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VITRE-GRAF COATING ON MULLITE

Low Cost Silicon Solar Array Project
Large Area Silicon Sheet Task

FINAL REPORT

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Technical Content Statement

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ABSTRACT

A technical and economic evaluation was made of a proprietary glass-like carbon glaze coating applied to mullite and graphite to be used either in thin-film silicon manufacture or in container ware applications. Preliminary evaluations had indicated that the glassy carbon coating reacts with molten silicon to form a silicon carbide reaction layer that may serve as a diffusion barrier to prevent silicon reaction with the substrate material.

The technical evaluation consisted of manufacturing test samples by varying materials and processing parameters in conformance with a pre-selected matrix. Various tests, primarily coating appearance, adherence and silicon reaction behavior was observed as a function of the test parameter variation. The results of these tests indicated that most graphite and carbonaceous materials used as substrates will produce a visually acceptable coating having excellent adherence over a wide range of processing parameters. However, no set of parameters produced a coating that could withstand the chemical attack from molten silicon and prevent reaction with a graphite substrate. The primary consideration of graphite substrates was in container ware applications requiring long-time molten silicon exposure. The conclusion of this study suggested that the glassy carbon coating might provide protection for time periods of 30 minutes or less, and therefore was not suitable for the intended application.

The results of tests conducted on the glassy carbon glaze applied to porous mullite made from a standard ceramic formulation indicated that a performance optimization did take place for the application of manufacturing silicon film solar arrays. When these optimized parameters were tested on Type K mullite developed specifically for the intended application it was found that performance was generally insensitive to processing parameters and the selected parameters were then cost optimized.

The economic analysis generated a process based on the selected parameters for coating glassy carbon onto newly developed mullite substrate material. By using the interim standard price estimating equation a projected cost of \$1.30/m^2 was calculated based on 1975 dollars. If further development of the Type K mullite could eliminate the requirement for HF etch preparation of the substrate surface, a unit cost of \$1.05/m^2 is calculated on 1975 dollars. Additionally, if normal advance in the Vitre-Graf technology is assumed, a unit cost of \$0.85/m^2 is projected on the 1975 dollar basis.

Acknowledgements

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SECTION I

INTRODUCTION

The Tylan Corporation processes a glass like carbon called Vitre-Graf made from a decomposed polymeric resin that is dissolved in an organic solvent to make a solution with the characteristics of lacquer. When applied to porous graphite by paint techniques and cured at elevated temperatures, a coating results that looks like a baked enamel finish. The coating material fills and seals surface pores to render the graphite impervious to gas or liquid penetration. The coating also strengthens the graphite, increases its rigidity, makes it less susceptible to chipping and provides a hard surface that does not easily mar or scratch. Coating thicknesses are typically 5-10 µm and does not interfere with normal tolerances. The coating material closely matches the thermal expansion of the graphite substrate allowing it to be applied to large graphite forms without checking or cracking. Although the coating is chemically pure carbon, it has greater chemical resistance and oxidation resistance than other forms of carbon and can be used against a wide range of corrosive gases, chemicals and molten metals for which no other material has adequate resistance.

The Tylan Corporation manufactures Vitre-Graf coated graphite that is used as susceptors in processing semiconductor materials. Other uses have included fuel cell plates, crucibles for molten metals, mandrels and an assortment of other specialty applications which have taken advantage of one or more of its unique properties.

Besides graphite substrates, the Vitre-Graf coatings have been applied successfully to several types of oxide ceramic substrates when there exists sufficient porosity in the ceramics (usually 5-10 percent) to allow an adequate mechanical bond to develop between coating and substrate. Previous to this program, a Vitre-Graf coating on a mullite substrate was found to provide the wettability required for the silicon on ceramics (SOC) process of solar cell fabrication developed by Honeywell Corporation.[1] Micrographic inspection of the interface between mullite and silicon, shown in Fig. 1, had revealed that the Vitre-Graf coating showed very little erosion by the molten silicon. Sessile drop experiments conducted by JPL[2] on Vitre-Graf coated graphite confirmed this behavior and showed further that after twenty minutes in contact with molten silicon, the coating had reacted to form a silicon carbide layer. Fig. 2 shows the interface between the silicon and substrate revealing minimal reaction with the graphite substrate.

These observations suggested that the Vitre-Graf coating could be an effective barrier to silicon-mullite interaction. Moreover, the supposition was made that the silicon carbide reaction layer might serve as a diffusion barrier to prevent unwanted impurities originating in the mullite from contaminating the silicon. The further possibility appeared to exist that the Vitre-Graf coating might serve as a protection layer for graphite crucibles, dies and container ware for molten silicon.

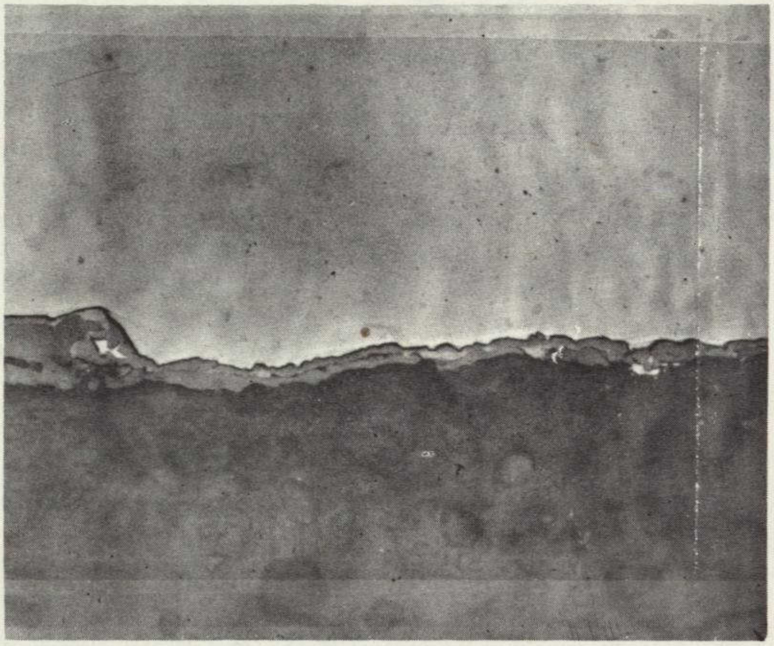

Fig. 1 Interface between mullite (lower) and silicon (upper) shows the Vitre-Graf coating intact and partially reacted with silicon to form a silicon carbide layer. (450x)

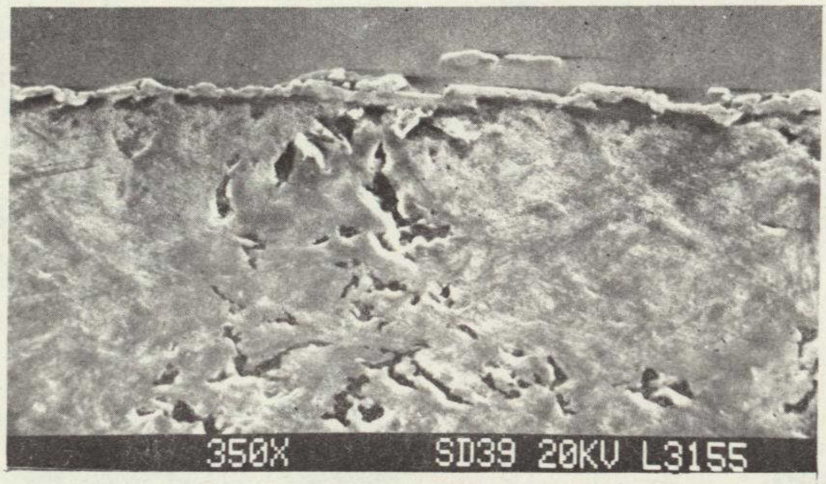

Fig. 2 Interface between silicon (upper) and graphite (lower) showing a continuous silicon carbide layer and unreacted (thin dark layer) Vitre-Graf dark. (350x)

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SECTION II

PROGRAM OBJECTIVES

The overall program objective was to determine processing parameters of the Vitre-Graf coating for optimal performance and economy when applied to mullite and graphite as substrates. (A minor effort was also performed on slip-cast fused silica substrates.)

The development of the coating had evolved in response to the high technological but relatively low volume requirements of the semi-conductor application. Although cost is always an important factor in product development, it had not entered into the original development work at a level of priority as high as that required for the LSSA program. Therefore, specific objectives were to perform both technical and economic evaluation of every process step so as to best meet the over-all program objectives. Thus, the following parameters were selected for evaluation in consecutive series of experiments (a) preparation of substrates, (b) coating application methods, (c) coating thickness, (d) cure temperature, (e) heating rate, and (f) alternate furnace atmospheres. Additionally, sufficient latitude was left in the program for a series of discretionary experiments to be determined as the program progressed.

SECTION III

MATERIALS AND PROCESSING

A. Materials

1. Mullite

All mullite used in this program was manufactured by the Coors Porcelain Co. under *JPL Contract. The initial set of experiments included the Coors standard mullite designated S-1-SI and a modification of this mullite fired to approximately 10% porosity and refered to in this report as porous mullite. All succeeding experiments used the porous mullite except for the final experimental set which used a new mullite designated "K" developed by Coors to match the thermal expansion of silicon and includes excess silica in its composition.

2. Test Graphite

The initial test graphite was manfactured by Poco Graphite Inc.** and designated DFP-2. After the second set of experiments this graphite was replaced with the control graphite, and dropped from the program after the fourth set of experiments.

3. Control Graphite

The graphite used as control was manufactured by Stackpole Carbon Co. 3* and designated grade 2020. After the second test series this graphite was used as the test graphite.

4. Silica

A slip-cast fused silica manufactured by Thermo-Sil Co. 4* was used in the third and fourth test series. It is a coarse grained material having approximately 21% porosity.

5. Carbon-Carbon Composite

Carbon-Carbon Composite made by American Automatic Engineering 5* consisting of rayon fabric and a pyrolyzed polyimide binder was used in the sixth test series.

6. Vitre-Graf

Vitre-Graf is manufactured by Tylan Corporation from decomposed resin dissolved in a suitable solvent. During the course of this program it was learned that the vendor of the resin initially used did not provide compositional control to his product and the composition was subject to variation over a period of time. Moreover, the vendor acknowledged that as much as 5 percent parafin might be contained in this material.

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* Coors Porcelain Co, Golden, Colorado, JPL Contract No. 954878.
** Poco Graphite, Inc., Decatur, Texas
3* Stackpole Carbon Co. St. Marys Pennsylvania
4* Thermo-Sil Co., Santa Ana, Calif.
5* American Automatic Engineering, Huntington Beach, Calif.

The presence of parafin is suspected of promoting peeling and flaking in Vitre-Graf. Starting in test series five and thereafter, a second resin was used of high purity and long term compositional reliability, but at a higher cost.

7. Filler

A filler material was used in test series six that is a two part graphite cement, C-34 made from fine graphitized powder and on organic binder and is manufactured by Union Carbide Corp.*

B. Processing

In the commercial manufacture of Vitre-Graf coatings certain values of processing variables were selected because they were found to provide acceptable performance in the finished product. They were selected on the basis of convenience, compatibility with existing apparatus, and behavior in a specific end-use environment. They are not necessarily the least costly, nor likely to give optimal performance in a different final application.

A description of this manufacturing process is given here to define the baseline from which the processing variables of this program were selected.

1. Pre-Process Preparation

Vitre-Graf is typically applied to a fine-grain, molded graphite that is machined before coating. The pores of the graphite are generally filled with graphite fines from the machining operation. Washing (or wiping) with benzene removes those particles that are easily dislodged and would otherwise become dislodged in the coating process.

2. Application Method

In practice, the Vitre-Graf solution has been applied by paint techniques, dipping, brushing or spraying without discernible differences in the quality of the cured coating. However, the techniques are not used interchangeable, that is the brushing technique is used for large flat pieces, dipping is used on small parts and spraying is used on blind holes and inaccessible recesses.

3. Coating Thickness

The thickness of the Vitre-Graf coating is not an independent variable but is dependent upon both the concentration of decomposed resin that is dissolved in the solvent and the number of coating layers applied. Typically a solution of 250 grams dissolved in one liter is applied and cured in five layers.

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* Union Carbide Corp. Chicago, Illinois.

The selection of this concentration was made arbitrarily because the resulting solution has suitable paint-like properties and it was then found that five layers were necessary to assure an impermeable coating.

4. Cure Temperature

The properties of the Vitre-Graf coating was not found to differ over a broad range of cure temperatures starting at about 950°C up to 1600°C. A temperature of 1050°C had been chosen because it represented a favorable position on the themal gravimetric analysis of this material.

5. Heating Rate

A heating rate of 3°C/min had been found to be the fastest rate at which a coating is produced with a minimal tendency to flake or delaminate and without problems created by cross contamination of hydrocarbons outgassing from the curing resin. This parameter is dependent upon furnace characteristics.

6. Furnace Atmosphere

Vitre-Graf coatings are cured in a vacuum environment to assist removal of decomposition products that outgas from the curing resin and to minimize the opportunity for redeposition and contamination of adjacent parts. Neutral atmospheres have previously been used with success for hardware that is not critically sensitive to contamination.

7. Cooling Rate

The cooling rate from maximum cure temperature is the cooling rate of the furnace. A very wide range of rates have been experienced with no adverse effects. Cooling rate does not appear to be a parameter in Vitre-Graf processing.

SECTION IV

DESCRIPTION OF PROCESS EVALUATION EXPERIMENTS

Table I is presented at the end of this section to facilitate understanding the many parameters evaluated in this program

A. Test Series I: Evaluation of Substrate Preparation

A major problem with the Vitre-Graf coating on ceramics has been a tendency for peeling or delamination of the coating. Flaking or delamination is observed occasionally with graphite substrates as well. Since the adherence of the coating is primarily mechanical, various methods of substrate surface roughening was tried in an attempt to increase mechanical attachment of the coating. Alternatively, a pre-fire of the substrates was performed to determine whether previous difficulties with adherence may have been a consequence of adsorbed water, grease or oxide layers on the surface. Each of these variations in a sample set of three was compared with control substrates in the as-received condition.

1. Variations in Mullite Surface Preparations

The following methods of surface preparations were performed:

a. As-received - mullite was coated after being washed in concentrated HCl, rinsed in distilled water and dried at 120°C. No other surface treatment was used.

b. Prefired - after being washed in HCl and water rinsed, the substrates were heated in vacuum to 1200°C.

c. Etched - after being washed in HCl and water rinsed, the substrates were etched in concentrated HF for 45 seconds.

d. Porous - an alternative mullite substrate having 10% open porosity were HCl washed, water rinsed, and dried at 120°C.

2. Variations in Test Graphite Surface Preparations

The following methods of surface preparations were performed:

a. As-received - the graphite was a purified grade which had experienced a high temperature process by the manufacturer and had not been physically handled at the time of our receipt. The substrates were rinsed in benzene and air dried before coating.

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b. Prefired - the substrates were heated in vacuum to 1200°C.

c. Roughen Surface - the substrate surfaces were roughened with a stiff steel brush to create a coarse surface and then benzene rinsed.

d. Polished Surface - the substrate surfaces were polished with fine silicon carbide paper to provide maximum contrast to surface preparation methods and thereafter they were benzene rinsed.

3. Surface Preparation of Graphite Controls

A graphite control sample was prepared in an identical manner with each test-graphite preparation method. The as-received surface condition was a typical machined surface prepared by an end-mill machining tool.

4. Processing Description

All samples were coated and cured by using the base line process which included brush application of a 250 g/l solution and heating at 3°C/hr to 1050°C. Five coats were applied.

B. Test Series II: Evaluation of Application Methods

The application of Vitre-Graf solutions have been successfully performed by dipping, brushing and spraying paint methods. Each is used in normal Vitre-Graf processing to accomplish specific coating requirements. No technological difference has been previously observed but a potential cost difference exists among them for large volume applications.

1. Dipping Process

Each sample was lowered into a beaker of solution, held submerged for about two seconds and withdrawn. The solvent rapidly evaporates and they were air dried in minutes.

2. Brushing Process

Brushing was accomplished with a 1 inch polyfoam brush. Each side of a sample was coated and allowed to dry for several minutes, then turned over and the process was repeated on the reverse side.

3. Spraying Process

A small air brush was used with the spray nozzle held about 2 inches from the surface to be coated and traversed in a back and forth motion typical of spray paint techniques.

4. Processing Description

All graphite was used in the as-received condition, and porous mullite was used after acid washing. Baseline processing was used for all other variables.

C. Test Series III: Evaluation of Coating Thickness

The thickness of the Vitre-Graf coating is controlled by two variables, the concentration of dissolved resin in the solution and the number of layers applied to build up the coating. The baseline process uses 250 g/l solution with five layers and produces a final coating that is 5-10 μm thick depending somewhat on the porosity of the substrate. Since cost is heavily dependent upon numbers of layers and far less dependent upon solution concentration, the objective of this evaluation was to determine the minimal layers needed to produce a technically adequate coating. A matrix was devised using light, medium and heavy coating concentrations at various number of layers.

1. Light Solution Concentration

The light solution was made at a resin concentration of 150 g/l and applied in eight (8), six (6), and four (4) layers.

2. Medium Solution Concentrations

The medium solution was made at a resin concentration of 250 g/l and applied in five (5), four (4), and three (3) layers.

3. Heavy Solution Concentrations

The heavy solution was made at a resin concentration of 350 g/l and applied in four (4), three (3), and two (2) layers.

4. Processing Description

Porous mullite and silica as-received were used after acid washing. Graphite was used in the as-received condition; the control graphite and test grade graphite were exchanged at this time relative to their role in the program. Coatings were applied by dipping. The cure cycle step used baseline processing of 3°C/hr to 1050°C.

D. Test Series IV: Evaluation of Cure Temperature

Cure temperatures for Vitre-Graf coatings have been used as low as 850°C and as high as 1600°C with little change in performance except at the lower cure temperature where the coating tends to be soft. Also at the lower temperatures there exists a greater propensity for peeling then at higher temperatures. The lower temperatures, however, represents a cost savings so that this evaluation series is designed to determine the optimum cure temperature relative to both performance and cost.

1. Cure Temperature Variation

Each of five sample sets were heated to five different temperatures ranging from 850°C to 1250°C in 100°C increments.

2. Processing Description

Porous mullite and silica as-received were used after acid washing. Graphite was used in the as-received condition. Samples were dip coated in 350 g/l solution; two layers were applied. Each coating layer was cured at the temperature of variation at a heating rate of 3°C/hr.

E. Test Series V: Evaluation of Alternate Gas Atmospheres

All commercial Vitre-Graf coatings are cured in vacuum. Previous attempts to process in neutral atmospheres, even at greatly reduced pressures has resulted in the deposition of contaminating tars on the ware surfaces as a consequence of redeposition of hydrocarbon that outgas from the curing resin. Vacuum processing adds heavily to processing costs and is prohibitively costly in high volume applications. This series was designed to demonstrate the technical acceptance of neutral atmospheres for the cure cycle under conditions where the source of hydrocarbons is small relative to furnace volume and deposition is minimized. This condition can be reproduced in high volume, continuous production operations by using flowing gas at atmospheres pressure.

1. Alternative Gases

Both nitrogen and argon were evaluated as media gases in the cure cycle for Vitre-Graf coatings. Pressures were nominally 5 in. of Hg, slightly below atmosphere pressure so that the experiments could be performed by using existing vacuum furnaces.

2. Processing Description

Porous mullite as-received was used after acid washing. Graphite was used as-received. Samples were dip coated in 350 g/l solution, cured at 1150°C/hr. and two layers were applied. Additionally, an alternative resin was used in nitrogen atmosphere for one sample set because of an uncertainty in the long-term performance characteristics of the primary resin source.

F. Test Series VI: Evaluation of Discretionary Alternatives

The evaluation results of previous test series indicated that different processing of Vitre-Graf was advisable for mullite to be used as a substrate for the SOC process than for graphite to be used as a container ware. Specifically, for container ware applications with graphite as substrate, the reaction layer performance was inferior to initial preliminary performance of Vitre-Graf coating on mullite. Several reasons were postulated including number of coating layers, temperature of curing and the pore structure of the graphite substrate.

1. Re-evaluation of Cure Temperature

Both mullite and graphite were re-evaluated at cure temperatures of 1150°C and 1450°C. The higher temperature representing a value greater than its expected use temperature. Additionally a graphite sample was cured at 1050°C for comparison with baseline.

2. Re-evaluation of Number of Coating Layers

Both mullite and graphite were re-evaluated with respect to number of coating layers on the supposition that one layer may be as effective as two for wettability. Additionally for graphite as a container material, a coating of five layers was evaluated.

3. Evaluation of an Alternative Form of Carbon

Because of the nature of the reaction product that was formed between silicon and graphite, an alternative carbonaceous substrate, a carbon-carbon composite, was evaluated.

4. Evaluation of Pore Structure Variable

A second alternative relating to the nature of the reaction product between silicon and graphite suggested a need to change pore structure; thus, both graphite and the carbon-carbon composite were evaluated after a carbonaceous filler material was rubbed into surface pores.

5. Processing Description

Porous mullite as-received was used after acid washing, graphite and the carbon-carbon composite were used as-received. Samples were dip coated in 350 g/1 solution of resin #2 and cured at selected temperatures with a heating rate of 3°C/hr. The number of coating layers was a selected variable. For the graphite and carbon-carbon composites which were filled, a two part carbon-based cement was used in a fluid state and the cement was rubbed into the open surface pores. Subsequently, the parts were heated to 700°C before applying the dip coating.

G. Test Series VII: Re-Evaluation of Parameters for Mullite as Substrate

At this point in the program, graphite and the container ware concept was dropped from the program and all effort was addressed toward mullite substrates and the SOC application. Moreover, a new mullite, Type K was developed by Coors Porcelain Co.[3] that exactly matched the thermal expansion of silicon. This material was manufactured with slots to accommodate back face contacts. One of our objectives was to determine whether Vitre-Graf could be applied to one face of the mullite without allowing the coating to cover the slot edges since it is undesireable to permit silicon to enter the slotted regions. Other objectives were to evaluate heating rate for the cure cycle and a general re-evaluation of parameters selected in previous test series on porous mullite but not confirmed for the new mullite. The objective was to systematically change variables to assure that optimal parameters had been selected.

1. Evaluation of Heating Rate for Type K Mullite

The optimal parameters selected from previous test series for S-1-SI porous mullite used resin #2 at 350 g/l solution, two coats applied by dipping and cured at 1150°C in nitrogen atmosphere at a heating rate of 3°C/min. An initial experiment at 10°C/min was run, subsequent heating rates would be selected at either 5°C/min or 20°C/min depending on the outcome so that the optimal rate may be bracketed by the existing baseline rate and an excessive rate.

a. 10°C/min - The samples run at 10°C/min severely flaked such that a wipe with a paper tissue removed the coating completely. These samples were re-run in the same condition but in vacuum rather than nitrogen.

b. 10°C/min in Vacuo - The flaking problem was just as severe as the previous experiment conducted in nitrogen. Excessive heating rate was deduced.

c. 5°C/min in N_2 - Reducing the heating rate by a factor of two had no effect on the results. The coating completely flaked off.

d. 3°C/min in N_2 - The Vitre-Graf coating flaked completely off even at baseline heating rate. It was apparent that the type "K" mullite had not only a new composition but also new surface characteristics.

