities of substrates can, and are, being manufactured, the cost of these substrates is high because of the labor intensive methods of manufacture being used. Furthermore, while projections of low cost substrates have been made for larger quantities and the basic processing methods have been developed and demonstrated, the details and optimization of these processing steps still need to be developed. If we look through cost areas individually, we can evaluate what needs to be done at each level.

a. Raw materials - The present use of a calcined clay and amorphous silica are as low a cost as can be foreseen.

b. Body preparation - This is a minimal cost adder at this time although it is a substantial capital cost.

c. Roll compaction - The cost in roll compaction is dependent on the rate of square meters produced. The linear rate is fairly fixed but substantial savings could be realized if wider rolling equipment were used. To date, 8-inch wide rolls are State-of-the-Art. However, discussions with the equipment manufacturer suggest at least 14-inch rolls are a probable improvement while 24-inch rolls are an "expensive" possibility.

d. Forming - This area refers to the post rolling shaping such as the slotting. A continuous roll punching would be required to minimize the cost here. To roll punch optimization of the roll compaction organic binder formulation would be necessary to maximize rates and yields.

e. Firing - Firing efficiency can be improved in two ways. A near term solution would be to develop an improvement in kiln loading density. This would require optimization of some existing techniques being used in the manufacture of thick film alumina substrates. The second method, a more ambitious effort, would be to couple the firing of the substrate with the coating in the SOC scim coater. This would eliminate heating the substrate twice. To accomplish this, the substrate have to be fired at the same rate as the coating which is presently projected at 0.3 cm/sec. Several of quick trials demonstrated the ability to feed a one-inch wide x twenty-inch long substrate into a 1525°C hot zone at 1.0 cm/sec. Binder burnout and some shrinkage took place. These tests indicate followup of this idea is feasible.

f. Specifications - Before embarking on these programs, some consideration of future specifications needs to be taken. Specifications such as surface finish, surface defects, flatness, straightness, dimensional tolerances, and property tolerances of density, strength, chemical purity and uniformity, and thermal expansion will affect the probability of success in meeting these, or any, future cost goals.

2. Evaluate additional "K" modification containers for molten silicon to determine if they can be heated and cooled without fracture of the container or the silicon. Determine what techniques can be used to minimize impurity contamination of the silicon.

NEW TECHNOLOGY:

A method of varying the thermal expansion of mullite ceramics by control of composition has been registered as an item of new technology.

☆ U.S. GOVERNMENT PRINTING OFFICE: 1980—640-258/2010