255
4/7/78

HA. 2012

DOE/JPL/954878-1

DEVELOPMENT OF MULLITE SUBSTRATES AND CONTAINERS

Silicon Sheet Growth Development for the Large Area Silicon Sheet
Task of the Low-Cost Silicon Solar Array Project. Quarterly
Report No. 1, October 6, 1977–November 14, 1977

MASTER

By
D. G. Wirth
J. D. Sibold

December 5, 1977
Date Published

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

Coors Porcelain Company
Golden, Colorado

U.S. Department of Energy

Solar Energy

DISCLAIMER

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

DISCLAIMER

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

NOTICE

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

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

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

Price: Paper Copy \$4.00
Microfiche \$3.00

DEVELOPMENT OF MULLITE SUBSTRATES AND CONTAINERS
SILICON SHEET GROWTH DEVELOPMENT FOR THE LARGE AREA
SILICON SHEET TASK OF THE LOW-COST SILICON SOLAR ARRAY PROJECT

QUARTERLY REPORT NO. 1

By:

D. G. Wirth and J. D. Sibold
Period Covered: 10/6/77 - 11/14/77

Published 12/5/77

JPL Contract No. 954878

COORS PORCELAIN COMPANY
Golden, Colorado 80401

This work was performed for the Jet Propulsion Laboratory California Institute of Technology, sponsored by Department of Energy and forms part of the DOE Photovoltaic Conversion Program to initiate a major effort toward development of low-cost solar arrays.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

TABLE OF CONTENTS

	Page
1.0 Introduction.....	1
1.1 Materials Selection.....	1
1.1.1 Mullite Substrates.....	1
1.1.2 Mullite Containers.....	2
2.0 Development of Materials.....	2
2.1 Mullite Substrates.....	2
2.1.1 Geometry.....	3
2.1.2 Hole Configuration.....	3
2.1.3 Composition and Microstructure.....	3
2.1.4 Surface Interaction with Silicon....	4
2.1.5 Processing Method of Manufacture....	4
2.2 Mullite Containers.....	4
2.2.1 Composition and Microstructure.....	5
2.2.2 Thermal Shock.....	5
2.2.3 Geometry.....	5
2.2.4 Processing Method of Fabrication....	5
3.0 Technical Discussion.....	5
3.1 Substrate Characterization.....	5
3.1.1 Chemical Characterization.....	5
3.1.2 Physical Characterization.....	7
3.1.3 Microstructure Characterization....	7
3.2 Substrate Production.....	11
3.2.1 Dry Press.....	11
3.2.2 Roll Compaction.....	11

TABLE OF CONTENTS (CONCLUDED)

	Page
3.3 Conclusions.....	12
3.4 Recommendations.....	12
3.5 Projected Activities for fourth quarter..	13

LIST OF TABLES

TABLE I.....Chemical Characterization.....	6
TABLE II....Phase Analysis.....	7

LIST OF FIGURES

Figure 1....High Silica Thermal Expansion ...	8
Figure 2 thru 9....Photo micrographs.....	9 & 10

SUMMARY:

Eight mullite bodies of varied compositions and microstructures have been prepared and are being characterized. These compositions will be submersed in molten silicon to study the impurity and surface effects. These various mullite materials will be analyzed for use as substrates for Honeywell Contract No. 954356, silicon on ceramic program and for use as a container of molten silicon.

Low cost processing methods are being developed and evaluated for manufacturing large mullite sheets and mullite containers. At present, a state-of-the-art roll compaction process has shown promising initial results for substrates. However, these 0.5mm x 10cm x 1m are extremely fragile. Slip casting or iso pressing are anticipated for containers.

TECHNICAL CONTENT STATEMENT

This report contains information prepared by COORS PORCELAIN COMPANY under JPL subcontract. Its content is not necessarily endorsed by the Jet Propulsion Laboratory, California Institute of Technology, National Aeronautics and Space Administration or the U. S. Energy Research and Development Administration, Division of Solar Energy.