2. Evaluation of Surface Preparation Methods (Type K)

The sample set used to investigate heating rate was etched in HF for fifteen seconds before coating with a brush. A second sample set was physically abraded with silicon carbide (240 grit) sanding paper before brush coating. Both sets were run under initial conditions i.e. optimal parameters but at 5°C/min in nitrogen.

a. Etched substrates - The etched samples coated completely and uniformily with one coat. No peeling, flaking or delamination was apparent. A second coating was not considered necessary.

b. Abraded substrates - The samples that were sanded appeared indistinguishable from those that were etched. Apparently in both cases a surface layer (presumable a silica glaze) was removed but the physical integrity of the abraded samples suffered as a consequence of that operation.

c. Etched substrates at 10°C/min - Another sample set was then etched before coating and the previous experiment was run at 10°C/min. The results were equally as good as those for 5°C/min.

3. Re-Evaluation of Cure Temperature (Type K)

The apparent effect of etching was to greatly increase adherence. On the basis of cost, a reduction in cure temperature was next considered most cost effective. This evaluation series was conducted with resin #2 at 350 g/l solution, single coat applied with brush and cured at reduced temperatures in nitrogen at a heating rate of 10°C/min.

a. 1050°C - The sample set cured at 1050°C appeared as well coated as previous samples cured at 1150°C.

b. 950°C - A cure temperature of 950°C did not appear to adversely affect the quality of the coating from previous higher cure temperatures.

4. Re-Evaluation of Solution Concentration (Type K)

Solution concentration was then re-evaluated at reduced temperatures. These experiments were conducted with resin #2 at 250 g/l and at 150 g/l and at cure temperatures of 950°C and 850°C. A single coat was applied and cured by heating at 10°C/min in nitrogen.

a. 250 g/l and 950°C - This sample set coated as well as any previous set.

b. 150 g/l and 850°C - An operator error was responsible for a cure temperature of 1225°C. Although the planned cure temperature was exceeded, the light solution covered and adhered well.

c. Repeat 150 g/l and 850°C - By appearance, this coating is equivalent to any previously produced.

Table I Sample Process Description

Variable	Material	Vitre-Graf Coating	Pre-process Treatment	Coating Method	Solution Concentration	No. of Layers	Cure Temperature	Furnace Atmosphere	Heating Rate
Test Series I **Evaluation of Pre-process Treatment**	DM	#1	AR	B	250	5	105	V	3
	DM	↑	PF	↑	↑	↑	↑	↑	↑
	DM		AE						
	PM		AR						
	FG		AR						
	FG		PF						
	FG		RS						
	FG		PS						
	MG		AR						
	MG		PF						
	MG		RS						
	MG		PS	↓					
Test Series II **Evaluation of Application Method**	PM		AR	B					
	PM		AR	D					
	PM		AR	S					
	FG		AR	B					
	FG		AR	D					
	FG		AR	S					
	MG		AR	B					
	MG	↓	AR	D	↓	↓	↓	↓	↓
	MG	#1	AR	S	250	5	105	V	3

Variable	Material	Vitre-Graf Coating	Pre-process Treatment	Coating Method	Solution Concentration	No of Layers	Cure Temperature	Furnace Atmosphere	Heating Rate
Test Series III **Evaluation of Thickness Parameters**	PM	#1	AR	D	150	4	105	V	3
	PM	↑	↑	↑	150	6	↑	↑	↑
	PM				150	8			
	PM				250	3			
	PM				250	4			
	PM				250	5			
	PM				350	2			
	PM				350	3			
	PM				350	4			
	MG				150	4			
	MG				150	6			
	MG				150	8			
	MG				250	3			
	MG				250	4			
	MG				250	5			
	MG				350	2			
	MG				350	3			
	MG				350	4			
	FG				150	4			
	FG				150	6			
	FG				150	8			
	FG				250	3			
	FG				250	4			
	FG				250	5			
	FG				350	2			
	FG				350	3			
	FG				350	4			
	FS				150	8			
	FS	↓	↓	↓	250	5	↓	↓	↓
	FS	#1	AR	D	350	4	105	V	3

MATERIALS

PM - porous mullite
DM - dense mullite
XM - type "K" mullite
FG - fine-grained graphite
MG - molded graphite
FS - slip-cast fused silica
CC - carbon-carbon composite

VITRE-GRAF COATING

#1 - Baseline resin
#2 - Hi-purity resin

PRE-PROCESS TREATMENT

AR - as received
PF - pre-fired
RS - roughened surface
PS - polished surface
AE - acid etched
MA - acid etched
MA - mechanically abraded
CF - carbon particle filled

APPLICATION METHOD

B - brush
D - dip

Variable	Material	Vitre-Graf Coating	Pre-process Treatment	Coating Method	Solution Concentration	No of Layers	Cure Temperature	Furnace Atmosphere	Heating Rate
Test Series IV Evaluation of Cure Temperature	PM	#1	AR	D	350	2	85	V	3
	PM	↑	↑	↑	↑	↑	95	↑	↑
	PM						105		
	PM						115		
	PM						125		
	MG						85		
	MG						95		
	MG						105		
	MG						115		
	MG						125		
	FG						85		
	FG						95		
	FG						105		
	FG						115		
	FG						125		
	FS						85		
	FS						95		
	FS						105		
	FS						115		
	FS	↓	↓	↓	↓	↓	125	↓	↓
Test Series V Evaluation of Furnace Atmosphere	PM	#1	AR	D	350	2	115	A	3
	PM	#1	↑	↑	↑	↑		N	↑
	PM	#2						N	
	MG	#1						A	
	MG	#1						N	
	MG	#2						N	
	FG	#1						A	
	FG	#1	↓	↓	↓	↓		N	↓
	FG	#2	AR	D	350	2	115	N	3

Variable	Material	Vitre-Graf Coating	Pre-process Treatment	Coating Method	Solution Concentration	No of Layers	Cure Temperature	Furnace Atmosphere	Heating Rate
Test Series VI Evaluation of Discretionary Alternatives	PM	#2	AR	D	350	1	115	N	3
	PM	↑	↑	↑	↑	2	115	↑	↑
	PM					1	145		
	PM					2	145		
	MG					1	115		
	MG					2	115		
	MG		↓			1	145		
	MG		AR			2	145		
	MG		CF			1	145		
	MG		AR			5	105		
	MG		AR			5	145		
	MG		CF			5	145		
	CC	↓	AR	↓	↓	1	105	↓	↓
	CC	#2	CF	D	350	5	145	N	3
Test Series VII Re-Evaluation of Parameters	KM	#2	AR	B	350	1	115	N	10
	↑	↑	↑	↑	↑	↑	↑	V	10
			↓		↓		↓	N	5
			AR		350		115	N	3
			MA		350		↑	N	5
			AL		↕		↓	N	5
			↑		350		115	N	10
					350		105	N	10
					350		95	N	10
					250		95	N	10
	↓	↓	↓	↓	150	↓	125*	N	10
	KM	#2	AL	B	150	1	85	N	10

SOLUTION CONCENTRATION

150 - 150g resin/liter solvent
250 - 250g resin/liter solvent
350 - 350g resin/liter solvent

HEATING RATE

3 - 3°C/min
5 - 5°C/min
10 - 10°C/min

COATING LAYERS

1 - 1 coating layer
2 - 2 coating layer
3 - 3 coating layer
4 - 4 coating layer
5 - 5 coating layer

CURE TEMPERATURE

85 - 850°C
95 - 950°C
105 - 1050°C
115 - 1150°C
125 - 1250°C

FURNACE ATMOSPHERE

V - vacuum
A - argon
N - nitrogen

SECTION V

EVALUATION RESULTS AND DISCUSSION

The evaluation of each test series was directed toward two primary technical objectives. The first was a determination of adherence, or stated conversely, the elimination of flaking or delaminations. The second objective was the determination of the reaction characteristics between silicon and the coating. In the initial experiments, only adherence was determined. The test for adherence consisted of applying an adhesive tape to the coating layer and stripping the tape away. The relative amount of coating adhering to the tape was noted and its weight gain determined. In support of this measurement, one sample from each test series was cut, the cross section polished and the interface between substrate and coating observed with a scanning electron microscope (SEM).

Evaluation of the silicon-coating reaction was made either through Sessile drop experiments conducted by JPL to determine the suitability of the coating for container materials, or by silicon dip experiments conducted by Honeywell to determine its suitability for the SOC applications. Only selected samples were evaluated by either of these methods based on the apparent suitability of the particular parameters to the intended application.*

Additional data were collected on each sample run to support the overall evaluation. Visual evaluation of the coating quality was recorded, the thickness of the coating was calculated from weight gain and also measured from SEM cross section micrographs. Additionally, a surface analysis with an ion microprobe was made of each test series to provide background chemical analysis of the coating material and establish a level of contamination potential originating from the substrates that might be expected in solar cells.

In retrospect, decisions and selections were not necessarily made on a rigorous method of evaluation, but rather many were made on subjective evaluation. As will become apparent in the following discussion, most variables produced equally satisfactory results and selection was made primarily on the basis of the lowest projected production cost for the variable.

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*The results and data on silicon reaction presented in this report are the work of Mr. Tim O'Donnell of JPL and Dr. J. Dave Zook of Honeywell Research Center.

A. Test Series I: Evaluation of Substrate Preparation

1. Visual

From visual observation all samples accepted a coating but flaking or delaminations varied widely among the samples. Of the mullite samples, the etched samples attained a significantly greater coating weight but the porous samples had the least amount of flaking and the best appearance. All of the test graphite samples flaked; the heaviest flaking occurred in the polished sample, the least in the roughened sample. The behavior of the control samples was similar to that of the test samples but the degree of flaking was significantly reduced. Except for the polished control, all graphite control samples appeared superior to the test graphite samples. No appearance difference was apparent between the as-received and the pre-fired samples of any samples in this series.

2. Adherence

One sample was arbitrarily selected from each sample set of three and tested for delamination by the adhesive tape method. The gain in weight of the tape after being stripped from the coating surface is used as an indication of the relative adherence of the coating. For some samples that had experienced heavy flaking, the adherence test did not provide a correct indicator because much of the surface layer was lost by flaking before the adherence test could be conducted. A ranking of the samples by the amount of peeling that was measured is presented in Table II.

TABLE II: Ranked from least amount of weight loss to greatest amount of weight loss.

	Preprocess Conditions	Tape Wt. Increase (mg)
Mullite:	Etched	0
	Porous	0
	As-Received	0.5
	Pre-fired @1250°C	0.8
Test Graphite:	As-Received	0*
	Polished	0*
	Coarsened	0.1
	Pre-fired	0.4
Control Graphite:	Polished	0*
	Coarsened	0
	Pre-fired @1250°C	0
	As-Received	0.1

*Surface loss by flaking occurred before adherence test.

The adherence test indicated that the etched and porous mullite samples were best, probable because they each provided a surface onto which the coating could mechanically attach. For both the test graphite and control graphite when pre-test flaking is taken into account the coarsened sample was best in both cases. Again, mechanical attachment appears to be the primary consideration.

3. SEM Observations

Examination of mullite samples with a scanning electron microscope (Figure 3) revealed that all samples delaminated between the fourth and fifth layers, and all samples, showed some evidence of separation between the coating and substrate. The etched sample contained a broad band of exposed crystals around which the coating adhered but the resulting surface was highly irregular. Surface flatness of the sample was improved considerably by coating in the other three cases. The micrographs did not show a significant difference between the porous sample and the as-received or pre-fired sample even though other tests showed a discernible difference between them.

The test graphite samples (Figure 4) showed the delamination problem observed in mullite but no separation of coating and substrate was observed on any. Some sections of the polished sample showed no delamination at all but this observation could be traced to a surface step where it becomes apparent that the outer layer had already flaked away.

The control graphite appeared much as the test graphite except its coarser porosity suggests a greater interface bond.

4. Thickness Measurements

The calculated thickness in this test series indicated a consistency that ranged between 7.5 and 4.5 μm. among all samples and with a strong distribution median at 6.0 μm. Thickness measured from SEM photos revealed an average thickness of 5 μm, about 80% of the calculated value and this difference is indicative of the coating contribution that has entered and filled pores. The measured thickness of as-received and pre-fired mullite samples that did not have pores, matched nearly precisely the calculated value. However, a much greater deviation in thickness is seen within a single sample where measured thickness ranged from about 1 μm to greater than 10 μm. Much of this deviation appears to be associated with the surface roughness of the substrate and the tendency for the coating to increase the flatness of the surface by filling in surface depressions.

5. Surface Chemical Analysis

The chemical analysis of the coating for each sample set was measured with the ion microprobe that analyzes the sputtered outer surface layer of the sample with a mass spectrometer. Mass Spectrometric data from these samples are presented in Fig. 5-8.

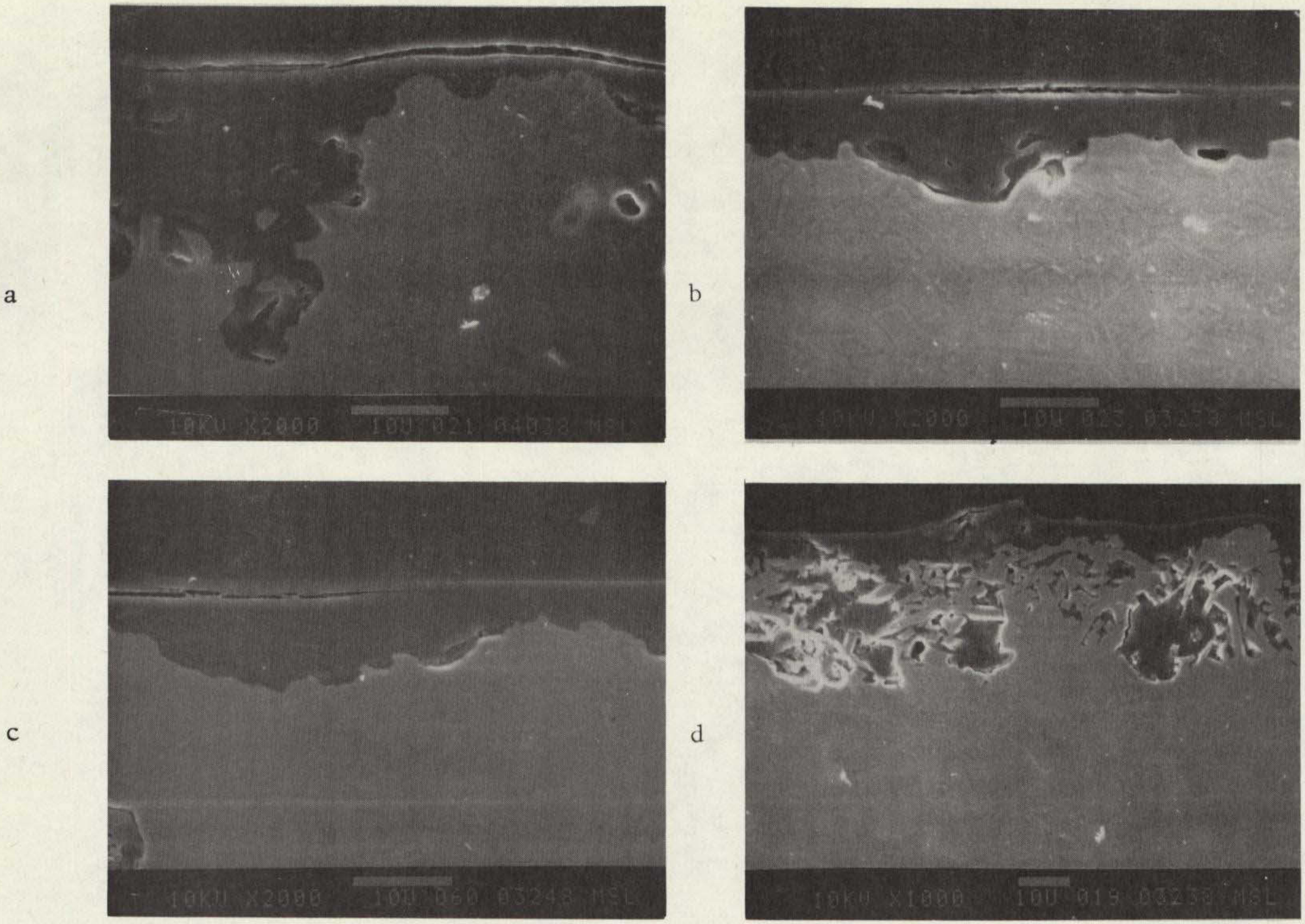


Fig. 3 Vitre-Graf coated mullite substrate: (a) as-received, (b) prefired, (c) porous, (d) etched. Photo margin contains 10 μm magnification marker.

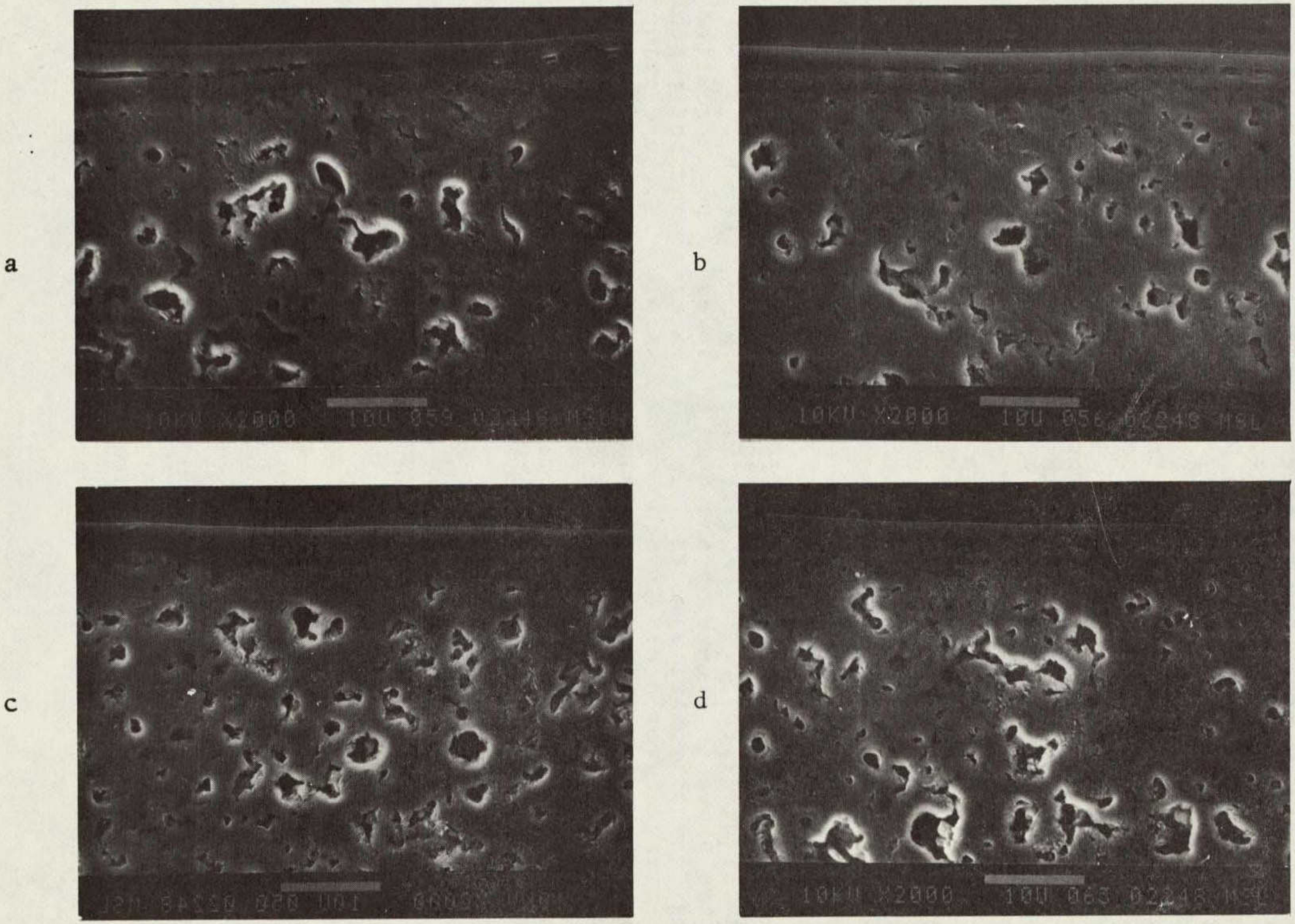


Fig. 4 Vitre-Graf coated fine-grained graphite: (a) as-received, (b) pre-fired, (c) polished, (d) roughened.

Figure 5 is for the polished test graphite sample and is fairly representative of the spectra that is expected from Vitre-Graf applied to purified graphite. Total impurities measured on this sample are less than 20 ppm. The spectra of the test graphite in the as-received condition is shown in Figure 6. Considerably greater amounts of impurities are apparent and include sodium, magnesium, aluminum, silicon, potassium and calcium. A total impurity level of about 100 ppm exist in this coating. The coating is a highly purified material but readily transmits substrate impurities to the surface by diffusion during the cure cycle. The greater impurities in the as-received sample relative to the polished sample suggests the presence of a surface layer of contamination that was removed in the polishing operation. The spectra of the coarsened and pre-fired samples are nearly identical with that of the as-received sample and supports this contention.

The mullite mass spectra are shown in Fig. 7 for the as-received sample and Fig. 8 for the porous sample. The mass spectra of the mullite samples show considerably more impurities and greater impurity concentrations than the test graphite samples. Notably, sodium, aluminum, silicon, potassium and calcium are present in concentrations that exceed 0.01% in most cases. The pre-fired and etched samples were similar to the as-received and all three are the same base mullite. The porous mullite is a material having the same composition as the others but processed slightly differently. The slight difference between the two spectra shown in Figures 5 and 6 is believed to be indicative of normal compositional variation in this material and not to this processing difference. In none of the samples is there evidence of fourth period transition metals but some evidence for copper contamination exists in all mullite samples. Although impurities are found in the coating of all samples and at total concentrations that may exceed 0.1% in mullite substrates, these data cannot serve to predict whether significant contamination of silicon in contact with the coating will occur in either end use application.

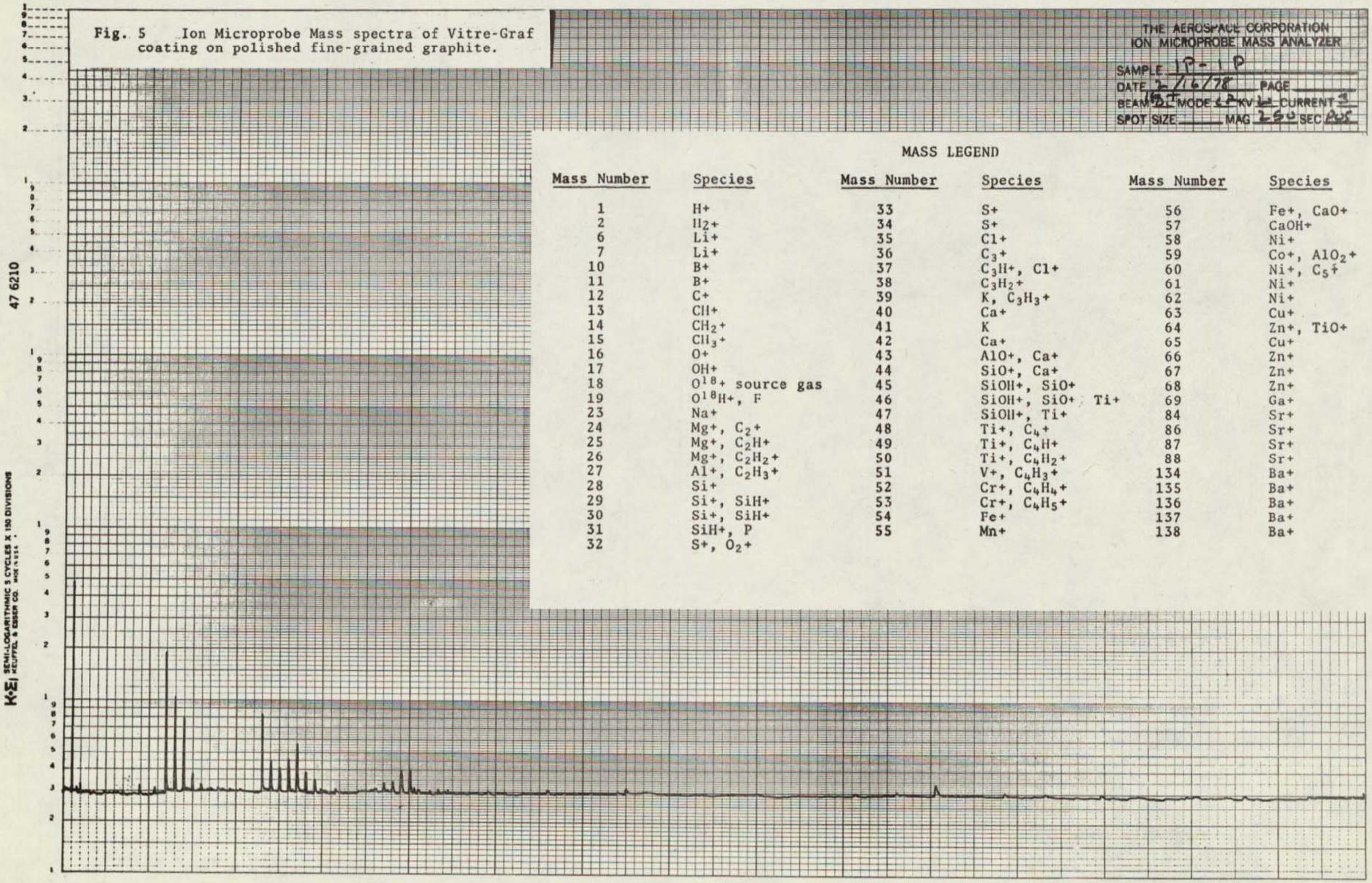
6. Conclusions

The substrate preparation technique selected for mullite was porous mullite used as-received. This selection was based primarily on visual observations and the adherence test which indicated a decisive advantage for the porous mullite. These criteria also suggested an advantage for etched mullite but the additional projected cost for an etching operation did not appear to favor this selection.

The various preparation techniques used in the test graphite did not show a decisive advantage that would offset any additional cost of an operation beyond that of an as-received condition.

Therefore, porous mullite and the test graphite both in the as-received condition were selected for the continuation of the program.

Fig. 5 Ion Microprobe Mass spectra of Vitre-Graf coating on polished fine-grained graphite.



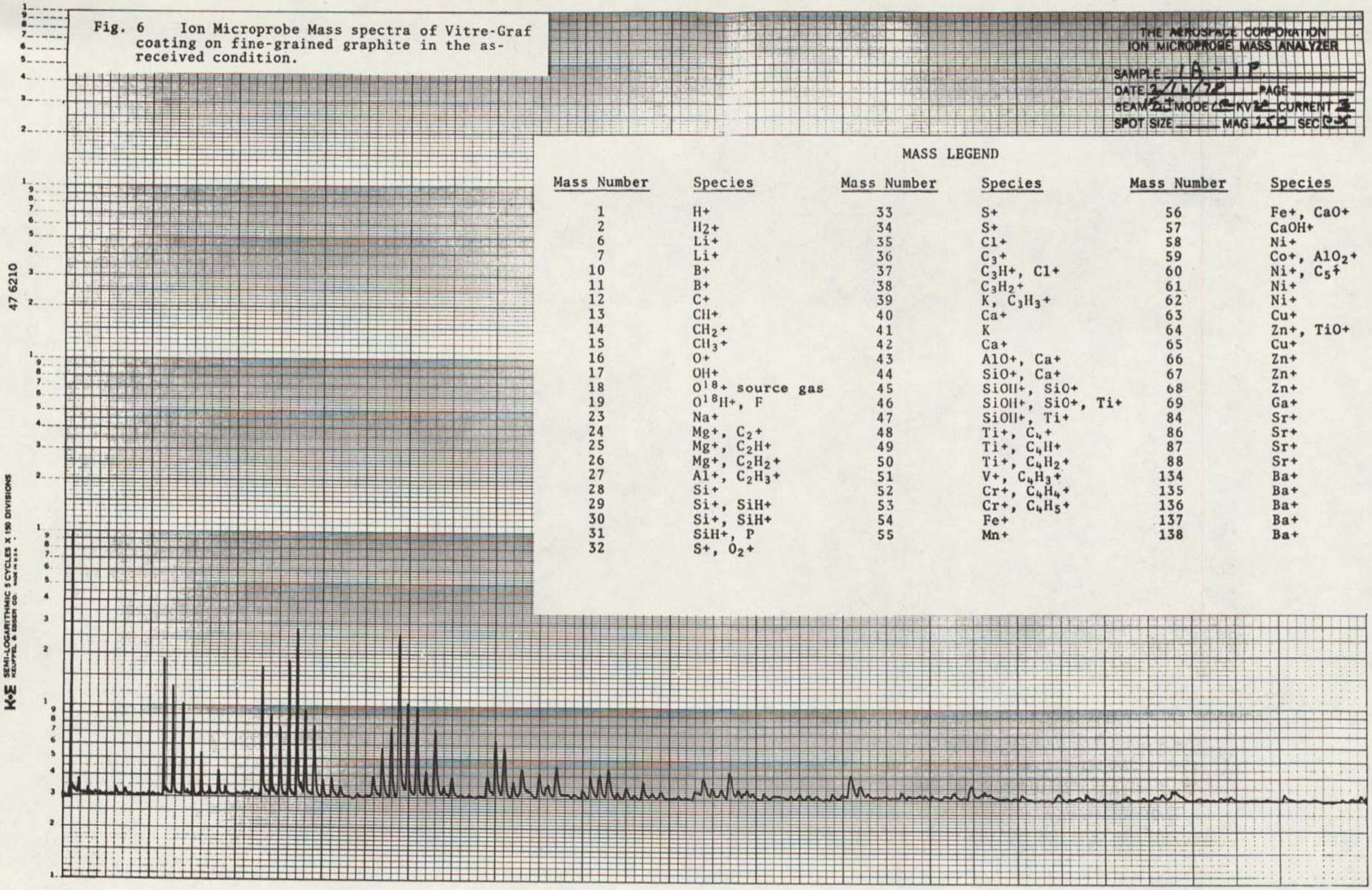
THE AEROSPACE CORPORATION
ION MICROPROBE MASS ANALYZER

SAMPLE 1P-1P
DATE 2/16/78 PAGE
BEAM $^{16}O^{-}$ MODE CP KV 12 CURRENT 3
SPOT SIZE MAG 250 SEC Pos

MASS LEGEND

Mass Number	Species	Mass Number	Species	Mass Number	Species
1	H+	33	S+	56	Fe+, CaO+
2	H_2+	34	S+	57	CaOH+
6	Li+	35	Cl+	58	Ni+
7	Li+	36	C_3+	59	Co+, AlO_2+
10	B+	37	C_3H+, Cl+	60	Ni+, C_5+
11	B+	38	C_3H_2+	61	Ni+
12	C+	39	K, C_3H_3+	62	Ni+
13	CH+	40	Ca+	63	Cu+
14	CH_2+	41	K	64	Zn+, TiO+
15	CH_3+	42	Ca+	65	Cu+
16	O+	43	AlO+, Ca+	66	Zn+
17	OH+	44	SiO+, Ca+	67	Zn+
18	O^{18}+ source gas	45	SiOH+, SiO+	68	Zn+
19	$O^{18}H$+, F	46	SiOH+, SiO+ Ti+	69	Ga+
23	Na+	47	SiOH+, Ti+	84	Sr+
24	Mg+, C_2+	48	Ti+, C_4+	86	Sr+
25	Mg+, C_2H+	49	Ti+, C_4H+	87	Sr+
26	Mg+, C_2H_2+	50	Ti+, C_4H_2+	88	Sr+
27	Al+, C_2H_3+	51	V+, C_4H_3+	134	Ba+
28	Si+	52	Cr+, C_4H_4+	135	Ba+
29	Si+, SiH+	53	Cr+, C_4H_5+	136	Ba+
30	Si+, SiH+	54	Fe+	137	Ba+
31	SiH+, P	55	Mn+	138	Ba+
32	S+, O_2+				

Fig. 6 Ion Microprobe Mass spectra of Vitre-Graf coating on fine-grained graphite in the as-received condition.



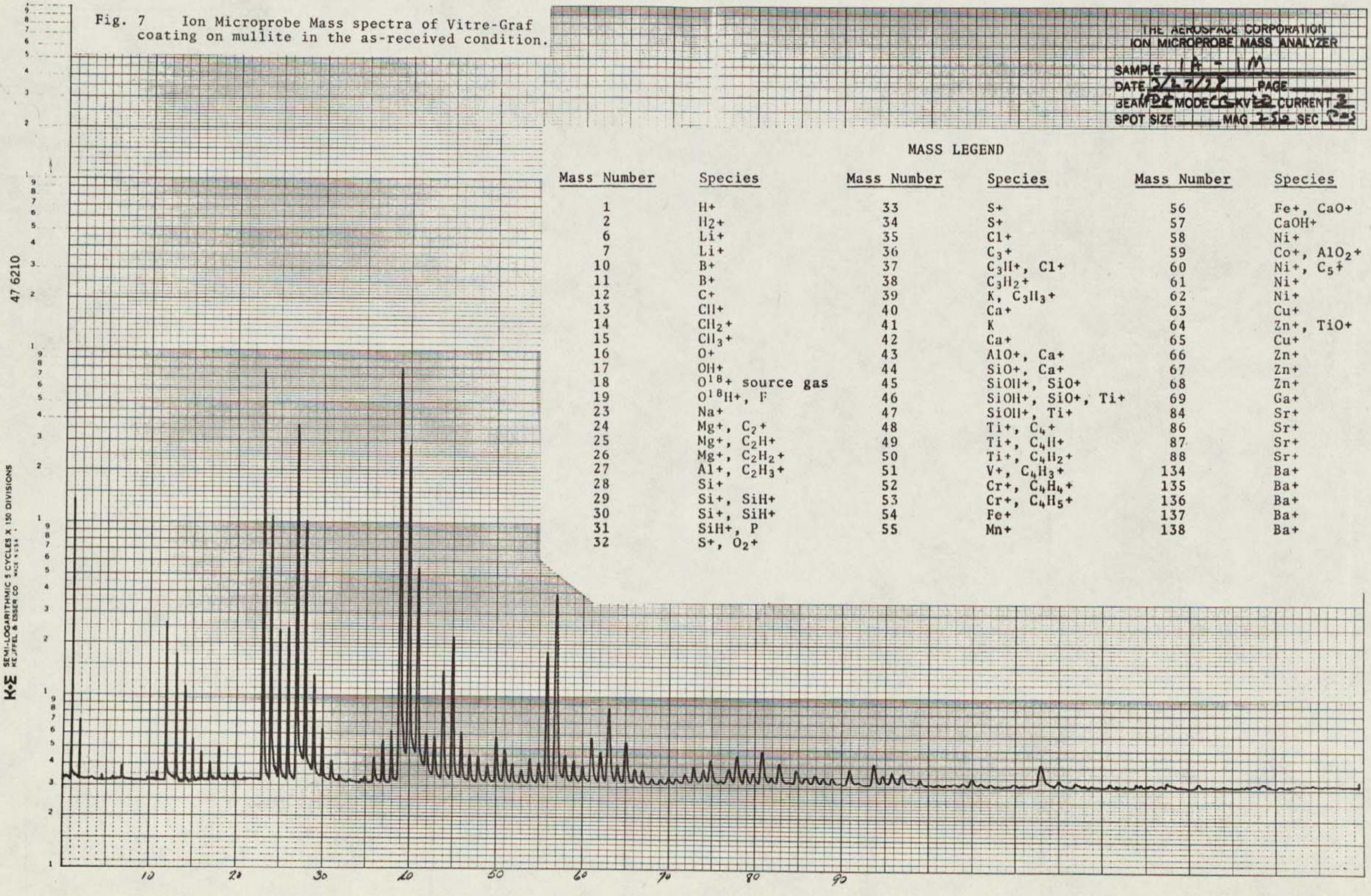
THE AEROSPACE CORPORATION
ION MICROPROBE MASS ANALYZER

SAMPLE IA - 1P.
DATE 2/16/78 PAGE
BEAM O_2^+ MODE CP KV 12 CURRENT 3
SPOT SIZE MAG 250 SEC 0.25

MASS LEGEND

Mass Number	Species	Mass Number	Species	Mass Number	Species
1	H+	33	S+	56	Fe+, CaO+
2	H_2+	34	S+	57	CaOH+
6	Li+	35	Cl+	58	Ni+
7	Li+	36	C_3+	59	Co+, AlO_2+
10	B+	37	C_3H+, Cl+	60	Ni+, C_5^+
11	B+	38	C_3H_2+	61	Ni+
12	C+	39	K, C_3H_3+	62	Ni+
13	CH+	40	Ca+	63	Cu+
14	CH_2+	41	K	64	Zn+, TiO+
15	CH_3+	42	Ca+	65	Cu+
16	O+	43	AlO+, Ca+	66	Zn+
17	OH+	44	SiO+, Ca+	67	Zn+
18	O^{18}+ source gas	45	SiOH+, SiO+	68	Zn+
19	O^{18}H+, F	46	SiOH+, SiO+, Ti+	69	Ga+
23	Na+	47	SiOH+, Ti+	84	Sr+
24	Mg+, C_2+	48	Ti+, C_4+	86	Sr+
25	Mg+, C_2H+	49	Ti+, C_4H+	87	Sr+
26	Mg+, C_2H_2+	50	Ti+, C_4H_2+	88	Sr+
27	Al+, C_2H_3+	51	V+, C_4H_3+	134	Ba+
28	Si+	52	Cr+, C_4H_4+	135	Ba+
29	Si+, SiH+	53	Cr+, C_4H_5+	136	Ba+
30	Si+, SiH+	54	Fe+	137	Ba+
31	SiH+, P	55	Mn+	138	Ba+
32	S+, O_2+				

Fig. 7 Ion Microprobe Mass spectra of Vitre-Graf coating on mullite in the as-received condition.



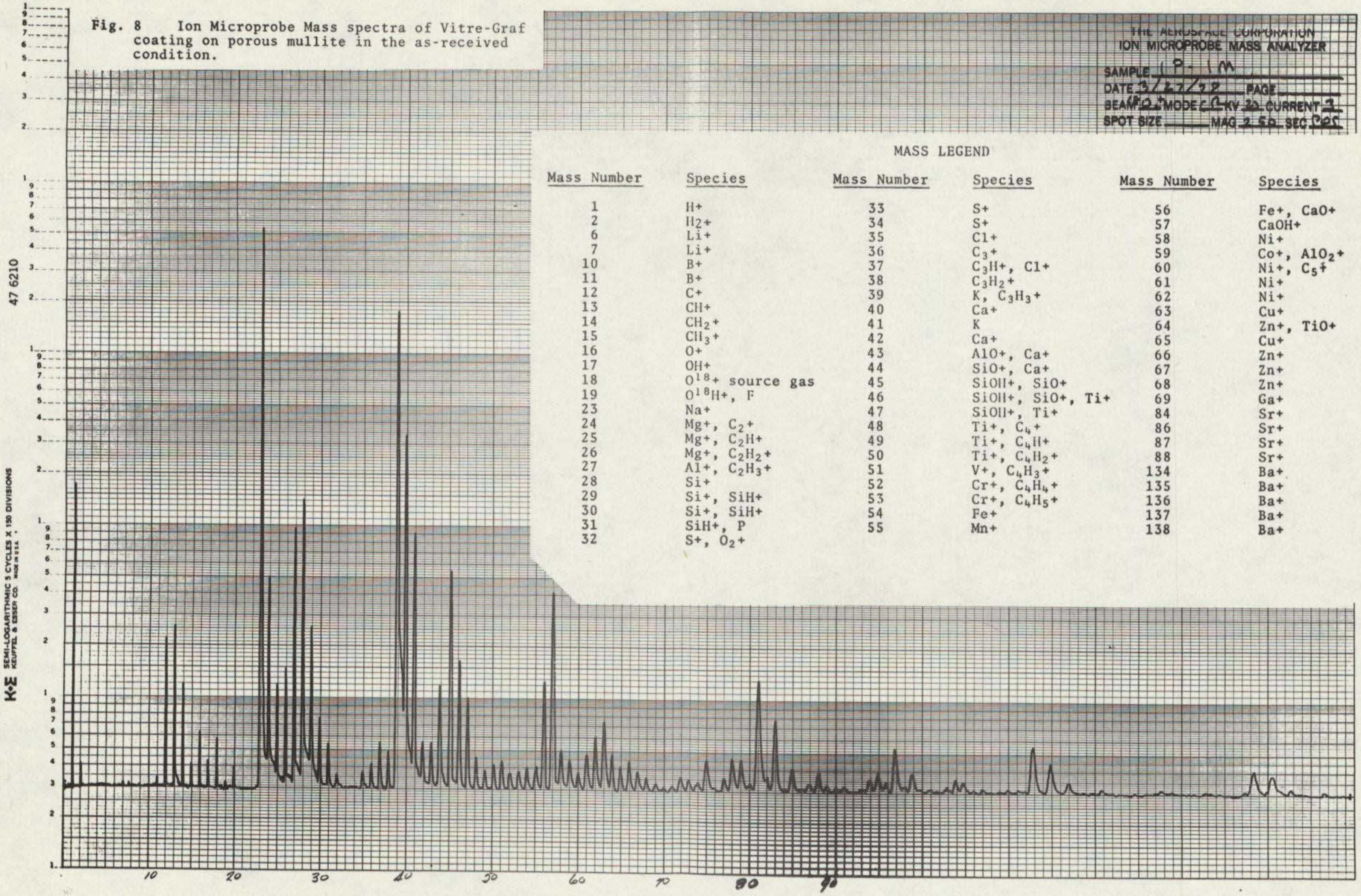
THE AEROSPACE CORPORATION
ION MICROPROBE MASS ANALYZER

SAMPLE 1A - 1M
DATE 3/27/78 PAGE
BEAM [illegible] MODE CG KV 22 CURRENT 3
SPOT SIZE MAG 250 SEC [illegible]

MASS LEGEND

Mass Number	Species	Mass Number	Species	Mass Number	Species
1	H+	33	S+	56	Fe+, CaO+
2	H_2+	34	S+	57	CaOH+
6	Li+	35	Cl+	58	Ni+
7	Li+	36	C_3+	59	Co+, AlO_2+
10	B+	37	C_3H+, Cl+	60	Ni+, C_5+
11	B+	38	C_3H_2+	61	Ni+
12	C+	39	K, C_3H_3+	62	Ni+
13	CH+	40	Ca+	63	Cu+
14	CH_2+	41	K	64	Zn+, TiO+
15	CH_3+	42	Ca+	65	Cu+
16	O+	43	AlO+, Ca+	66	Zn+
17	OH+	44	SiO+, Ca+	67	Zn+
18	O^{18}+ source gas	45	SiOH+, SiO+	68	Zn+
19	O^{18}H+, F	46	SiOH+, SiO+, Ti+	69	Ga+
23	Na+	47	SiOH+, Ti+	84	Sr+
24	Mg+, C_2+	48	Ti+, C_4+	86	Sr+
25	Mg+, C_2H+	49	Ti+, C_4H+	87	Sr+
26	Mg+, C_2H_2+	50	Ti+, C_4H_2+	88	Sr+
27	Al+, C_2H_3+	51	V+, C_4H_3+	134	Ba+
28	Si+	52	Cr+, C_4H_4+	135	Ba+
29	Si+, SiH+	53	Cr+, C_4H_5+	136	Ba+
30	Si+, SiH+	54	Fe+	137	Ba+
31	SiH+, P	55	Mn+	138	Ba+
32	S+, O_2+				

Fig. 8 Ion Microprobe Mass spectra of Vitre-Graf coating on porous mullite in the as-received condition.



THE AEROSPACE CORPORATION
ION MICROPROBE MASS ANALYZER
SAMPLE 1P-1M
DATE 3/27/78 PAGE
BEAM O_2^+ MODE CC KV 20 CURRENT 3
SPOT SIZE MAG 250 SEC Pos

MASS LEGEND

Mass Number	Species	Mass Number	Species	Mass Number	Species
1	H^+	33	S^+	56	Fe^+, CaO^+
2	H_2^+	34	S^+	57	$CaOH^+$
6	Li^+	35	Cl^+	58	Ni^+
7	Li^+	36	C_3^+	59	Co^+, AlO_2^+
10	B^+	37	C_3H^+, Cl^+	60	Ni^+, C_5^+
11	B^+	38	$C_3H_2^+$	61	Ni^+
12	C^+	39	K, $C_3H_3^+$	62	Ni^+
13	CH^+	40	Ca^+	63	Cu^+
14	CH_2^+	41	K	64	Zn^+, TiO^+
15	CH_3^+	42	Ca^+	65	Cu^+
16	O^+	43	AlO^+, Ca^+	66	Zn^+
17	OH^+	44	SiO^+, Ca^+	67	Zn^+
18	O^{18+} source gas	45	$SiOH^+$, SiO^+	68	Zn^+
19	$O^{18}H^+$, F	46	$SiOH^+$, SiO^+, Ti^+	69	Ga^+
23	Na^+	47	$SiOH^+$, Ti^+	84	Sr^+
24	Mg^+, C_2^+	48	Ti^+, C_4^+	86	Sr^+
25	Mg^+, C_2H^+	49	Ti^+, C_4H^+	87	Sr^+
26	Mg^+, $C_2H_2^+$	50	Ti^+, $C_4H_2^+$	88	Sr^+
27	Al^+, $C_2H_3^+$	51	V^+, $C_4H_3^+$	134	Ba^+
28	Si^+	52	Cr^+, $C_4H_4^+$	135	Ba^+
29	Si^+, SiH^+	53	Cr^+, $C_4H_5^+$	136	Ba^+
30	Si^+, SiH^+	54	Fe^+	137	Ba^+
31	SiH^+, P	55	Mn^+	138	Ba^+
32	S^+, O_2^+				

B. Test Series II: Evaluation of Application Methods

1. Visual

The samples of mullite, test graphite and control graphite that had their coating applied by brush were virtually identical with like samples from the first test series with the possibility of a little less flaking on all three substrates. No discernible difference was apparent between the dip coated and brush coated samples except for a slight tendency toward streaking in the brush coated samples, especially with the test graphite. The spray coated sample was the worse of each set for each substrate material and poorest for mullite. The spray coating on the porous mullite did not appear to be strongly bonded and looked as if it could be removed by wiping it away.

Both dipping and brush coating produced acceptable looking coatings on mullite and control graphite but the test graphite flaked in both cases. Spray coating created flaky coatings on all samples.

2. Adherence

The adherence tests results were that as expected in most cases. For all substrates the results expected for brush coated samples are those experienced in test Series I where no loss of coating was experienced in the test. The same result was obtained for dip coated samples. However, from the flakiness of the spray coated samples, an expected massive loss of coating adherence was expected on all samples and especially on the mullite sample. The test showed no coating loss on the mullite nor control graphite and only 0.1 mg loss from the test graphite sample in spite of the appearance that suggested a weakly bonded coating.