1.0 INTRODUCTION

The primary objective of this proposed study program is to develop methods for processing and fabrication of selected "refractory mullite" materials into a form which is amenable to the production of substrates and containers for molten silicon. Specifically, the program objectives are: (1) a mullite substrate for silicon film preparation, and (2) a mullite container which does not contaminate, or is not contaminated by, molten silicon.

1.1 Materials Selection

1.1.1 Mullite Substrates

Already under way are the fabrication of candidate mullite substrate compositions from a standard production mullite body, SISI, and from seven chemical and physical variations to the basic body formulation and processing. These eight body variations are as follows:

- A. Standard Body SISI
- B. High Mullite Modification of SISI
- C. High Glass Modification of SISI
- D. Glass Property Modification of SISI
- E. Open Porosity Modification of SISI
- F. High Purity Modification of SISI
- G. Electrically Fused Mullite Body
- H. Reducing Fire Modification of SISI

These eight bodies are being characterized as to their chemical composition, pertinent physical properties and microstructure, and ultimately will be submitted to Honeywell, Inc. to be coated with silicon under contract 954356.

In addition, these materials will be exposed to molten silicon for various contact times, the silicon then being solidified in contact with the substrate and, consequently, the coated substrate analyzed and characterized. Test substrates will be fabricated by dry pressing and/or roll compaction process.

1.1.2 Mullite Containers

The same eight bodies which are being considered as candidates for mullite substrates will also be evaluated as mullite containers for the melting of silicon. Forming methods applicable to crucible fabrication, slip casting and/or iso-static pressing, will be employed in test crucible fabrication as opposed to dry pressing and/or roll compaction processes, which are applicable to substrate fabrication.

These materials fabricated in the form of test crucibles will then be used as containers in the melting of silicon for various holding times, and then analyzed and characterized.

2.0 DEVELOPMENT OF MATERIALS

2.1 Mullite Substrates

The material development of mullite substrates for growth of large silicon sheet will require fabrication methods suitable for shapes necessary for low cost solar arrays and material with necessary properties to allow minimal contamination of the silicon sheet to maximize the efficiencies of the solar cells.

2.1.1 Geometry

In order to make large area substrates - approximately 1 meter x 10 centimeters, a proprietary fabrication process will be used. This roll compaction process consists of rolling powders into flexible sheets of desired thickness which can be cut or punch pressed to necessary configurations. Generally, thicknesses of .030 to .060 inches are well within the capabilities of this process. Flatness and smoothness depend on the flatness and smoothness of the refractory setters the substrate is fired on. The refractory setters will be manufactured at Coors. This type of setter is currently being used to manufacture thick and thin film alumina substrates. Length and width capabilities will be expanded to make 1 meter x 10 centimeter sheets. Alumina substrates up to 0.5 meter x 10 centimeters have been successfully fired.

2.1.2 Hole Configuration

Feedthrough holes of different configurations will be punched in the roll compacted tape prior to firing. The hole configurations will consist of round, square and long slots of varying sizes. Length and width firing shrinkages may affect the hole locations and hole shape. This will be noted in this study.

2.1.3 Composition and Microstructure

A series of 8 compositions and microstructures are presently being prepared for Honeywell, Inc., under contract No. 954356. This series includes a standard mullite body with standard firing treatment. This same body, designated SISI is being under fired to study porosity effects and reducing fired to study surface chemistry effects. Additionally, composition variations with standard firing conditions are being examined. An excess silica body will have more glass phase and less potential for free alumina.

A higher purity clay body will minimize such impurities as iron and titania. A higher alumina content body will increase the amount of mullite formed at the expense of the glass phase. A mullite body consisting of ground electrically fused mullite should eliminate potential free alumina or silica and glass phase. The addition of boron attempts to alter the thermal expansion of the glass phase of the standard mullite formulation. The testing and evaluation of these bodies will direct the compositional and microstructural explorations. These bodies are being wet milled/spray dried/dry pressed for cost purposes.