3. SEM Observations

The brush coated and dip coated samples looked much like Series I samples with the same substrates as is shown in Figure 9. Delamination between coating and substrate is seen on the dip coated mullite sample, and delamination between layers is seen for both the mullite and test graphite substrates. Spray coating in all cases produced a foam-like coating that was not removed in adherence testing but crumbled at the interface in the grinding-polishing operation performed in preparing the sample for SEM observations. Although this test series showed generally less flaking than the previous test series, more inter-layer delamination was apparent in this series.

4. Thickness Measurements

The thickness of the second test series is slightly greater than that for the first test series with an average calculated thickness of about 8.0 μm. The test graphite had a calculated thickness less than the other two substrate materials pro-

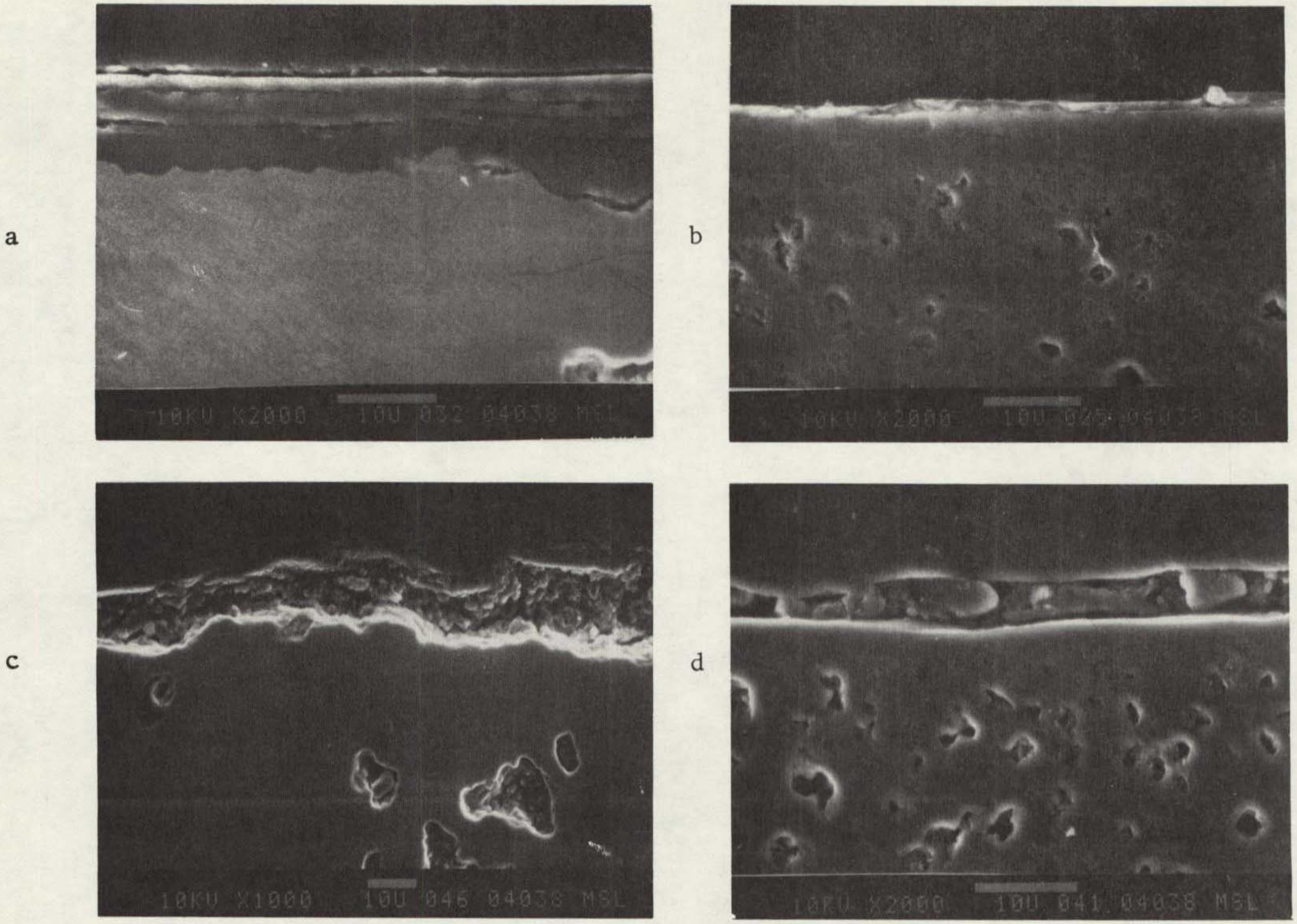


Fig. 9 Vitre-Graf coating on (a) mullite substrate (lower), dip coated; (b) fine-grained graphite (lower), brush coated; (c) mullite substrate (lower), spray coated; (d) fine-grained graphite (lower), spray coated.

bably because of a tendency for some weight loss between each layer due to flaking. As before, the measured thickness on SEM photos was about 80% of the calculated thickness. Thickness variations on a single sample was greater than average variations between any pair of samples.

5. Surface Chemical Analysis

In Test Series II the mass spectra of the mullite samples are virtually identical with each other and with the porous mullite sample of Series I. The same similarity exists between the spectra of Series I and Series II for test graphite samples. However, in all samples there appeared stronger alkali metal signals in Series II that are suspected of being caused by polyelectrolytes used in the recirculating water system for furnace cooling. A water jacket leak occurred during the course of this series and is believed responsible for this furnace contamination. No other effect of the leak was apparent from the mass spectra.

6. Conclusions

This test series clearly revealed that spray coating requires further development before it could become a viable technique. Between dip coating and brush coating there was no discernible technical difference. Dip coating was selected for continuation in this program because of a more favorable cost consideration.

(The greater tendency for inter-layer delamination observed in this series relative to Test Series I is believed to be related to the furnace water leak. The delamination observed in Test Series I occurred between the fourth and fifth coating; samples had experienced a weekend of ambient laboratory exposure between these two layers.)

As a consequence of the continuing flakiness of the test graphite the decision was made to substitute the control graphite for subsequent program testing and to continue the test graphite in the program but in a subservient role.

C. Test Series III: Evaluation of Coating Thickness

1. Visual

Visual observations were made after each layer cure.

a. For 350 g/l solution:

(1) Coating looked complete in some areas after 1st. layer.
(2) Cratering was noticed along the lower edge of each sample. Cratering is a condition that results from excessive build-up of resin solution.

b. For 250 g/l solution:

(1) Coating looked complete in some areas after the 2nd. layer.

(2) Minor cratering after each run along the lower edge.

c. For 150 g/l solution:

(1) Coating looked complete in some areas after 3rd layer.

(2) No cratering and very little streaking.

d. For all substrates, the best appearing surface was that with the greatest number of layers; however, acceptable coatings appeared with fewer layers on mullite and molded graphite. The fine-grained graphite showed some flakiness but less than in the previous test series. Very little flakiness appeared on any other substrate material. The silica substrate was so rough and porous that even with the maximum number of layers for each matrix set, the pores were not filled and the surface remained rough and irregular.

2. Adherence

Results of the adherence test showed little or no weight loss from flaking. No delamination occurred and no behavior pattern was observed. For the 250 g/l and 350 g/l solutions, only the silica substrate showed a weight loss in each case and the amount, 0.1 mg was negligible. For the 150 g/l solution, at least one sample from all substrates showed a similar negligible amount of weight loss from flaking. By comparison with series I and II, both flaking and delamination was significantly reduced.

3. SEM Observations

a. Mullite - Several anomalies were observed in the Vitre-Graf coating on the mullite substrates and are given in the following list:

(1) On some samples there existed delamination and/or tendency to delaminate between layers. Other samples showed no evidence for delamination.

(2) Separation between substrate and coating was often complete in areas of some samples, in other samples there was no evidence of separation.

(3) Where separation exists particulates appear in the gap that are probably polishing abrasive.

(4) Where separation does not exist there is evidence of good penetration into open pores.

This test series had been conducted before the water adsorption theory was postulated as cause for delamination. Therefore, no precautions were taken to protect surfaces between coating layers. The micrographs suggest that the adherence between the plastic mount and the coating often exceeded the strength of the inter-layer or interface bond. Abrasive powders appear to have collected in the resulting void. In general, the coatings from heavy solutions appeared superior to light solutions, and fewer layers were preferred over many layers. The contrast between these observed extremes are shown in Figure 10.

b. Graphite - The observations made of the Vitre-Graf coating on molded graphite substrates are as follows:

(1) Some delamination and tendency for delamination but generally far less than observed on mullite substrates.

(2) A wide variation in thickness on the same sample.

(3) Good adherence of the coating to the substrates.

(4) Occasional perpendicular cracking through a layer and subsequent flaking.

The micrographs of the coating on graphite samples exhibit better adherence to the substrate as well as between layers relative to mullite. Since samples of all substrates at each condition were processed together, the observed differences can not be ascribed to processing conditions. Figure 11 are micrographs showing typical examples of the above observations. Resin concentration did not seem to have an effect on coating quality but those samples having fewer layers seemed to have fewer defects.

c. Graphite - The characteristics of Vitre-Graf coating on fine-grained graphite substrates are given in the following observation:

(1) Delamination of the last coating layer and some tendency toward delamination between layers exists on some samples much like that observed on mullite substrates.

(2) Adherence at the interface is good. Figure 12 shows an example of these observations. No clear trends were observed relative to concentration or number of layers.

(3) The fine pore structure of the substrate does not allow deep penetration of the coating into the subsurface pores.

Much like the mullite samples, there exists evidence of inter-layer weakness that creates a tendency toward delamination.

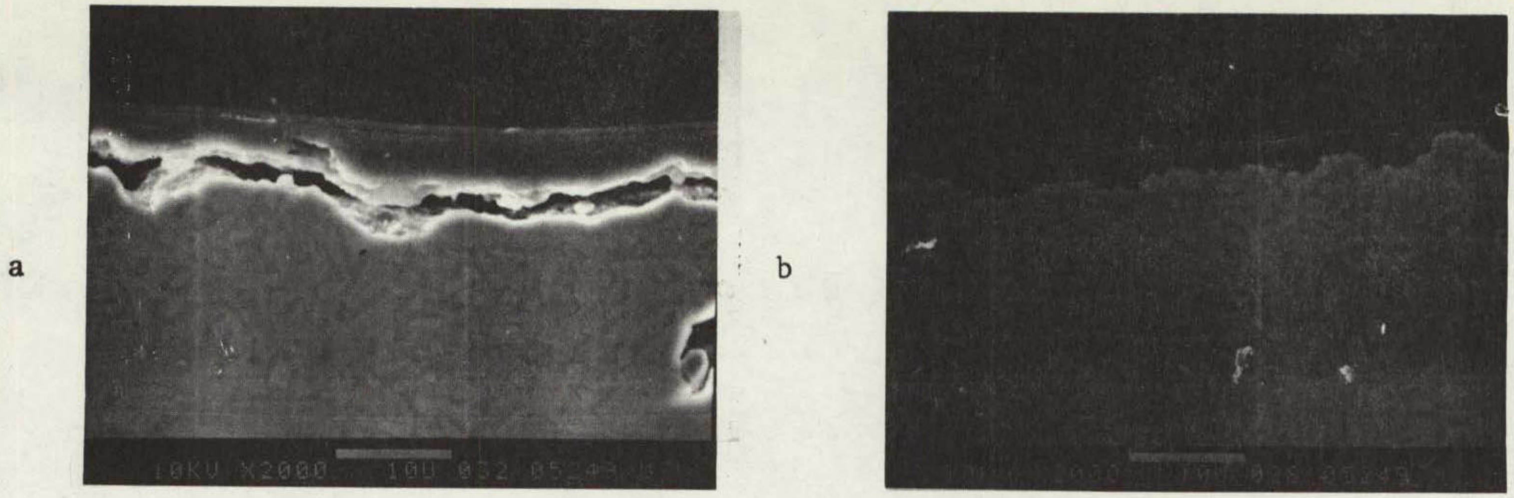


Fig. 10 Vitre-Graf coating on mullite substrates: (a) eight layers of light solution, and (b) two layers of heavy solution.

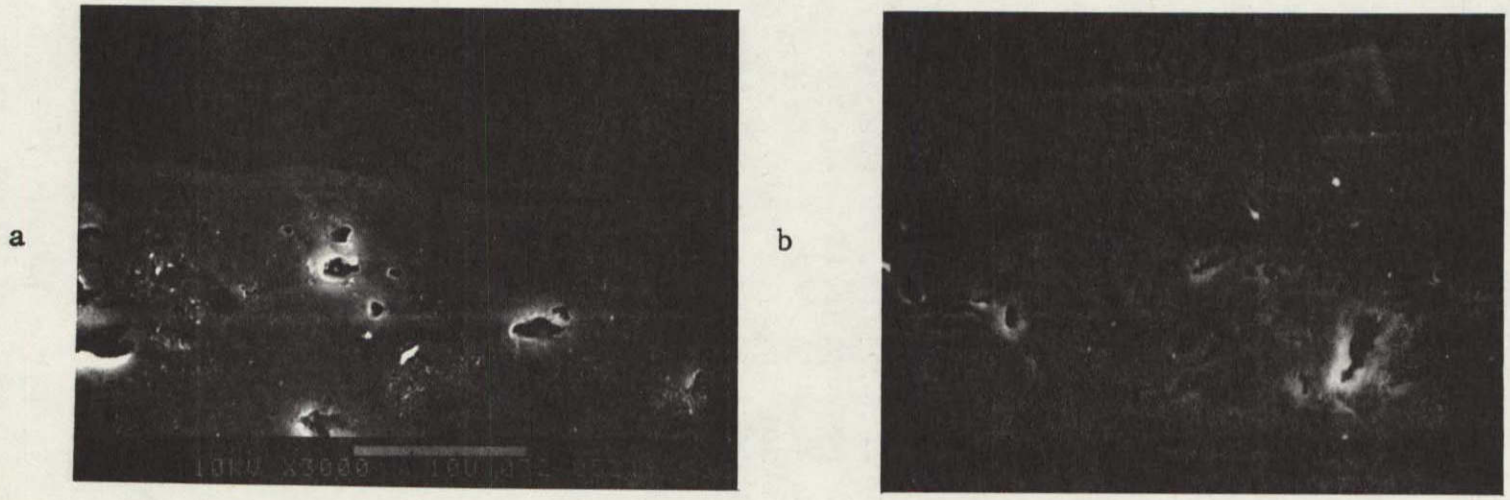


Fig. 11 Vitre-Graf coating on molded graphite substrates: (a) four layers of light solution, and (b) four layers of medium solution.

Nevertheless, except for peeling of the outer layer, the coating appears to be reasonably uniform and well adhered to the substrate.

d. Silica - The observations of the Vitre-Graf coating on slip-cast fused silica are the following:

(1) Because of the high open porosity of the substrate, neither multiple layers nor heavy solution built up a coating on the substrate.

(2) A great deal of cracking and incipient flaking is evident.

(3) As a consequence of an excessively rough surface and high open porosity, the coating was not able to fill the low spots in the substrate and the surface remained rough and irregular.

A serious problem to the integrity of the coating on silica results from the unfavorable thermal expansion difference between them. Upon cooling from cure temperature, the coating is placed in tension and perpendicular cracking occurs. The light solution with many layers was superior to the heavy solution probably because each successive layer was able to fill and heal some of the cracking that occurred on the previous layer. The above observations can be seen in the micrographs in Fig. 13.

4. Thickness Measurements

The weight gain and thickness, both measured and calculated, are presented in Table III. These data provide a great deal of understanding to the relationship between coating thickness and the interrelationship between concentration of solution and number of coating layers. The weight gain and thickness increase with an increase in concentration of the solution but not in proportion to their relative concentration. The higher viscosity of the heavier solutions results in a greater pickup of material when dipped; thus, the heavier concentrations have heavier and thicker coatings than expected solely from concentration increase.

The weight gain and thickness relative to the number of coating layers is also not linear; however, in this case, an increase in number of coating layers results in a decrease in weight gain and thickness for each successive layer. The data suggest in every case that the first coating and maybe the second as well gain the most weight. This effect is particularly pronounced in the more porous graphite and least pronounced in mullite, the least porous material. These results are indicative of the relative amount of solution that enters pores in the initial dipping. Apparently, after the pores are filled there is considerably less pickup of solution in succeeding layers. This effect is apparent also in a comparison of measured thickness relative to calculated thickness based on weight gain. For silica which is a very porous material, the average ratio is 0.35; the next most porous material is graphite which had an average ratio of 0.76. The fine-grained graphite had a ratio of 0.86 and mullite which has few interconnected

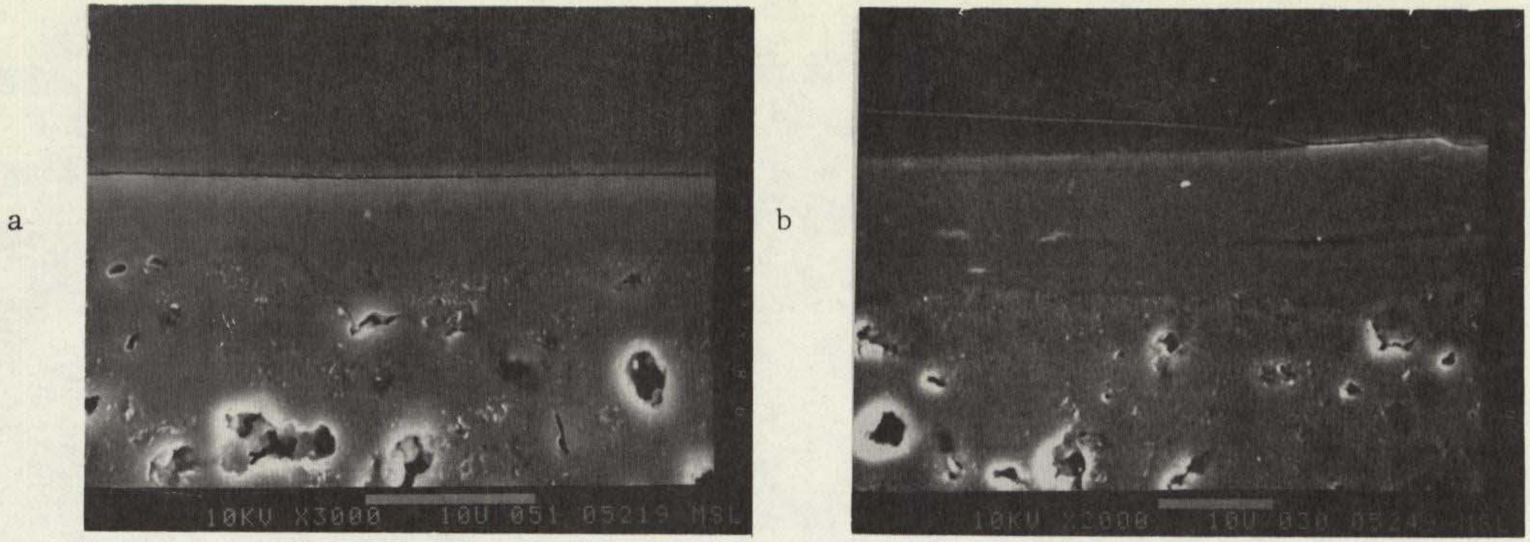


Fig. 12 Vitre-Graf coating on fine-grained graphite substrates: (a) six layers of light solution, and (b) four layers of heavy solution.

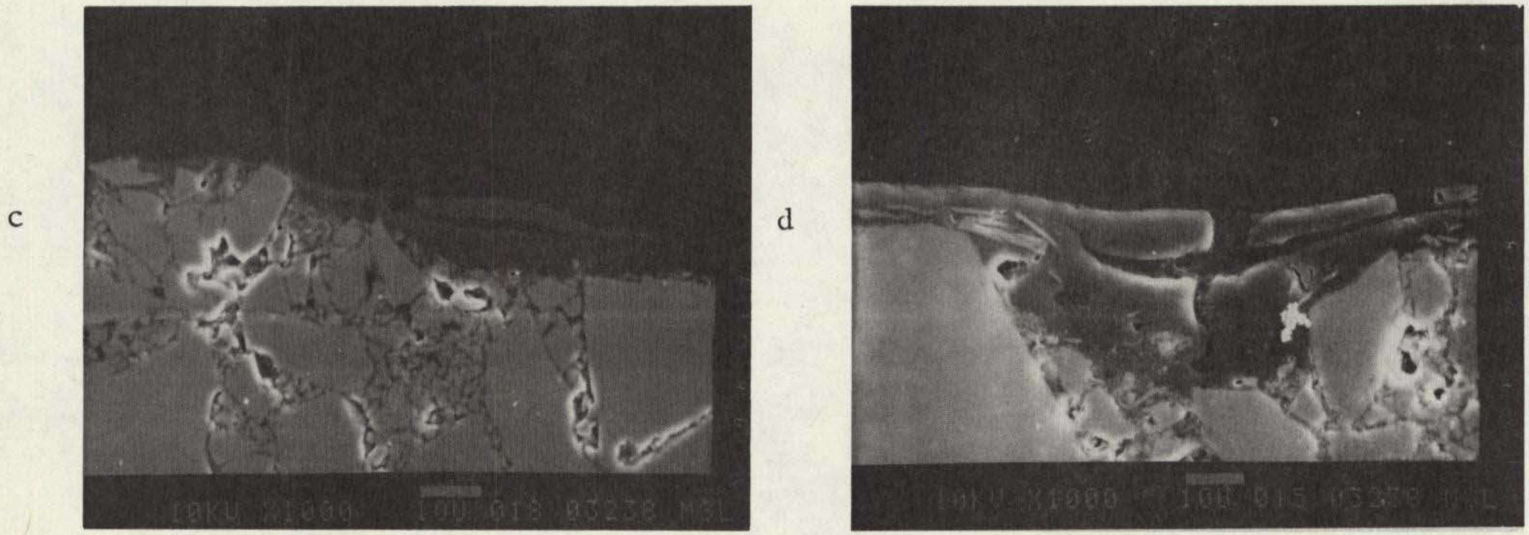


Fig. 13 Vitre-Graf coating on slip-cast fused silica: (a) eight layers of light solution, and (b) four layers of heavy solution.

Table III Average Weight Gain and Coating Thickness for Test Series III

		150 Solution			250 Solution			350 Solution		
		3154	3156	3158	3253	3254	3255	3352	3353	3354
Graphite (ave. 3 samples)	Wt. Gain (mg)	14.0	20.4	24.9	26.6	22.2	31.0	26.6	37.1	41.4
	Calc Thk.* (um)	4.4	6.4	7.6	8.4	7.0	9.8	8.3	11.7	13.0
	Meas Thk. (um)	3.0	3.2	5.2	6.5	7.8	8.1	6.5	9.1	10.0
Mullite (ave. 3 samples)	Wt. Gain (mg)	8.9	12.0	20.3	20.3	17.6	21.0	18.2	31.2	37.0
	Calc Thk.* (um)	2.3	3.2	5.4	5.4	4.7	7.4	4.8	8.3	9.9
	Meas Thk. (um)	2.1	3.6	4.8	5.2	4.5	6.8	4.3	6.7	9.3
Poco (1 sample)	Wt. Gain (mg)	14.4	18.3	29.2	22.8	23.9	31.3	21.8	32.2	27.2
	Calc Thk.* (um)	3.4	4.4	7.0	5.4	5.7	7.5	5.2	7.7	6.6
	Meas Thk. (um)	2.7	3.3	4.6	4.2	6.1	6.6	6.0	5.5	6.2
Silica (ave. 3 samples)	Wt. Gain (mg)			43.7			43.9			66.7
	Calc Thk.* (um)			17.0			17.1			26.0
	Meas Thk. (um)			6.2			6.1			8.3

* Thickness calculated from weight gain and surface area of each specimen.

pores had a ratio of 0.91.

Silica did not reveal the behavior previously noted between thickness and weight gain with solution concentration but rather the converse. In this case it is postulated that the volume of pores rather than viscosity of the solution controlled the amount of solution pick-up. Moreover, the lower viscosity solution more easily entered the pore spaces and undoubtedly offset the effect of greater surface pick-up due to viscosity.

On the basis of optimizing coating thickness relative to cost, it is apparent that the greatest economy can be gained with a few coats at heavy concentration.

5. Surface Chemical Analysis

The mass spectra of all samples were identical with those obtained in Test Series I for like substrate materials. The high alkali signals in Test Series II were not observed and substantiates the supposition that they were a consequence of peculiarities in that series and not characteristic of the material. In no case were there found any transition metals and only in the mullite was there found copper as a heavy metal (that is greater than mass 40).

The mass spectra of the silica sample is presented in Figure 14. This spectra shows the presence of sodium, aluminum, potassium and calcium in the 20-50 ppm range and also copper (mass 63, 65) as does mullite, but the intensity of this spectra is considerably lower than that for mullite (a glass-crystal mixture).

6. Sessile Drop Test Evaluation

Two samples each of graphite substrate and mullite substrate were evaluated by the Sessile Drop Test method * over a 40 minute melt period. In every case a silicon carbide reaction product is seen along the interface between substrate and silicon. For the samples having thicker coating, both mullite and graphite, there remains a layer of unreacted Vitre-Graf coating between the reaction product and substrate. Also, in each case there is evidence of silicon penetrating beneath the interface layer and reacting with the substrate. The silicon carbide crystals appear to be more perfect with sharp corners and flat faces on the graphite substrate relative to the mullite substrate probably because of a localized saturation of carbon in the silicon at the interface that is not possible to maintain on mullite substrates.

7. Conclusions

Several contradictory conclusions can be drawn from the

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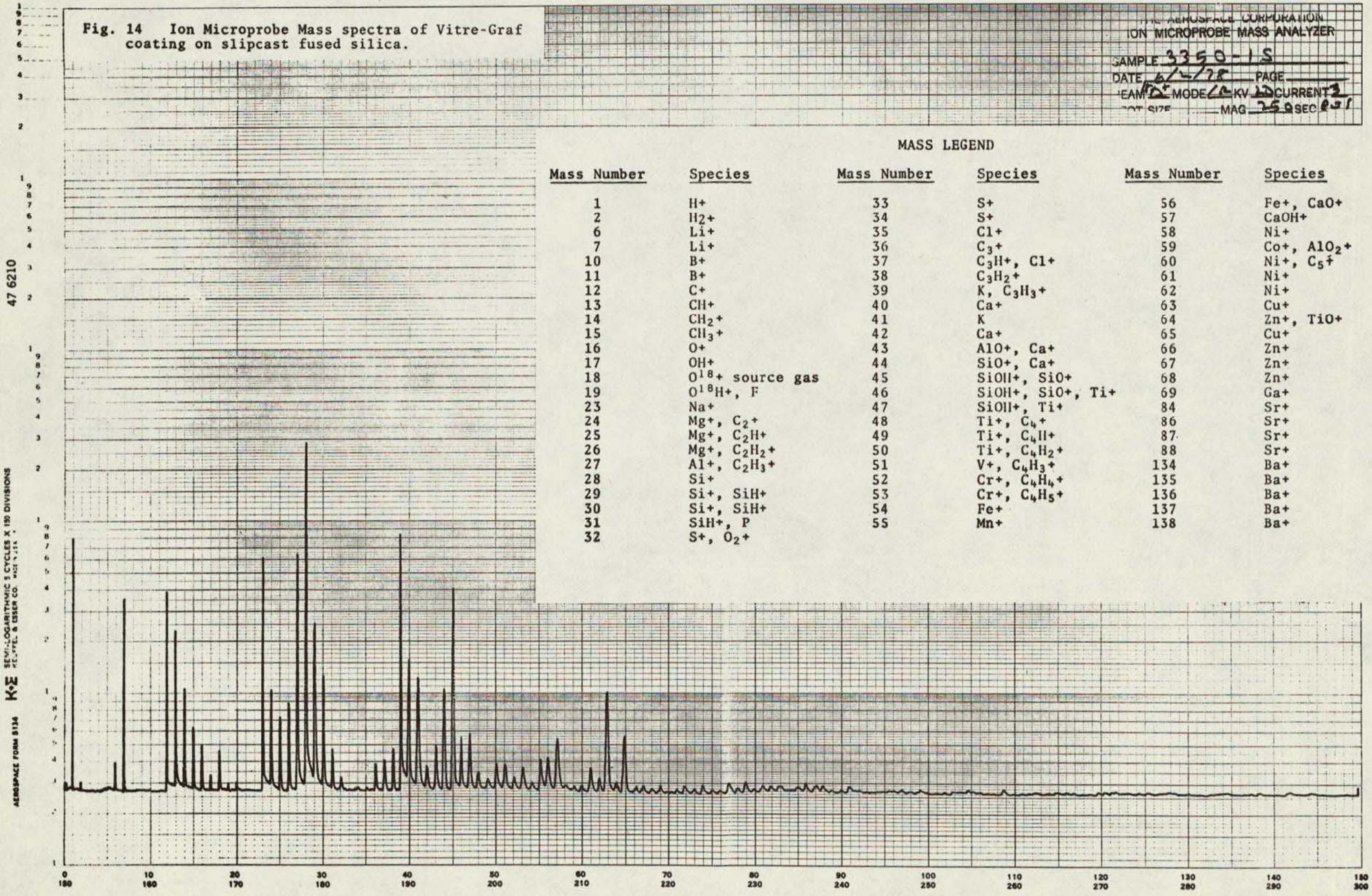
*Evaluation performed by Mr. Tim O'Donnell, JPL.

Fig. 14 Ion Microprobe Mass spectra of Vitre-Graf coating on slipcast fused silica.



MASS LEGEND

Mass Number	Species	Mass Number	Species	Mass Number	Species
1	H^+	33	S^+	56	Fe^+, CaO^+
2	H_2^+	34	S^+	57	$CaOH^+$
6	Li^+	35	Cl^+	58	Ni^+
7	Li^+	36	C_3^+	59	Co^+, AlO_2^+
10	B^+	37	C_3H^+, Cl^+	60	Ni^+, C_5^+
11	B^+	38	$C_3H_2^+$	61	Ni^+
12	C^+	39	K, $C_3H_3^+$	62	Ni^+
13	CH^+	40	Ca^+	63	Cu^+
14	CH_2^+	41	K	64	Zn^+, TiO^+
15	CH_3^+	42	Ca^+	65	Cu^+
16	O^+	43	AlO^+, Ca^+	66	Zn^+
17	OH^+	44	SiO^+, Ca^+	67	Zn^+
18	O^{18+} source gas	45	$SiOH^+$, SiO^+	68	Zn^+
19	$O^{18}H^+$, F	46	$SiOH^+$, SiO^+, Ti^+	69	Ga^+
23	Na^+	47	$SiOH^+$, Ti^+	84	Sr^+
24	Mg^+, C_2^+	48	Ti^+, C_4^+	86	Sr^+
25	Mg^+, C_2H^+	49	Ti^+, C_4H^+	87	Sr^+
26	Mg^+, $C_2H_2^+$	50	Ti^+, $C_4H_2^+$	88	Sr^+
27	Al^+, $C_2H_3^+$	51	V^+, $C_4H_3^+$	134	Ba^+
28	Si^+	52	Cr^+, $C_4H_4^+$	135	Ba^+
29	Si^+, SiH^+	53	Cr^+, $C_4H_5^+$	136	Ba^+
30	Si^+, SiH^+	54	Fe^+	137	Ba^+
31	SiH^+, P	55	Mn^+	138	Ba^+
32	S^+, O_2^+				

data generated in this test series. From visual and SEM observations, fewer coating layers appear to give the best results because of the lower concentration of defects. The thickness measurements strongly suggest that the heavy solution with few layers is best because it provides the most cost effective coating (relative to cost/unit thickness). However, from the Sessile Drop Test, the heavy solution with two coating layers was generally equivalent in appearance to the light solution with six coating layers and they both showed signs indicating a protective layer could form. Even with the heavy layer, it is apparent that the layer is breached, possibly through defects, and many coatings may be necessary in an attempt to heal, or at least minimize these defects. However, for the SOC application where contact time with molten silicon is measured in fractions of a minute, there may be insufficient time to breach even a thin coating.

The conclusion of this test series is that the heavy solution offers the most promise for both applications and the greatest cost effectiveness. Whereas possibly only two coating layers may be required for the SOC application, multiple layers appear to be required to provide a protective coating for the container ware application.

D. Test Series IV: Evaluation of Cure Temperature

1. Visual

The visual appearance of the test samples from this test series was superior to any previous series. Specific care was taken to assure that a minimal exposure to the ambient atmosphere occurred between coating runs. Either as a consequence of this precaution or because of the limited number of coating layers, there was a minimal amount of flaking on all samples. However, cratering, a defect that occurs with heavy solutions, appeared on every sample. No differences were observed on any substrate as a consequence of a 400°C differential in cure temperature among the samples.

In general, the samples appeared to be covered well with coating and, except for the cratering effect, they appeared similar to the coating expected from the baseline process that uses a medium solution and five coating layers.

2. Adherence

The adherence test results were as expected, that is, no loss of weight by flaking or delamination occurred on any sample.

3. SEM Observations

Although both visual appearance and adherence showed marked improvement over previous test results, the scanning electron micrographs did not show as great an improvement as might otherwise be expected. Many defects were observed similar to those seen on prior test samples. Conspicuously missing, however, is the tendency for delamination seen previously on all substrate materials. There was no discernible difference between the low and high cure temperatures for any of the substrates. Excellent interface bonding was apparent on all graphite samples whereas some interface de-bonding occurred with mullite substrates. Figure 15a shows a typically good segment of the coating on mullite as well as good pore penetration. All mullite samples revealed large regions of similarly well defined, well adhering coatings; other regions showed interface de-bonding such as in Figure 15b, or layer steps such as shown in Figure 15c. These steps appeared in both mullite and graphite samples, an example of the latter is shown in Figure 15d, and they occur as one of several defects that are associated with the cratering effect. In general, the surface defects caused by cratering was less disruptive on graphite substrates than on mullite.

4. Thickness Measurements

The average thickness measurements from this test series presented in Table IV closely matched the thickness from Test Series III samples with two coating layers of heavy solution (See Table III). Except for the fine grained graphite samples, thicknesses were about 25% greater in this series than Test Series III but this difference is not unexpected with heavy solutions because the amount of pick-up during the dipping process is strongly dependent upon technique. The relationship between the measured thickness and calculated thickness from all samples deviated from that of Test Series III by less than 3%. Thus this behavior for the different substrate materials appears to be consistent.

5. Surface Chemical Analysis

Essentially no difference was observed between the surface analysis of the samples in this series and those in previous series. No relationship appeared as a function of cure temperature and no new contaminant appeared. There were variations in signal intensities between samples but these appeared to be random and did not correlate with samples in the same cure cycle.

6. Silicon Dip Evaluation

Samples cured at 1050, 1150 and 1250°C for each substrate were selected for evaluation by dipping in molten silicon, followed by a 0.08 cm/sec withdrawal rate and characterized by its wettability and the qualities of the resulting silicon film.* All substrates were wetted by silicon but the silica substrate did not wet completely; the resulting silicon film incompletely covered the surface of the silica substrate and that which did adhere checked upon cooling because of the thermal expansion mismatch between them. An example of this behavior is shown in Figure 16a.

The mullite samples coated well but the silicon film was thinner than normally experienced. This behavior was predicatable because the present samples were coated on both sides rather than just one side, thereby creating a difference in thermal response

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*Evaluation performed by Dr. J. David Zook, Honeywell Corp.

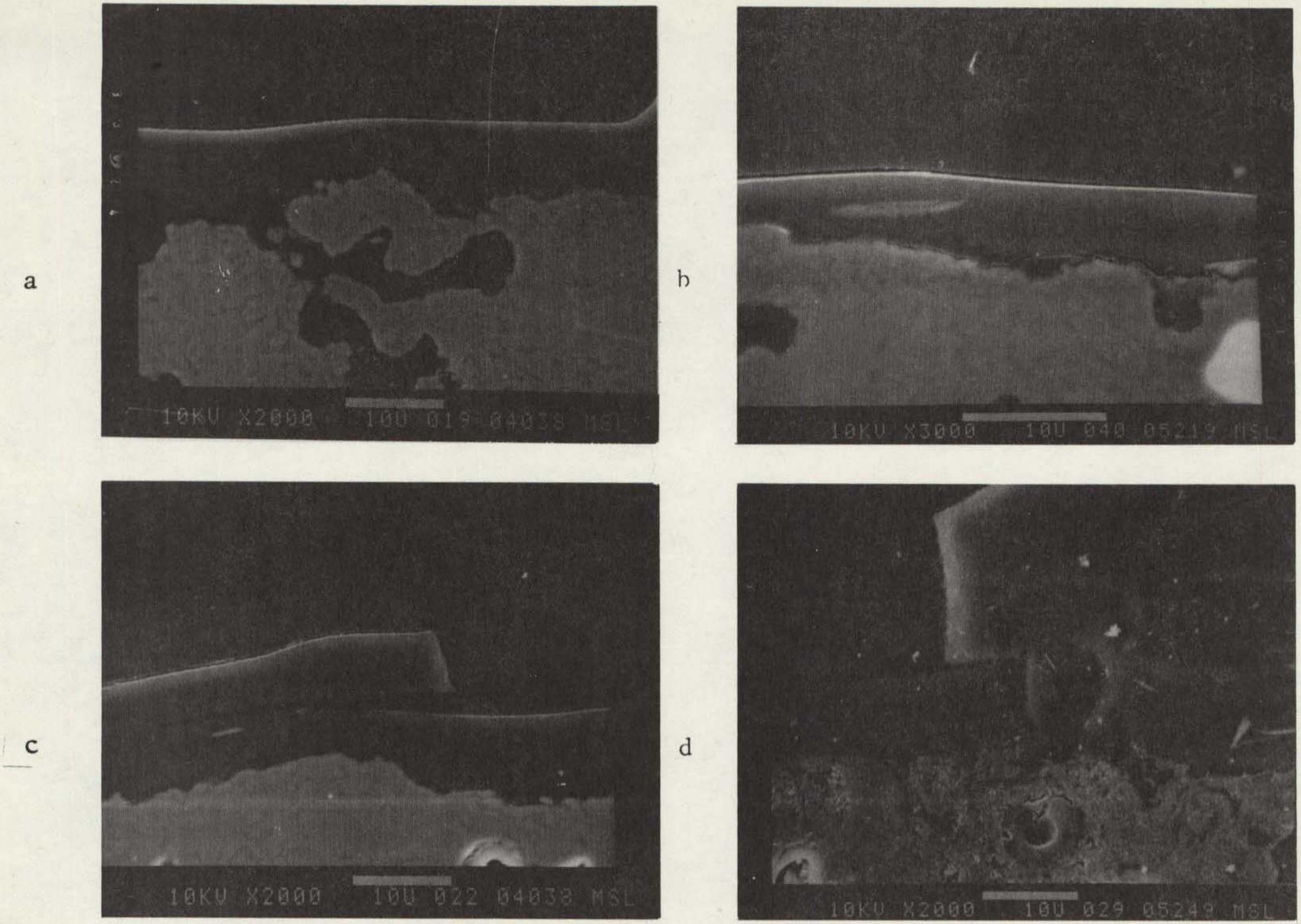


Fig. 15 Vitre-Graf coating on: (a) mullite substrate cured at 1250°C, (b) mullite substrate cured at 1150°C, (c) mullite substrate cured at 1250°C, and (d) molded graphite substrate cured at 1250°C.

Table IV Test Series IV: Weight Gain and Coating Thickness

CURE TEMPERATURE		850°C	950°C	1050°C	1150°C	**1250°C**
Molded Graphite (3 Samples)	Wt. Gain (mg)	28.5	32.5	32.0	21.1	**52.1**
	Calc. Thk. (um)	9.1	10.3	10.2	6.7	**16.5**
	Meas. Thk. (um)	6.7	7.3	7.2	6.0	**11.8**
Mullite (3 Samples)	Wt. Gain (mg)	21.2	31.1	37.4	26.4	**50.7**
	Calc. Thk. (um)	5.7	8.4	10.1	7.1	**13.7**
	Meas. Thk. (um)	5.6	7.8	9.3	6.8	**11.8**
Fine-gl. Graphite (1 Samples)	Wt. Gain (mg)	18.0	19.9	32.0	7.7	**54.1**
	Calc. Thk. (um)	4.3	4.8	7.7	1.8	**13.0**
	Meas. Thk. (um)	4.1	4.5	5.9	2.1	**11.3**
S-C Silica (1 Sample)	Wt. Gain (mg)	60.1	64.0	41.6	48.7	**72.9**
	Calc. Thk. (um)	23.5	25.0	16.2	19.0	**28.5**
	Meas. Thk. (um)	7.9	6.2	5.1	7.2	**9.4**

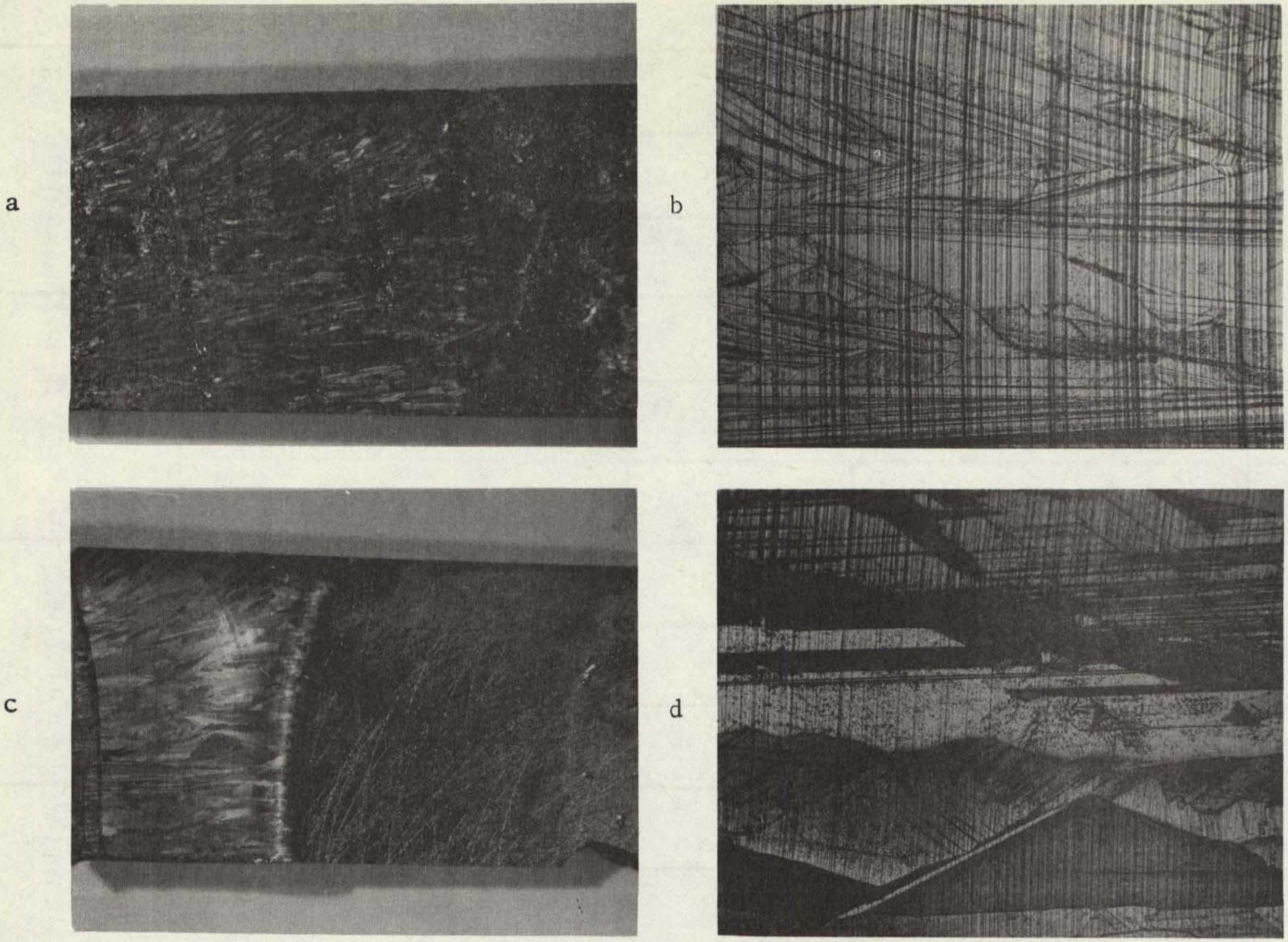


Fig. 16 Silicon dip evaluation: (a) silica substrate partially wetted with silica film; (b) grain structure of silicon film on mullite substrate coated with Vitre-Graf and cured at $1050^{\circ}C$; (c) fine-grained graphite substrate cured at $1150^{\circ}C$ with heavy silicon film; (d) grain structure of silicon film on molded graphite substrate coated with Vitre-Graf and cured at $1150^{\circ}C$ (a&c: 4x; b & d: 40x)

and resulting in a thinner silicon film. The films completely coated the dipped sample but the resulting silicon grains were finer than normally experienced. The sample cured at 1050°C produced possibly a slightly coarser grain structure shown in Fig. 16b. Based on previous experience, all samples would have expected to produce solar cell quality silicon films. Of the three samples evaluated, the 1250°C cured sample gave the poorest results with very little difference between the 1150°C and 1050°C samples except for the slightly coarser grain size of the 1050°C sample.

Both sets of graphite samples gave comparably good results characterized by thick complete films. The thickness of the silicon film was considerably greater than normally obtained and the grain size was coarser than normal. These results inferred the possibility of a faster dip process for carbonaceous substrates. There was little difference in wettability among the samples but the 1150°C samples produced a decisively coarser grain structure in the silicon film. A dipped sample and the grain structure are shown in Figs. 16c and d for 1150°C samples. Because of the thermal conductivity of the graphite, no difference was expected between a one or two sided dip sample.

7. Conclusions

Of the various evaluations performed, none provided a decisive preference as a function of cure temperature. Only the silicon dip evaluation suggested an advantage based on silicon grain size, 1150°C for graphites, 1050°C for mullite. However, because the Vitre-Graf coating on the 1150°C sample was about 2/3rds the thickness of the 1050°C, the decision was made without further substantiation that 1150°C would have optimized performance had all parameters been equal.

E. Test Series V: Evaluation of Alternate Gas Atmospheres

1. Visual

The test samples showed no difference between an argon atmosphere and nitrogen atmosphere during the cure cycle and these samples could not be easily discerned from those cured in vacuum in Test Series IV. A slightly greater tendency toward flaking was observed on all samples in this series relative to series IV but insignificant relative to the first three test series. Cratering also was observed but the amount was considerably less than Test Series IV because greater care was taken to prevent the solution from building-up at the lower edges during the dipping operation.

From visual appearance there is no evidence to suggest that the coating material could not be cured successfully in a neutral atmosphere as well as in vacuum. However, prior experience with neutral atmosphere curing resulted in hydrocarbon deposition on the surfaces of the ware. In this set of experiments the ratio of coating surface to furnace size is possibly 1/100 th of prior experience and redeposition, if it occurred would be unnoticed by visual observations.