2.1.4 Surface Interaction with Silicon

The aforementioned eight bodies will also provide large variation of surfaces which will be examined in contact with silicon.

2.1.5 Processing Method of Manufacture

The indicated compositions from 2.1.3 will be prepared in the roll compacted process from 2.1.1 to prepare final samples. Projections of manufacturing capability, production rates, and cost will be made from this section of the study.

2.2 Mullite Containers

Mullite containers for molten silicon will require different compositional and microstructural constraints to minimize contaminating the silicon thermal shock failures.

2.2.1 Composition and Microstructure

Since the composition and microstructure study has begun for the substrates, it will be extended to the container material development with appropriate change in the material testing program.

2.2.2 Thermal Shock

Compositions and microstructures should cover the necessary thermal shock improvements through thermal expansion alterations and increased porosity.

2.2.3 Geometry

Geometrical considerations may necessarily be taken to minimize thermal shock. Minimal surface exposure to the melt will help corrosion as will any methods to reduce silicon bath convection currents.

2.2.4 Processing - Method of Fabrication

For the size containers indicated in the statement of work, slip casting and/or iso-pressing will be used to fabricate samples. Both these methods are capable of shape flexibility, good production rates, and therefore, low costs.

3.0 TECHNICAL DISCUSSION

3.1 Substrate Characterization

3.1.1 Chemical Characterization

Each of the candidate compositions is being characterized chemically by calculating from the formulation and vendor analyses of the raw materials. These are listed in Table I. In addition, analyses of the fired samples is being made by wet chemistry and emission spectroscopy. This analysis is not complete.

TABLE I

T A S K	BODY	APPROXIMATE % OXIDE COMPOSITION									PROPERTIES		LAB ANALYSIS			
		Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	B ₂ O ₃	DENSITY %	POROSITY %	THICKNESS SHRINKAGE	LENGTH SHRINKAGE	X-RAY MULLITE %	THER. EXP. RT-1000°C
1A	STD S-1-SI Coor's Composition	57.6	38.9	0.62	0.13	0.25	0.92	0.25	1.12	0.00	2.70	0.32	12.06	16.66	76.5	5.41 X10 ⁻⁶
1B	982HPM High Mullite	67.2	31.4	0.45	0.02	0.01	0.16	0.18	0.54		2.86	.22	12.10	12.69	70.2	5.0 X10 ⁻⁶
1C	996HPM High Silica	52.2	44.7	0.56	0.13	0.22	0.83	0.22	1.01	0.00	2.58		14.2	12.3	56.1	4.95 X10 ⁻⁶
1D	7 HPM Boric Acid	56.7	38.3	0.61	0.13	0.24	0.30	0.24	1.10	1.50	2.50	.19	11.72	13.72	66.8	5.52 X10 ⁻⁶
1E	STD S-1-SI Open Porosity	57.6	38.9	0.62	0.13	0.25	0.92	0.25	1.12	0.00	2.55	7.27	11.56	13.75	66.4	5.41 X10 ⁻⁶
1F	979HPM High Purity	57.6	39.1	0.44	0.21	0.13	0.34	0.05	0.30	0.00	2.70	0.53	14.91	19.49	66.8	5.26 X10 ⁻⁶
1G	995HPM Electrically fused	77.5	21.9	0.12	0.00	0.00	0.00	0.35	0.05	0.00	2.62	13.89	10.40	11.34	84.2	5.46 X10 ⁻⁶
1H	S-1-SI Reducing Fire	57.6	38.9	0.62	0.13	0.25	0.92	0.25	1.12	0.00	1)2.88 2)2.67	0.38 11.4	12.50	18.06	66.4	5.31 X10 ⁻⁶

1) All dark part

2) 50% dark part

COMMENTS

3.1.2 Physical Characterization

Physical properties of each candidate material are listed in Table I. In general the data are as expected except the x-ray analysis. This will be discussed in the following section. The thermal expansion data appear to indicate the high silica composition to be the lowest expansion. It is also the highest glass content material. The Boron addition evidently did not form a low expansion glass phase. One must conclude that the glass phase in the other compositions is the low expansion phase and must be very high silica content. As Figure 1 shows, the expansion is linear to 1000°C, thus no yielding is taking place. It appears that it is necessary to analyze the composition of the glass phase to determine the cause of the expansion changes.