2. Adherence

The adherence test was also very similar to Test Series IV in that no measured loss of weight occurred by flaking; however, contrary to the previous series some flakes were observed on the adhesive tape of nearly every sample but in no case did the weight exceed 0.1 mg., our limit of sensitivity. The samples that were coated with resin #2 and cured in nitrogen showed no evidence of flaking or delamination in the adherence test. However, the solution was light concentration (150 g/1) and the previous experiments with light solutions in Test Series III had also showed a lack of flakiness, thus, these results can not be attributed unequivocally to the particular resin solution.

3. SEM Observations

The scanning electron micrographs of Test Series V was very similar to those of Test Series IV. Delamination was no longer present but interface de-bonding and defects caused by cratering were apparent in all mullite samples. The graphite samples showed generally excellent interface adherence but also showed evidence of the cratering defects. Elimination of the cratering suggests the possibility of a good quality coating for both substrate materials.

The SEM photos of resin #2 do not have crater defects because this resin solution was a light concentration but interface de-bonding was commonly seen on mullite substrates. The light solution had penetrated deeply within the pores, more so than previously observed even with light solutions, but this penetration did not prevent separation at the interface.

4. Thickness Measurements

The average weight gain and thickness, calculated and measured are presented in Table V. The weight gain and thickness of these samples are considerably greater than those previously measured. This difference is attributed to a change in dipping technique which was directed toward an elimination of the cratering effect. Craters tend to appear along the edge and lower portions of the sample apparently as a consequence of the solution flowing to these locations immediately upon withdrawing the part from the dipping vat. The problem is especially pronounced with heavy solutions, not only because there is greater solution pick-up but also because the greater amount means a slower drying and a longer time in which the solution will flow. The changed technique slowly withdrew the sample from the solution so that the drying interface was slightly above the solution level as withdrawn. This technique did, in fact reduce flowing but the much prolonged time in the solution resulted in considerably more pore penetration, more weight pick-up and consequently greater thickness.

The average ratio of measured to calculated thickness, MT/CT in this series for mullite is 0.82 in contrast to a value of 0.91

Table V Test Series V: Average Weight Gain and Coating Thickness.

		RESIN #1		RESIN #2
ATMOSPHERE		ARGON	NITROGEN	NITROGEN
Molded Graphite (3 Samples)	Wt. Gain (mg)	30.1	38.4	49.3
	Calc. Thk. (um)	9.5	12.6	15.6
	Meas. Thk. (um)	6.5	8.8	9.2
Mullite (3 Samples)	Wt. Gain (mg)	45.4	35.9	47.1
	Calc. Thk. (um)	12.1	9.6	12.6
	Meas. Thk. (um)	10.1	7.8	9.8

in Test Series III and 0.92 in Test Series IV. For graphite the average ratio was 0.69 in contrast with 0.76 in Test Series III and 0.74 in Test Series IV. The ratio was even more extreme for the light solution of resin #2 where the mullite ratio was 0.78 and graphite ratio was 0.59. These contrasting values strongly reflect the extent of pore penetration that can occur as a consequence of a slow dip process, especially in the light solution that most easily penetrates the fine pore structure of these materials.

5. Surface Chemical Analysis

The presence of argon or nitrogen during the cure cycle had no effect on the impurities or their concentration in the coating material. Furthermore, no evidence of hydrocarbon redeposition was seen as a consequence of either argon or nitrogen atmosphere.

Resin #2 is a much more pure initial material than resin #1 used as baseline; nevertheless, no difference was observed in the mass spectra between them because the impurities observed in the coating originates primarily in the substrate.

6. Sessile Drop Test Evaluation

A single sample with a mullite substrate and cured in nitrogen was evaluated by the sessile drop test method for a 40 minute melt period. The silicon carbide reaction layer forms, apparently in the first minutes, and subsequently the carbide crystals dissolve in the molten silicon as evidenced by the rounded corners as seen in the cross-section of Fig. 17a. Molten silicon has penetrated deeply into the pore structure and silicon carbide is seen along the walls of the pores. The broken line of inclusions in the silicon that appear to lead away from the large surface pore is evidence that a silicon mullite reaction has occured. In a second area, shown in Figure 17b, the extent of the silicon mullite reaction can be more clearly seen. The primary reaction is a reduction of metal oxides by the silicon followed by metal dissolution in the molten silicon and inclusion precipitation at regions of saturation upon cooling.

This test confirmed the observations seen previously where by the Vitre-Graf coating on mullite does not provide a protective barrier when in contact with molten silicon for times greater than possibly several minutes. Although the particular sample had a relatively thick coating (∿ 8.0 μm based on the calculated thickness and coating ratio), no residual layer of the Vitre-Graf coating between the reaction layer and substrate was seen in this sample as had been seen in thick coated samples of previous sessile drop tests. On the basis of a single sample, this difference could not be credited to the nitrogen atmosphere used in the curing process.

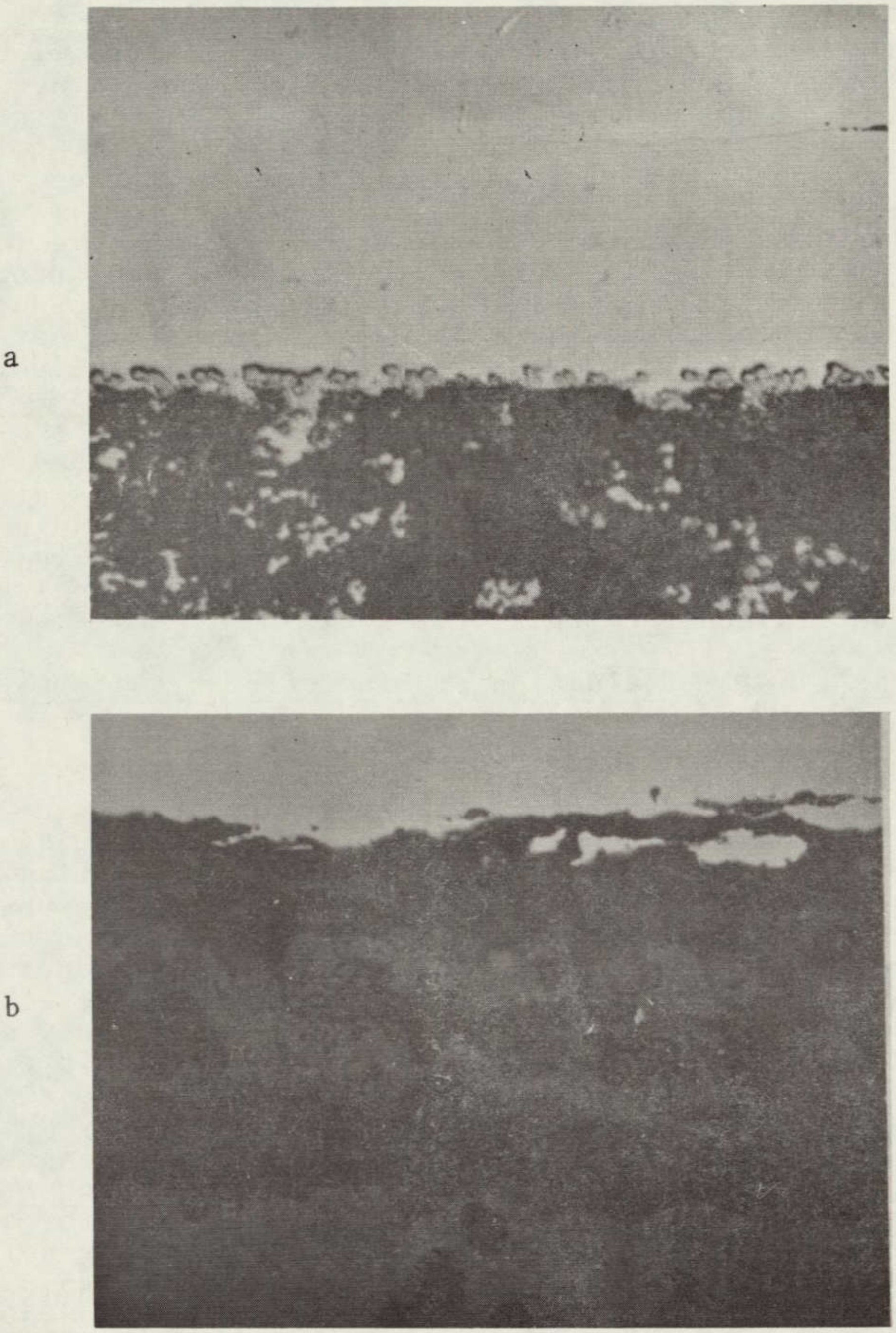


Fig. 17 Cross section of Sessile drop evaluation sample, (a) silicon (upper) has reacted with the Vitre-Graf coating to form silicon carbide at the interface with the mullite substrate, (b) the silicon (upper) has reacted with mullite (lower) to form a massive reaction layer (center). (a & b: 200x)

7. Conclusions

The results of Test Series V indicate that the use of argon or nitrogen at atmospheric pressure during the curing process is not discernibly detrimental to the performance of the Vitre-Graf coating. The coating in either case does not provide a protective layer on mullite for extended time exposure to molten silicon.

The depth of penetration of porous substrates by the resin solution was seen to be a function of the time the substrate was immersed and the fluidity of the solution. Deeper penetration of the coating material into the mullite pores did not effect a hinderance to molten silicon penetration into the pores when in contact for a 40 minute time period.

The reaction of molten silicon with Vitre-Graf coated mullite is an initial formation of silicon carbide crystals at the interface followed by a dissolution of these crystals and a reduction of mullite. The contribution of crater defects to the molten silicon breaching of the silicon carbide reaction layer could not be determined from this test series.

F. Test Series VI: Evaluation of Discretionary Alternatives

1. Visual

The samples in this test series were exposed to a wide range of variables which included one, two and five coating layers, three cure temperatures, one new substrate material and an alteration of the pore structure of the carbonaceous substrates. The appearance among them differed widely because of the differences in processing. Nevertheless, several general observations can be made. Four mullite sample sets were evaluated. Of the two sets cured at 1150°C, those having only one coat did not seem to have a complete coating because of a blotchy appearance, whereas the samples receiving two coating layers were covered completely and looked as good as any mullite samples to date in the program. The sample sets receiving both one and two coating layers and cured at 1450°C were even more blotchy than the one layer sample at 1150°C. However, the set that was scheduled for two layers at 1450°C mistakenly received a third coating layer at 1150°C. The final result was a good appearance nearly comparable to the two layer samples cured at 1150°C. There was no flaking, delamination or cratering on these samples and they appeared to be completely free of defects.

The graphite samples that received one coating layer appeared to have no coating whether they were cured at 1150°C, or 1450°C. However, the samples that were treated with a filler material showed evidence of being coated but the coating had a blotchy appearance. The graphite samples receiving two coating layers, both 1150°C and 1450°C cure temperatures, showed a slight evidence of a blotchy layer, but less complete than the samples with one coat and a filler.

The graphite samples that received 5 coating layers and cured at 1050°C (nominally baseline process) had an obsidian-like luster. Those 5 layer samples that were cured at 1150°C, including one set that was treated with a filler, had a good, uniform coating but lacked the glass-like luster.

Two sets of carbon-carbon composites were introduced in this test series. The one set receiving one coating layer and cured at 1450°C revealed a slight coating appearance but this coating could be removed by brisk rubbing across the surface. The samples receiving 5 coating layers and cured at 1450°C had a dull glossy luster and the coating could not be abraded away by rubbing.

In this entire test series no samples showed a flakiness or delamination tendency. (The flakiness described for the C-C composite required a physical abrasion to effect.) However, all graphite samples except those receiving only one coating layer showed cratering inspite of attempts to eliminate this defect. While dipping, the lower portion of the sample was kept in contact with the surface of the resin solution for several seconds until sufficient drying had occurred on the sample. The technique minimized the extent of cratering but did not eliminate it. Neither the mullite nor the C-C composites showed this defect.

2. Adherence

The adherence Test showed no weight loss nor evidence of delamination. The results were the best thus far in the program.

3. SEM Observations

The micrographs of mullite cured at 1150°C were similar to others previously presented. The thin coating from one layer did not appear to completely coat over the rough surface of the mullite substrate and correlates with the visual observation that had suggested an incomplete coating layer. The sample with two coating layers had coated well but had debonded from the substrate as had all previous mullite samples.

The mullite samples cured at 1450°C had a completely different surface characteristic than any previously seen. On the sample receiving only one layer, no coating was seen on the surface but some Vitre-Graf was seen occasionally in surface pores and usually in pores below the surface. The surface itself was rough and appeared to be chemically attacked as seen in Fig. 18a. The micrograph of the mullite sample that received two coating layers, cured at 1450°C and mistakenly given a third coating layer and cured at 1150°C is shown in Figure 18b. The chemically attacked surface is seen as in Fig. 18a but also seen is a very thin Vitre-Graf layer that has flowed in and around the surface particles that appear to be residue from the chemical attack. The interpretation of these data and correlation with visual observations strongly suggest that the mullite had been chemically attacked by

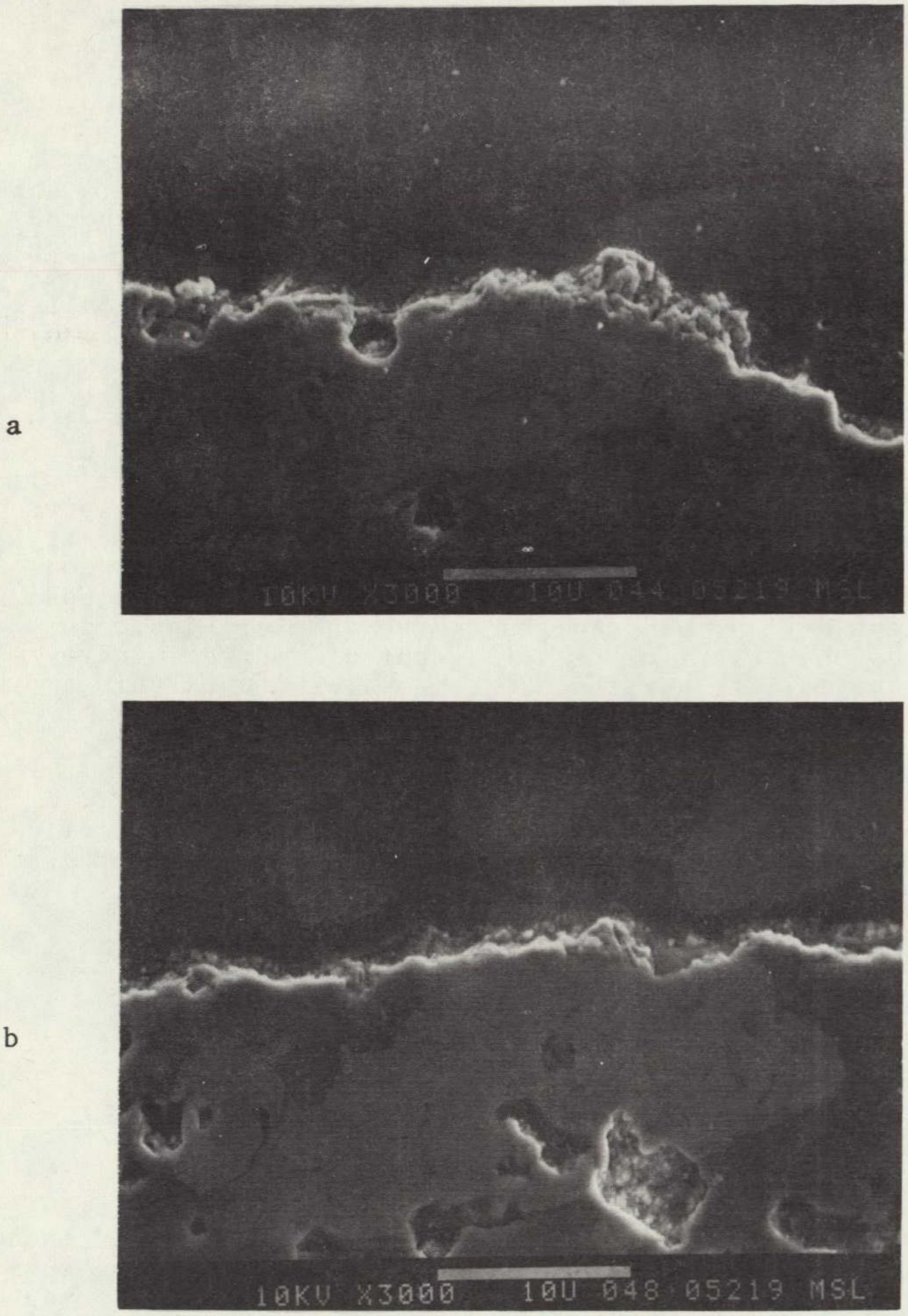


Fig. 18 Vitre-Graf coating on mullite substrates and cured at 1450^{o}C: (a) one coating layer; (b) two coating layers followed by one layer cured at 1150^{o}C

the Vitre-Graf coating presumably by reduction of the oxides and by oxidation of the carbon. The blotchy visual appearance of these samples is presumed to be a consequence of the loss of the carbon coating through oxidation.

Scanning electron microscopy was conducted on neither the graphite nor composite samples.

4. Thickness Measurements

The average weight gain and thickness are presented in Table VI. For the mullite samples cured at 1150°C, the results are generally consistent with previous test series. However, the samples cured at 1450°C showed a loss in weight rather than a gain in weight. From the blotchy appearance of these samples, a chemical reduction of the mullite is postulated as the cause for this weight loss. Moreover, the sample mistakenly receiving a third coating layer and cured at 1150°C gained weight of an amount again consistent with previous data.

The results for graphite samples are self-consistent at each temperature of cure but not consistent between the two cure temperatures. These values tend to be lower than data of previous test series at 1150°C and higher than previous data at 1450°C. No other explanation besides possibly an inconsistency in dipping technique is offered for this behavior. Otherwise the thickness measurements are much as expected. For the graphite with filler particles added, a large weight gain is experienced with the first coating layer but the weight gain for subsequent layers appear to be equivalent with those samples without filler. The actual coating thickness in these samples are not expected to be represented by the calculated thickness values because of pore penetration.

The carbon-carbon composites reveal the role of the filler material more clearly. The gain in weight in the sample with one layer without the filler exceeded the gain in weight of the sample first coating layer including filler material was less than one-half that of the sample without filler. The very high porosity of this material absorbed a considerable amount of solution in both cases, but when filler particles had been added with the intent of filling surface pores, then had inhibited the penetration of the solution into the interior pore structure. The actual thickness (not measured) of these samples are not expected to be represented by the calculated value because much of the solution has penetrated below the surface of the sample.

5. Surface Chemical Analysis

The ion microprobe analysis was conducted only on the mullite samples. The results correlated well with both visual and SEM observations. The surface analysis of the sample receiving one coating layer and cured at 1150°C was very similar to the analysis previously obtained except for an approximate one order of magnitude increase for both silicon and aluminum and

Table VI Test Series VI: Average Weight Gain and Thickness

			1150°C			1450°C		
		Layers	1	2	5	1	2**	5
Mullite (Ave. 3 Samples)		Wt. Gain (mg)	7.5	31.4		-48.2	-75.8 (12.3)	
		Calc Thk. (um)	2.0	8.5		--	-- (3.3)	
		Meas. Thk. (um)	1.6	7.6			(1.0)	
Graphite (Ave. 3 Samples)	W/O Filler	Wt. Gain (mg)	18.0	41.9	110.7 *	55.5	96.2	131.6
		Calc. Thk. (um)	2.1	5.2	13.7 *	6.7	10.0	16.3
	W/Filler	Wt. Gain (mg)			102.9			145.7
		Calc. Thk. (um)			11.2			15.9
C-C Composite (Ave. 3 Samples)	W/O Filler	Wt. Gain (mg)			632.7			
		Calc. Thk. (um)			65.5			
	W/Filler							468.3
								47.9

* 1050°C

** Parenthesis refers to 3rd. layer at 1150°C.

a strongly increased intensity of their oxides. Additionally, titanium and its oxide are strongly present whereas this element had not been observed in previous analysis. The mass spectra of this sample is presented in Fig. 19. The most likely explanation for these changes in mass spectra arise from the incomplete surface covering that is afforded by a single coating layer. The ion beam that sputters material from the surface during the analysis will sputter not only the carbon layer but also the exposed substrate as well. Thus, the observed changes are as expected and correlate well with the SEM observations that showed an incomplete coating layer.

The sample receiving two coating layers had a normal spectra similar to those obtained in previous test series. These results again correlate with the SEM micrographs that showed normal coverage for two coating layers.

The sample receiving one coating layer and cured at 1450°C resulted in a nearly unintelligible mass spectra that arose from surface charging effects. This effect appears on insulating material whenever their is insufficient conduction across the surface to dissipate the imposed ion current. The SEM micrographs had revelaed only isolated coating in pores and again the results correlated.

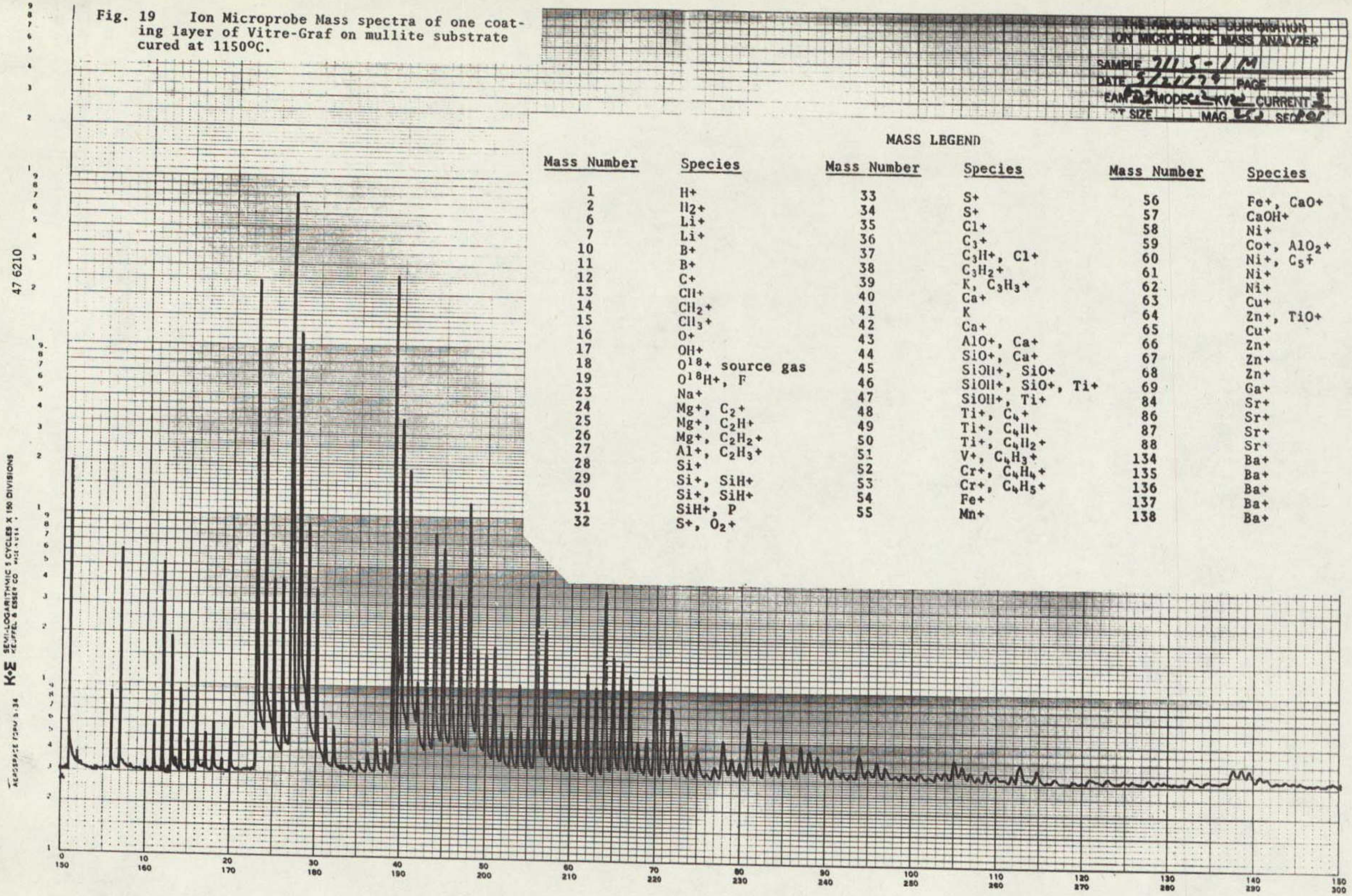
The sample that received two coating layers, cured at 1450°C had mistakenly received a third coating layer which was cured at 1150°C. From SEM micrographs the resulting coating was similar to the sample receiving one layer and cured at 1150°C with the exception that the sample surface had been roughened by chemical attack. The resulting mass spectra shown in Fig. 20 is also similar to that of Fig. 19 with the exception of the intensity of the signals. The weaker signal intensity and the appearance of charge spikes are indicative of maginal surface conductivity in this coating layer.

6. Silicon - Graphite Reaction

In an independent experimental effort complementary to a portion of this program a graphite crucible coated with Vitre-Graf was used to melt silicon at 20 minute melt cycles with a total melt time of about 10 hrs.; a second crucible experienced a total melt time of about 20 hrs. At the conclusion of these melting runs the crucibles were cut in half and the cross-section of the interface between the silicon and graphite was polished and examined microscopically. The Vitre-Graf coating had been applied by using the baseline process except that in both cases eight coating layers rather than five were applied. The coatings were free of visual defects and had appeared to be able to serve as a protective layer to the graphite crucibles.

Examination of the micrographs from both of the crucibles showed that a silicon carbide layer had formed along the interface and had retained the layer morphology of the Vitre-Graf coating. This layer, appearing to be protective was seen at various places along the cross-section of the crucible experiencing the shorter

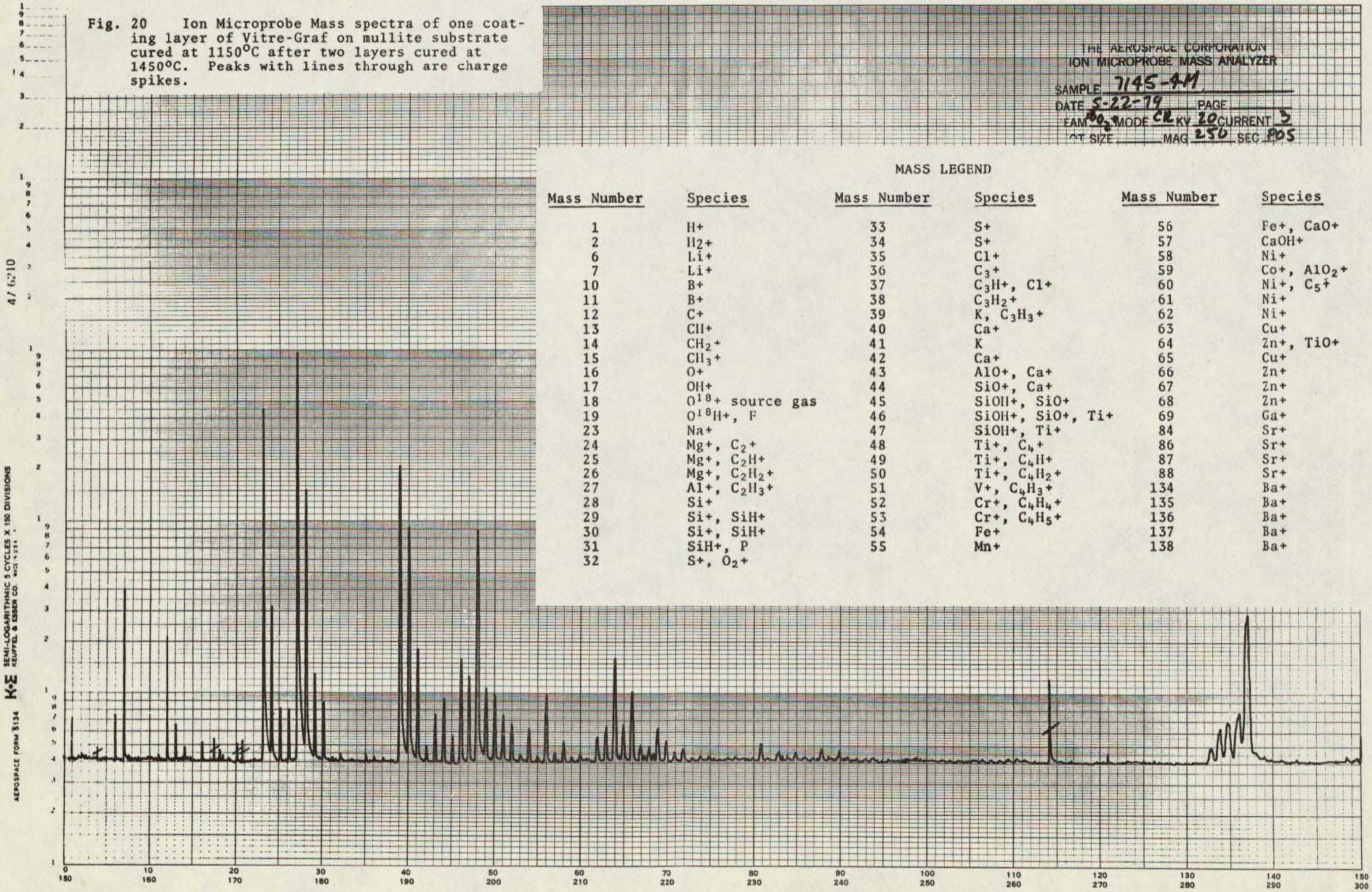
Fig. 19 Ion Microprobe Mass spectra of one coating layer of Vitre-Graf on mullite substrate cured at 1150°C.



MASS LEGEND

Mass Number	Species	Mass Number	Species	Mass Number	Species
1	H+	33	S+	56	Fe+, CaO+
2	H_2+	34	S+	57	CaOH+
6	Li+	35	Cl+	58	Ni+
7	Li+	36	C_3+	59	Co+, AlO_2+
10	B+	37	C_3H+, Cl+	60	Ni+, C_5+
11	B+	38	C_3H_2+	61	Ni+
12	C+	39	K, C_3H_3+	62	Ni+
13	CH+	40	Ca+	63	Cu+
14	CH_2+	41	K	64	Zn+, TiO+
15	CH_3+	42	Ca+	65	Cu+
16	O+	43	AlO+, Ca+	66	Zn+
17	OH+	44	SiO+, Ca+	67	Zn+
18	O^{18}+ source gas	45	SiOH+, SiO+	68	Zn+
19	$O^{18}H$+, F	46	SiOH+, SiO+, Ti+	69	Ga+
23	Na+	47	SiOH+, Ti+	84	Sr+
24	Mg+, C_2+	48	Ti+, C_4+	86	Sr+
25	Mg+, C_2H+	49	Ti+, C_4H+	87	Sr+
26	Mg+, C_2H_2+	50	Ti+, C_4H_2+	88	Sr+
27	Al+, C_2H_3+	51	V+, C_4H_3+	134	Ba+
28	Si+	52	Cr+, C_4H_4+	135	Ba+
29	Si+, SiH+	53	Cr+, C_4H_5+	136	Ba+
30	Si+, SiH+	54	Fe+	137	Ba+
31	SiH+, P	55	Mn+	138	Ba+
32	S+, O_2+				

Fig. 20 Ion Microprobe Mass spectra of one coating layer of Vitre-Graf on mullite substrate cured at 1150°C after two layers cured at 1450°C. Peaks with lines through are charge spikes.



THE AEROSPACE CORPORATION
ION MICROPROBE MASS ANALYZER
SAMPLE 7145-4M
DATE 5-22-79 PAGE
EAM $^{18}O_2^+$ MODE CR KV 20 CURRENT 3
OT SIZE MAG 250 SEC 805

MASS LEGEND

Mass Number	Species	Mass Number	Species	Mass Number	Species
1	H^+	33	S^+	56	Fe^+, CaO^+
2	H_2^+	34	S^+	57	$CaOH^+$
6	Li^+	35	Cl^+	58	Ni^+
7	Li^+	36	C_3^+	59	Co^+, AlO_2^+
10	B^+	37	C_3H^+, Cl^+	60	Ni^+, C_5^+
11	B^+	38	$C_3H_2^+$	61	Ni^+
12	C^+	39	K, $C_3H_3^+$	62	Ni^+
13	CH^+	40	Ca^+	63	Cu^+
14	CH_2^+	41	K	64	Zn^+, TiO^+
15	CH_3^+	42	Ca^+	65	Cu^+
16	O^+	43	AlO^+, Ca^+	66	Zn^+
17	OH^+	44	SiO^+, Ca^+	67	Zn^+
18	$O^{18}+$ source gas	45	$SiOH^+$, SiO^+	68	Zn^+
19	$O^{18}H^+$, F	46	$SiOH^+$, SiO^+, Ti^+	69	Ga^+
23	Na^+	47	$SiOH^+$, Ti^+	84	Sr^+
24	Mg^+, C_2^+	48	Ti^+, C_4^+	86	Sr^+
25	Mg^+, C_2H^+	49	Ti^+, C_4H^+	87	Sr^+
26	Mg^+, $C_2H_2^+$	50	Ti^+, $C_4H_2^+$	88	Sr^+
27	Al^+, $C_2H_3^+$	51	V^+, $C_4H_3^+$	134	Ba^+
28	Si^+	52	Cr^+, $C_4H_4^+$	135	Ba^+
29	Si^+, SiH^+	53	Cr^+, $C_4H_5^+$	136	Ba^+
30	Si^+, SiH^+	54	Fe^+	137	Ba^+
31	SiH^+, P	55	Mn^+	138	Ba^+
32	S^+, O_2^+				

melt exposure, but on the other crucible experiencing twice the melt time this layer was found only at the top edge where the molten silicon had formed a meniscus against the crucible wall. Fig. 21a shows this reaction layer and also some of the pores in the graphite substrate that were protected from silicon intrusion. However, 21b is more representative of the total interaction and shows massive intrusion of the graphite by silicon and its conversion to silicon carbide. Sharp clean silicon carbide crystals are seen at the interface and these crystals were also seen throughout the melt but were found predominantly floating along the top surface.

From these data and examination of Sessile drop experiments at 20 and 40 minutes the following reaction steps were deduced.

(1) Silicon carbide forms by diffusion of silicon into the Vitre-Graf coating and creates an initial SiC barrier.

(2) Carbon diffuses through the SiC barrier.

(3) Carbon saturates at the SiC-Si interface creating SiC crystals that subsequently float away.

(4) Formation of SiC crystals and their subsequent separation creates defects such that the SiC barrier is breached and silicon invades the graphite.

(5) Silicon penetrates and invades open pores.

(6) Silicon carbide reacts at all interfaces by:

   a. diffusion of silicon into the binder phase or the Vitre-Graf that had previously entered the pores.

   b. diffusion of carbon from filler particles into silicon.

(7) Growth of silicon carbide reaction phase within pores.

(8) Continued growth of silicon carbide along macroscopic interface.

The effect of Vitre-Graf in protecting graphite used as a container for molten silicon appears to serve not as a true protective layer but only as a slight inhibitor of the silicon-graphite reaction. From the data thus far examined, the Vitre-Graf appears to provide only a short time, 30 - 60 minute advantage over un-coated graphite. Thereafter, the coating appears to serve no useful purpose.

7. Conclusions

The variables evaluated in this Test Series did not result in useable test samples for silicon melt evaluation. Except for the mullite sample receiving two coating layers and cured at

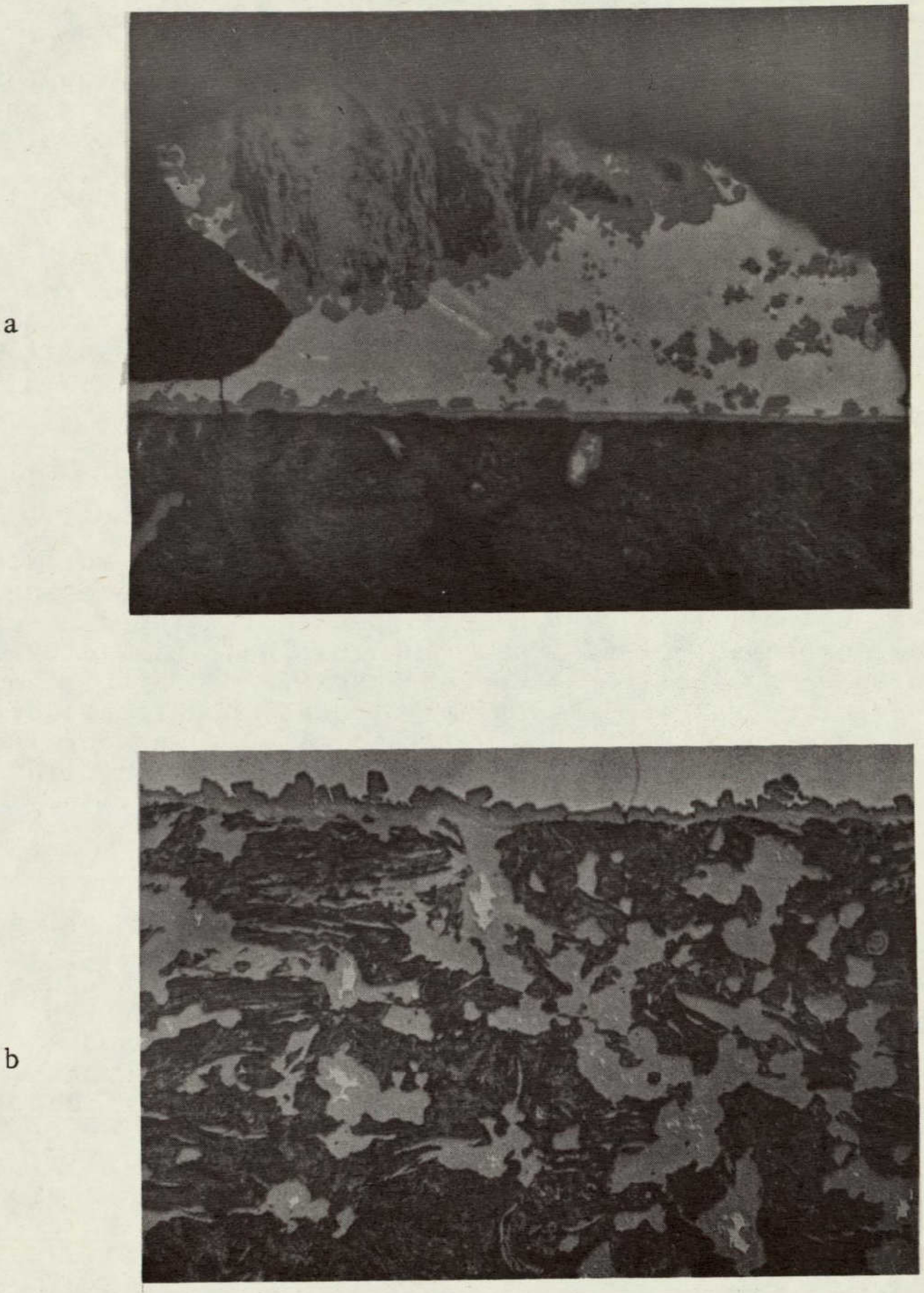


Fig. 21 Cross-section of silicon interface with Vitre-Graf coated graphite crucible after 20 hrs. showing (a) Silicon carbide reaction layer near miniscus, (b) penetration of silicon and reaction within pores of the graphite crucible. (a & b: 150x)

1150°C, the mullite was either not adequately coated or its coating was chemically oxidized during the cure cycle.

The graphite samples, at least those receiving 5 coating layers were adequate for testing but the independent data presented in the previous sub-section strongly suggested that the use of Vitre-Graf in the container ware application is not now possible because of the present understanding of its reaction with molten silicon.

Thus, from these data it was possible to conclude that graphite and all carbonoceous substrates be dropped from the program. Also concluded is that temperatures greater than 1150°C and fewer than two coating layers on mullite substrate are diverting from optimal performance.

G. Test Series VII: Re-Evaluation of Parameters for Mullite as Substrate

At this point in the program all parameters for mullite substrates had been evaluated except for optimizing heating rate. However, a new mullite had been developed that matched precisely the thermal expansion of silicon. In addition, this material was manufactured with slots to accomodate back face contacts and one of our objectives was to demonstrate or develop a technique to coat the face of only one side. At this time it was our further objective to demonstrate that parameters optimized on porous mullite were valid for the type "K" mullite modification.

1. Visual

The first parameter to be examined in this Test Series was the effect of heating rate which had been originally scheduled earlier in the program but had been postponed because of delays in obtaining results of prior Test Series. Heating rates of 10°C/min, then 5°C/min and finally 3°C/min were used on the type K mullite and vacuum atmosphere was also used in one case with exactly the same results, i.e. the first layer of coating completely flaked off. The complete lack of adherence inferred a marked difference in surface characteristics of this mullite even though it also contained some porosity. On the knowledge that this material contained considerable excess silica it was speculated that the lack of adherence arose from a silica glaze on the sample surface.

The second parameter examined was surface preparation methods: HF acid etch and mechanical abrasion. Samples prepared by both of these methods were heated at 5°C/min and a third which was acid etched was heated at 10°C/min. All three samples produced a uniformly coated, matte finish with one coating layer. The resulting surface finish was qualitatively better than all but possibly the multiple layer coatings in the early test series and much superior to any two layer coatings in more recent test series.

The fourth parameter re-examined was the solution concentration which was reduced to 250 g/l and cured at 950°C. Again the resulting coating was of excellent quality. A simulataneous reduction of concentration to 150 g/l and 850°C was attempted but an actual cure temperature of 1225°C was reached. This set of samples also had a uniform coating but from the experience of the former test series, some evidence of reaction between the mullite and the coating could be discerned. The experiment was repeated, again with good results.

Generalizing these observations, when using type "K" mullite after HF etching, high visual quality coatings can be obtained by brushing from solutions between 150 and 350 g/l, cured at temperatures between 850 and 1150°C and heated at 10°C/min in one atmosphere of nitrogen. At least from visual evaluation, the uniformity and general appearance of the coating was of such high quality that at no time during the conduction of this series did it appear that a second layer was necessary to obtain satisfactory results.

2. Adherence

No visual sign of flaking, peeling or delamination was seen on any of the mullite samples which were etched before coating. The adherence test has been able in some previous series to remove a slight amount of coating material although often too little to be measured with an analytical balance. In these samples, there was absolutely no removal of coating. In contrast, those mullite samples that were not etched lost their complete coating just by brushing lightly with a paper tissue.

These data as well as the predominance of flaking experienced in the earliest test series when adsorbed water was known to be present, and in later series where sections of interface were debonded strongly suggest that satisfactory Vitre-Graf coatings on mullite are strongly dependent upon the character of the mullite surface and possibly far less dependent upon the parameters of the Vitre-Graf coating than had been suspected at the start of this program.

3. SEM Observations

Scanning electron microscopy was performed on only a single sample, the last of the series experiencing one layer of the 150 g/l solution and cured at 850oC. On the basis of the close visual similarity in all etched samples in this series, it was presumed that this sample might adequately represent all samples in the series. The micrograph in Fig. 22 is typical of the surface of this sample and reveal the following: (1) the coating layer is generally poorly defined, (2) the substrate is severely etched and extends several microns below the coating interface, (3) the coating and exposed crystals are intermixed in the coating layer, (4) the etching treatment was so severe that insufficient bonding existed among exposed crystals such that they were broken away from the interface during the polishing operation, (5) depressions from these crystals exist in the plastic mount

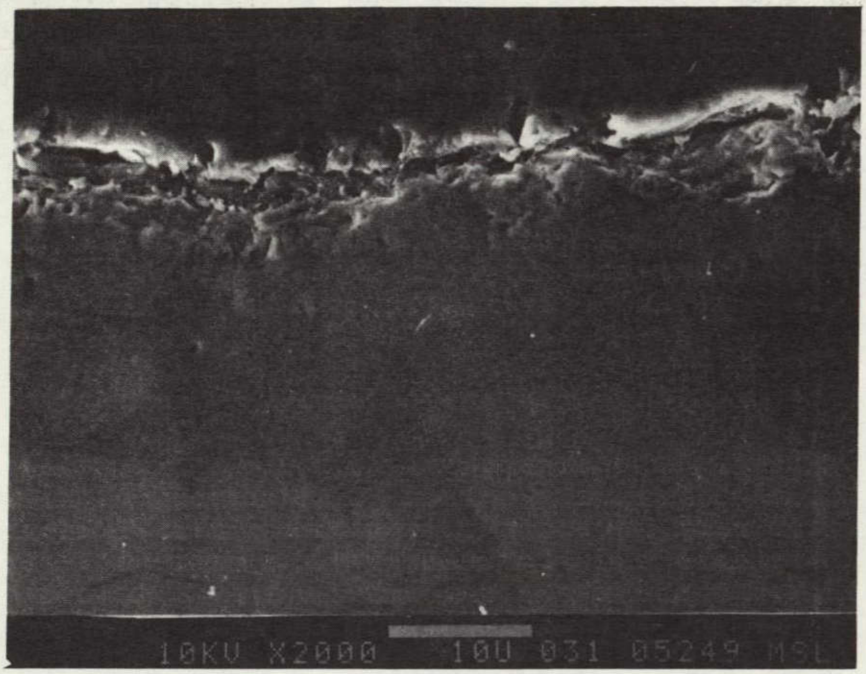


Fig. 22 One layer of Vitre-Graf coating cured at 850°C on heavily etched mullite substrate (lower). Upper portion of micrograph is the plastic mount.

above the surface of coating layer, (6) the interface between substrate and coating is too irregular to determine whether the coating had debonded although some areas appear to indicate that partial debonding may have occurred (This effect may also be a consequence of the polishing operation).

These observations suggest that a 15 sec. etch in concentrated HF is far too long to remove a surface glaze. The resulting surface is apparently devoid of the silica matrix and thereby has high porosity and an intrinsic weakness. The micrographs suggest that crystals protruded above the surface of a single coating layer when etched for this time period.

4. Thickness Measurements

The thickness measurements presented in Table VII are those calculated from weight gain of the etched mullite samples. Whereas in prior presentation of thickness data in this report the values presented were usually an average value of three samples, the data in Table VII is presented for individual samples. The reason for this is a consequence of an observation made while brushing on the coating in that the surface accepted the solution in a manner that was suggestive of a highly porous surface. Depending upon the loading of solution in the brush and the pressure applied while brushing, a heavy or light layer could be applied. During the course of this test series, variations in application of coating were made among the three samples in a test set. Sometimes the coatings of a set were made intentionally light on one, intentionally heavy on the second, and the third was applied to match one or the other. Sometimes an attempt was made to determine how reproducible a particular layer weight could be and other times how deviant the coating could be and appear acceptable. The values in Table VII reflect each of these variations. Interestingly, the difference between even the most diverse layer weights in the series was not easily discerned visually and no way detracted from the excellent visual quality of the coating.