3.1.3 Microstructure Characterization

Photo micrographs of each of the candidate materials are shown in Figures 2-9. These are polished sections which were relief polished to bring out phase contrast. Magnification is 500X. Phase analysis by linear intercept is present below in Table II with corresponding x-ray analyses.

TABLE II

	<u>Microstructural</u>	<u>X-Ray</u>
SISI	61.5	76.5
High Mullite	78.5	70.2
High Silica	47.0	56.1
Boric Acid	74.0	66.8
Open Porosity	79.2	66.4
High Purity	86.6	66.8
Electrically Fused	98.6	84.2
Reducing Fire	82.0	66.4

Figure 1 - High Silica

Figure 2 - SISI

Figure 3 - High Mullite

Figure 4 - High Silica

Figure 5 - Boric Acid

Figure 6 - Open Porosity

Figure 7 - High Purity

Figure 8 - Electrically Fused

Figure 9 - Reducing Fire

It is difficult to resolve these variations since they were samples from the same firing but not of the same piece. Possibly other crystalline phases, such as Al_2O_3 are present in the microstructures.

3.2 Substrate Production

3.2.1 Dry Press

The samples being evaluated were wet milled, spray dried and dry pressed. They were then fired at 1650°C in gas/air tunnel kiln at cone 32. Two exceptions to this firing procedure were the open porosity and the reducing fire. The open porosity was fired at 1540°C (cone 28) and the reducing fire was 1650°C for four hours in dry hydrogen atmosphere. The H_2 firing gave very mixed results. In each 1.5 x 2.1 inch plate, there is variation in density and color. A dark area of about 2.88 g/cc and beige-pink area of about 2.67 g/cc. It is felt that this is due to partial reduction of the silica. Furthermore, many of the plates stuck to the molybdenum setters. Another H_2 firing is planned in which the plates will not have the binder burned out before H_2 fire. The idea is to leave carbon in the fired substrate to promote wetting during silicon coating.

3.2.2 Roll Compaction

A formula of SISI has been prepared by roll compaction into continuous sheet approximately 5.5 inches wide by .025 inches thick. Samples of this have been cut and fired to lengths of 16 inches. The limitation has been setter length. These sheets fired quite straight with no cracking. Slots up to $1/8 \times 2$ inches and holes were cut and punched into the sheet at various positions. These slots and holes maintained their geometries very well through

firing. Recently setter 48 inches in length have been manufactured. To date, two lengths of sheet approximately 43 inches x 4.51 inches have been fired in one piece. The first was fired without a cover and it appears that impurities dripped from the kiln onto the part. The second stuck to the setter. Both pieces were extremely fragile and were slid off the setter onto a supporting aluminum plate. This weakness may require thicker parts. Another roll compaction run will be scheduled to attempt to make thicker sheet. To alleviate the sticking problem, the setters will be coated with a refractory grain.

3.3 Conclusions

Single sheets up to 1 meter long and 10 cm wide still appear feasible. Still to be determined is the necessary thickness required to allow reasonable handling. Higher porosity variations of the compositions will be weaker and, therefore, more prone to this failure.

Thermal expansion appears dependent upon glass phase amount and composition as would be expected. Perhaps unexpectedly the glass phase is the lower expansion phase.

3.4 Recommendations

Calculate necessary thicknesses to support this length of sheet given the strength of the mullite materials now being produced.

Consider whether or not to coat exposure samples with carbon since that is how the substrates will be coated.

3.5 Projected Activities for Next Quarter

Completion of the initial characterization of the eight composition and microstructure variations is anticipated. The erosion/corrosion studies will begin upon receipt of the materials. More large sheets of SISI will be fired. Additionally, initial cost projections should be complete.