The seemingly minor differences in dipping technique that was experienced by samples in the prior three test series was seen to have a marked effect on the resulting weight gain and coating thickness. Where as the coating thickness of a single sample of a set of three might have deviated from the average value by 20% in prior test series the coating thickness of a single sample of the abraded set, Table VII was seen to vary by a factor of 2. This difference in coating thickness was unintentional but resulted as a consequence of the high surface absortivity. On the next set, care was taken to apply the solution uniformly among the samples in the set and the results are similar to previous coating experience. On the followed sample set (etched, 10°C/min, 350 solution, 1150°C) one sample was intentionally coated as lightly as possible and the final thickness was less than one-half the thickness as "normally" applied. In the next set (1050°C cure), the solution was applied to two of the samples in the set as heavily as considered reasonable. The resulting coating was

Table VII Test Series VII: Wt. Gain and Calculated Thickness for Mullite Substrates

	Solution Concentrations	350 g/l	350 g/l	350 g/l	250 g/l	150 g/l	150 g/l
	Cure Temperature	1150°C	1050°C	950°C	950°C.	1225°C	850°C
Abraded, 5°C/min	Wt. Gain (mg)	12.1 13.0 6.1					
	Calc. Thk. (um)	3.8 3.7 1.9 3.75 ave.					
Etched, 5°C/min	Wt. Gain (mg)	12.5 10.9 10.4					
	Calc. Thk. (um)	3.8 3.4 3.0 3.4 ave.					
Etched, 10°C/min	Wt. Gain (mg)	13.1 10.0 4.3	11.5 19.9 15.0	15.9 18.1 14.3	11.1 8.4 11.2	3.8 4.0 6.8	7.8 6.5 5.3
	Calc. Thk. (um)	3.6 3.0 1.4 3.3	3.6 6.2 4.3 5.3	4.9 5.6 4.1 4.8	3.4 2.6 3.1 3.0	1.3 1.2 2.0 1.25	2.6 1.8 1.9 1.85

about 50% thicker but most significantly, no cratering occurred as expected. All samples in the 350 g/1, 950°C cure were then given a heavy coating, the results were as expected.

In the following experiment which used a 250 g/1 solution, an attempt was made to apply a normal coating as uniformly as possible. The thickness of the coating, 3.0 μm is greater than expected from results of Test Series III which would predict a thinner coating based on the dipping method on porous mullite.

The last two experiments using the 150 g/1 solution were conducted in the same manner with an attempt to coat one sample "normally", the other two as thin as possible. Although both sets were coated as similarly as possible, the set that had experienced a 1225°C temperature had both weight gain and thickness that was 50% less than the sample set cured at 850°C. A definitive conclusion is not possible based on just these two sample sets, neverthe less supported by visual appearance, the higher temperature samples appear to have reached a temperature high enough to have induced some loss through reaction with the mullite.

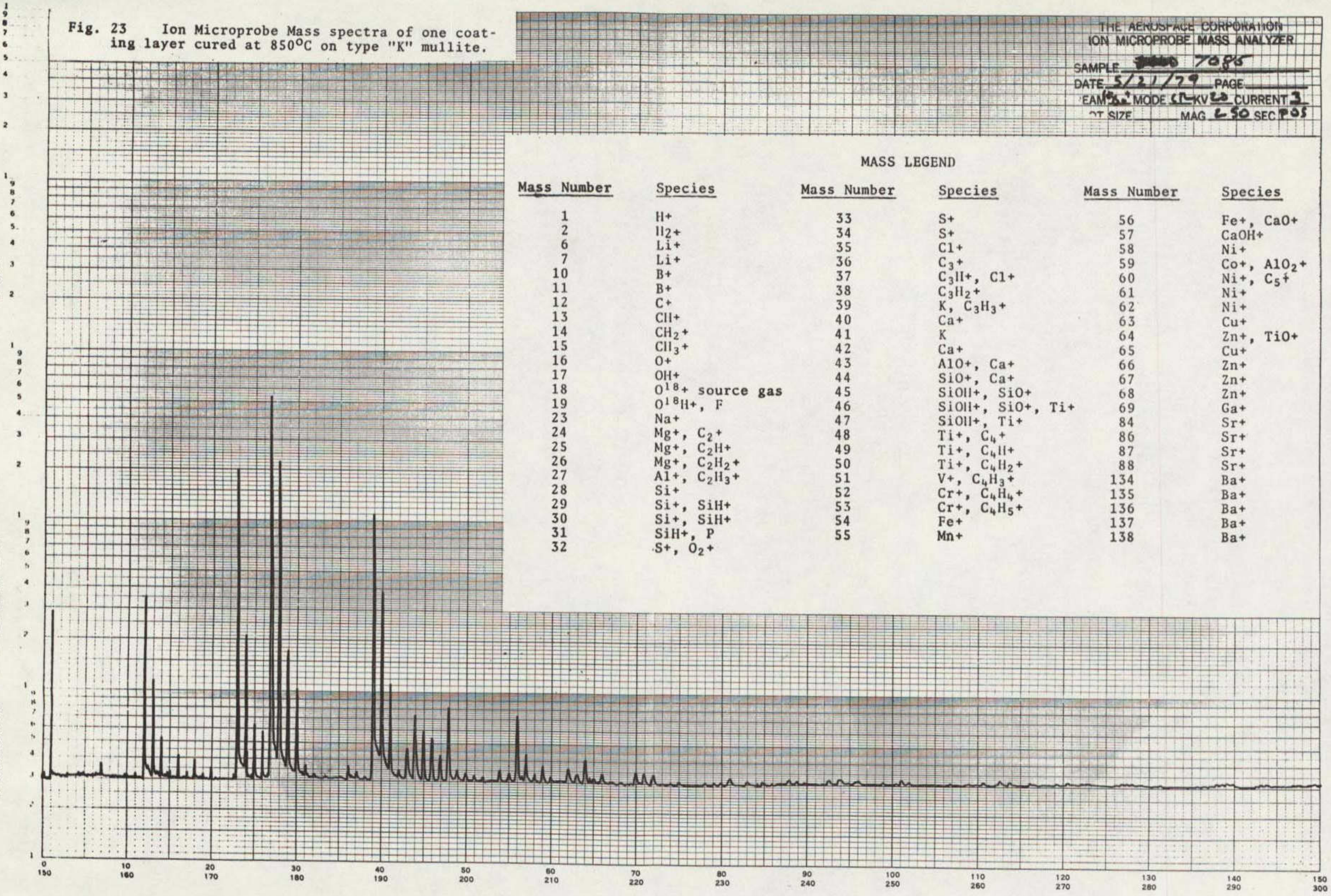
These data suggest that the effect of applying a heavy or light solution layer when brushing on an etched mullite surface is to vary the thickness of the resulting coating. In the extreme case a factor of four difference between a thin and thick layer was observed for a 350 g/1 solution. The typical heavy layer was generally about 50% thicker than a "normally" applied layer, and a typical light layer thickness was generally about one-half the normally applied layer thickness.

Direct comparison of coating thickness with previous Test Series is not possible because no other data is available for a single coating layer, some inferences can be made by comparison with Table III as a function of solution concentration. By taking the thickness value of 3.5 μm for the 350 g/1 solution, 3.0 μm for 250 g/1, and 2.5 μm for 150 g/1 from Table VII as "normally" applied, the thickness for the 350 g/1 compared with Table III is approximately that expected for a single coating layer. However, the thickness from the 250 g/1 solution and especially the 150 g/1 solution from Table VII is considerably greater than that expected from Table III. Moreover, at 150 g/1, the single layer coating thickness is greater than four layers applied to porous mullite by dipping method. The relationship of coating thickness from the dipping experiments were explained on the basis of the viscosity of the solutions. In the latter case, in which the solution was brushed, the parameter that appeared to have the most effect on the coating thickenss is the absorptivity of the etched mullite surface and solution viscosity did not appear to be influential.

5. Surface Chemical Analysis

The sample that was examined with the SEM was the only sample on which surface chemical analysis was performed. The mass spectra is presented in Fig. 23. The intensity of the peak signals appear suppressed much as in Fig. 18 but contrary to that data

Fig. 23 Ion Microprobe Mass spectra of one coating layer cured at 850°C on type "K" mullite.



THE AEROSPACE CORPORATION
ION MICROPROBE MASS ANALYZER
SAMPLE 7086
DATE 5/21/79 PAGE
EAM O_2^+ MODE CP KV 20 CURRENT 3
OT SIZE MAG 250 SEC POS

MASS LEGEND

Mass Number	Species	Mass Number	Species	Mass Number	Species
1	H+	33	S+	56	Fe+, CaO+
2	H_2+	34	S+	57	CaOH+
6	Li+	35	Cl+	58	Ni+
7	Li+	36	C_3+	59	Co+, AlO_2+
10	B+	37	C_3H+, Cl+	60	Ni+, C_5+
11	B+	38	C_3H_2+	61	Ni+
12	C+	39	K, C_3H_3+	62	Ni+
13	CH+	40	Ca+	63	Cu+
14	CH_2+	41	K	64	Zn+, TiO+
15	CH_3+	42	Ca+	65	Cu+
16	O+	43	AlO+, Ca+	66	Zn+
17	OH+	44	SiO+, Ca+	67	Zn+
18	O^{18}+ **source gas**	45	SiOH+, SiO+	68	Zn+
19	$O^{18}H$+, F	46	SiOH+, SiO+, Ti+	69	Ga+
23	Na+	47	SiOH+, Ti+	84	Sr+
24	Mg+, C_2+	48	Ti+, C_4+	86	Sr+
25	Mg+, C_2H+	49	Ti+, C_4H+	87	Sr+
26	Mg+, C_2H_2+	50	Ti+, C_4H_2+	88	Sr+
27	Al+, C_2H_3+	51	V+, C_4H_3+	134	Ba+
28	Si+	52	Cr+, C_4H_4+	135	Ba+
29	Si+, SiH+	53	Cr+, C_4H_5+	136	Ba+
30	Si+, SiH+	54	Fe+	137	Ba+
31	SiH+, P	55	Mn+	138	Ba+
32	S+, O_2+				

no charge spikes are visible and the carbon signal used as the basis for normalization is of proper magnitude. The aluminum, silicon and titanium intensities are greater than that expected but their oxides are not strongly present.

The data are interpreted as being truly representative of the sample. The presence of titanium in the spectra suggests that the ion beam sputtered substrate as well as coating since titanium from the substrate had not been seen in the coating previous to Test Series VI. This explanation is reasonable considering that the SEM micrographs revealed crystals protruding above the coating surface. (However, the uniformly black surface in this series suggests that a coating film covered the crystals in contrast with the blotchy appearance of Series VI).

The reduced signal can be a consequence of a reduction in the impurity content of the Type "K" mullite, a consequence of a cleaner resin material, or a consequence of curing at a lower temperature where impurity migration is thermally inhibited. The signal intensity for this sample may, in fact, be a consequence of a combination of all three of these explanations. Nevertheless, the impurity signal on the surface of this sample is lower than that of any mullite substrate examined in the program. Moreover, on the presumption that the titanium and some portion of the aluminum and silicon signal arise from sputtered substrate crystals, those elements then are not dissolved in the coating and the actual contaminant level in the coating may be even less than that indicated by these data.

6. Conclusions

From results of this test series it was concluded:

(a) Parameters optimized for porous mullite were not optimal for type "K" mullite.

(b) Type "K" mullite produced equivalent appearing coatings over a wide range of parameters.

(c) Type "K" mullite as presently made has a surface glaze that must be HF etched before Vitre-Graf is applied.

(d) An etch time of 15 sec. in concentrated HF is excessive to remove the glaze.

(e) A single coating layer produces a uniform black coating layer that appears functional.

(f) A cure temperature as low as 850°C appears to be adequate.

(g) The weight and thickness of a coating can be controlled by controlling the etch-produced porosity of the surface under controlled application conditions.

(h) Dependent upon the porosity of the surface, a light resin solution may give results comparable to a heavy solution.

Qualifications required in making these conclusions are that an etch surface can be made such that a small and limited surface porosity exists to accomodate the application of the resin and executing an adherent bond with the coating. It is presumed that the favorable observations made in test samples in this series can be projected to properly etched samples without performance sacrifice and with the elimination of observations detrimental to performance.

An alternative to the requirement for etching the surface is the possibility that type "K" mullite could be made with adequate surface porosity such that an adherent bond with the coating can be made. The presumption is then made that the observations made on the test samples in this series are applicable to the type "K" mullite surface as prepared.

SECTION VI

CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS i.e.

1. Vitre-Graf coatings on either mullite or graphite substrates are not effective as a barrier to silicon substrate interaction when in contact with molten silicon for extended time periods (> 30 min).

2. Vitre-Graf coatings on graphite react with molten silicon to form a silicon carbide reaction layer which serves as an initial barrier, but growth of SiC crystals and their subsequent separation from the layer creates a breach in the barrier that allows the molten silicon to attack the graphite substrate.

3. Vitre-Graf coatings react with mullite substrates at temperatures of 1250°C and greater to create a reaction layer of reduced oxides and a loss of the coating, presumed to be by oxidation and vaporization.

4. Vitre-Graf coatings applied to porous mullite produces good quality coatings when cured at 1150°C. The most cost effective coating required two layers of a heavy solution.

5. Vitre-Graf coatings applied to type "K" mullite (developed to match the thermal expansion of silicon) require that the surface be HF acid etched.

6. When etched, type "K" mullite accepts the Vitre-Graf coating under a broad range of parametric conditions.

7. The most cost effective process condition for type "K" mullite is a single layer of 150 g/l solution cured at 850°C.

8. The effectiveness of the Vitre-Graf coating as a wetting surface for molten silicon on type "K" mullite substrates is unaffected by variations in processing parameters after a surface glaze has been removed by HF acid etching.

B. Recommendations

The primary objective of this program to establish cost effective processing parameters on a mullite substrate has been successfully completed. Moreover, the technical effectiveness of the Vitre-Graf coating as a wetting surface is shown to be relatively insensitive to variations in processing parameters, and thereby increasing its potential utilization. Nevertheless, two areas of further development are apparent that can significantly affect the economics of the Vitre-Graf coating (See Section VII).

1. Presently type "K" mullite requires HF acid etching to promote Vitre-Graf adherence to the substrate. It is

recommended that further development of this mullite be continued to eliminate the need for this process step possibly through surface porosity. Elimination of this step can reduce process cost by nearly 20%.

2. A major expense factor in the Vitre-Graf process is the cost of manufacturing the Vitre-Graf solution from decomposed resins. Whereas a sizable reduction in unit cost in projected solely through the use of high-volume, mass production methods, an additional cost reduction of 20% is believed to be possible through further advances in the decomposition technology. Thus, it is recommended that technology development leading to cost reduction of Vitre-Graf solution be initiated.

SECTION VII

ECONOMIC ANALYSIS

A. PHYSICAL MODEL

In order to determine the cost of processing a Vitre-Graf coating onto a mullite substrate for the SOC process, it is first necessary to construct a physical model for the required process steps. From the results of this program, the following assumptions are made:

(1) Type "K" mullite will be used.

(2) Substrates will be HF etched for times less than 15 sec.

(3) Substrates will be coated with a light resin #2 solution (∿ 150 g/l).

(4) Coatings will be single layers and cured at: (a) 900°C in (b) nitrogen atmosphere at atmospheric pressure, (c) at a heating rate consistent with furnace design.

In contrast with the batch processing used in experimentation, it is envisioned that a continuous tunnel furnace will be used. Coated substrates will be loaded onto kiln cars; kiln cars will enter the furnace through an air lock that will minimize oxygen entrainment and then follow through the furnace immediately behind the preceding car. The kiln cars will progress at a given rate through the furnace from a cold end through a central hot zone and exit again at a cold end through a second air lock.

A flow of nitrogen countercurrent to the passage of the kiln cars will serve to chill the parts at the exit end, pass through the central hot zone and heat the incoming parts in the entry end. The flow of nitrogen will also serve to carry away hydrocarbons that evolve from the curing resin solution and, by their counter current flow, prevent a redeposition onto previously cured parts. The nitrogen gas will be recirculated first through a trap to eliminate hydrocarbon tars, then through a heat exchanger and then blown back into the furnace at the exit end.

It is presumed that the mullite substrates will be received packaged, 80 to a pack, such that an automatic device can unwrap the package and feed a conveyor belt with an individual substrate. The substrate will then be automatically loaded onto a basket that will float the substrate on an HF etch bath for a given time period, followed by a water rinse and dried and then redeposited onto a conveyor belt. The substrate would then pass over a paint roller that will apply the coating at a preset pressure and then the substrate would be flipped over so that the coating surface is on top and again deposited onto a conveyer belt. Five such units will converge onto a single conveyer that will be automatically positioned so as to load the support plates of a kiln car. Each plate will be ¼in. thick and spaced ¼ in. apart and hold five substrates in a position transverse to the direction of motion. The five substrates will be loaded simultaneously and the conveyor belt will then automatically drop ½ inch to position for loading onto the next lower support plate.

Unloading the kiln car is a similar process in reverse whereby the substrates are pushed from one side of the kiln car onto a conveyor belt that when having traversed 40 inches, will drop ½in to a position so as to pick up the next row of coated substrates. The finished product will pass an inspection station and proceed to an automatic wrapping device that will create a finished package of coated parts that is exactly like the incoming package of substrates.

All loading and unloading machinery will be timed so as to exactly coincide with the rate of parts through the furnace. In order to minimize costs and conserve materials it is envisioned that wrapping material (foam padding) and crating materials will be reusable.

B. Process Parameters

1. Output Rate

Furnace size: $1m^2$ cross section nominal 100 ft. long.

Loading: 1 substrate at full width, 2 substrates per vertical inch, 80 substrates at full height (Substrate size: 1m x 10cm x 1mm)

Rate of motion: 1.8in/min

Utilization Factor: 0.96

Yield Factor: 0.965

No. of Furnaces: 3

Minutes per yr.: 525,600

Substrates per linear inch: 5 substrates/support plate = 20 inches, 1 inch vertical support stand = 21 inches. Eighty support stacks x5 substrate/support ÷21 inches = 19.05.

Square meter per substrate: 0.1

Yearly output: (1.8) (525,600) (0.96) (0.965) (3) (19.05) (0.1) = 5,008,900 m^2/yr.

2. Process speed(load/unload conveyor rate):

$$\frac{(5)(60)}{(1.8)(19.05)} = 8.75 \text{ sec/group (5 substrates)}$$

Conveyor rate:

Assume 1.5 sec/group for conveyer re-positioning

$$\frac{(40)}{(8.75-1.50)} = 5.517 \text{ in/sec.}$$

3. Time at Station = Time in furnace + load/unload time.

$(1.8)(12)(100) + 4(8.75)(80)(10)/60$

$2160 + 466 = 2626$ min. = 109.5 hrs.

4. Equipment Costs:

Furnace	-	$840,000
Handling Equip.	-	180,000
Etch & Rinse Baths	-	150,000
Ancillary Equip.	-	30,000
		$1,200,000
		x3
		$3,600,000

5. Space Requirement/furnace, including load/unload equip.

Furnace Length ≈ 100 ft.

Kiln car turntable, each end = 20 ft.

Total length = 140 ft.

Furnace width = 8 ft.

Load/Unload Equip. = 12 ft.

Total width = 20 ft.

$(140)(20) = 2800$ ft.^{2}/furnace unit

6. Direct Labor Costs (2100 hrs/yr/shift)
All subsequent costs are based on 1979 dollars.

	Unit Requirement	Rate	DLC/Unit
Chemical Operator	0.33/shift	$7.50	$ 5250
Furnace Operator	0.67/shift	7.50	10500
Material Handlers	0.67/shift	6.00	8400
Machine Packers	0.67/shift	6.00	8400
	2.34men/shift		32550

($32,550)(3 units)(4 shifts) = $390,600 yearly DLC.

7. Material Costs

Assume:

1 gal solution covers 40 m^2

1 gal solution (150 g/1) costs $20.

(5,190,570)($20)/(40) = $2,595,285

Assume:

1 gal Hydrofluoric acid etches 100 m^2

1 gal acid cost $20.

(5,190,570)($20)/100 = $1,038,114

Assume:

1 gal rinse water (de-ionized) rinses 3.6 m^2

Make-up water is 10%

Water cost is $0.008/gal.

(5,190,570)($0.008)(0.1)/(3.6) = $1154

Assume:

Replacement nitrogen - 1000 cu ft/hr./unit at $1/100 ft.

(1000)($0.01)(8423)(3) = $252,690

Assume:

Replacement part costs per unit per year = $50,000
yearly material costs = $150,000

Total Material Costs = $4,037,243

8. Utilities:

Electricity for furnace operation 86.4 kw/unit

(86.4)(3)(8423 hrs.)($0.03) = $65,500

Electricity for fans, motors and other operating equipment = 4.5 kw/unit.

(4.5)(3)(8423)($0.03) = $3400

Yearly Contract Maintenance = $50,000

C. IPEG Costs

The equation for the IPEG Cost Model is:

Cost = (0.49 Eqpt. + 97 sq ft + 2.1 DLAB + 1.3 MATS + 1.3 UTIL)/Quan.

(0.49)	$3,600.000 =	$ 1,764,000
($97)(3)	2800	814,800
(2.1)	$390,600	820,260
(1.3)	4,037,243	5,248,416
(1.3)	$ 118,900	154,570
Total Production Costs		$ 8,802,046

Unit Cost = ($13,825,360)/(5,008,009) = $1.76/m^2

Adjusting this cost to 1975 dollars by using a 1.35 inflation factor gives a unit cost of $1.30/m^2.

D. IPEG Costs for an Alternate Process

On the basis that the type "K" mullite could be manufactured so that surface etching until HF acid could be eliminated, the following changes can be made.

1. Eliminate etch and rinse baths: Subtract 450,000 from equipment.
   Equipment requirement = $3,150,000
2. No change in space requirement.
3. Elimination of chemical operators: subtract $63,000 from direct labor cost.
   DLC/yr = $327,600
4. Eliminate Hydrofluoric acid: subtract $1,038,114 from material costs.
   Total material costs/yr. = $2,999,129
5. Eliminate 1.5 kw/unit electricity from operating unit: subtract $1133 from utility cost.
   Utility/yr. = $117,769
6. IPEG Costs

(0.49)	$3,150,000	$1,543,500
($97)(3)	2800	814,800

(2.1)	$327,600	$ 687,960
(1.3)	$2,999,129	3,898,868
(1.3)	$117,767	153,097
Total production costs		$7,098,224

Unit cost = ($7,098,224)/(5,008,900) = $\$1.42/\text{m}^2$

Adjusting this cost to 1975 dollars by using a 1.35 inflation factor fives a cost of $\$1.05/\text{m}^2$

E. IPEG Costs Assuming Vitre-Graf Technology Advance

A major cost of the process is the cost of the Vitre-Graf solution. The cost of solution at 150 g/l concentration has been calculated at $20/gal based on volume production of the present decomposition technology. Assuming that a normal advance in this technology will take place in the coming years a 1979 dollar cost of $12/gal is considered attainable.

Thus solution costs becomes $1,557,171.

IPEG costs become $5,748,676 per year.

Unit cost becomes $\$1.15/\text{m}^2$

and adjusted for inflation become $\$0.85/\text{m}^2$ on 1975 dollar.

SECTION VII

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