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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. 2, November 14, 1977—March 31, 1978

By
D. G. Wirth
J. D. Sibold

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Coors Porcelain Company
Golden, Colorado

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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. 2

By:

D. G. Wirth and J. D. Sibold
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COORS PORCELAIN COMPANY
GOLDEN, COLORADO 80401

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"The JPL Low-Cost Silicon Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE".

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ABSTRACT

Compositional variations in Mullite formulations have been found to lower the thermal expansion of Mullite. Increased glass phase has been found to lower thermal expansion of fired Mullite bodies. Attempts to lower the thermal expansion to that of Silicon are underway.

Sessile drop experiments on a series of composition and firing variations of Mullite produced a drastic change in some of the materials after a 10 hour exposure time. At 5 and 20 minutes nothing unusual was noted. Mullite substrates 100 CM x 10 CM x 0.1 CM were fabricated and fired successfully. Slots and holes have been fabricated in smaller 3.75 x 5.0 CM substrates. Crucibles from the standard Mullite formulation have been fabricated both dense and porous. Cost projections have been made for large quantities of substrates.

1.0 Introduction

The JPL Low Cost Silicon Solar Array Project has been established with the goal of decreasing the cost of solar photovoltaic arrays for electrical power generation. There is a need for low cost refractory materials to be used with, or exposed to, molten silicon. Crystal-growing processes require a refractory crucible to hold the molten silicon while ribbon processes additionally require a shaping die of refractory material. In one sheet silicon process - silicon on ceramic - a refractory ceramic sheet is coated with silicon.

The objective of this study is to develop, evaluate and fabricate a refractory ceramic material for molten silicon containers and silicon sheet substrates. For these applications the refractory material must be mechanically stable to a temperature above that of the silicon melt point (1412°C). Thus it must not melt or undergo other destructive phase changes below this temperature. The refractory material must not erode, corrode or otherwise react with silicon and change dimensionally or contaminate the silicon. A further requirement is that the refractory material be low cost and readily fabricated to close tolerances.

The approach has been to use mullite as the basic material since it is derived from low cost clays. High alumina fabrication technology is being applied to mullite to make the required shapes. Mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ is the only stable phase between alumina and silica. It is normally manufactured to high density in the ceramic industry by blending alumino-silicate clays with aluminum oxide. Upon firing, fine needle-like mullite crystals form in a continuous glass phase. The ratio of mullite to glass phase is controlled by the proportion of alumina to clay. Most commercially available mullite bodies

contain 20-40% glass. Unfortunately although the clay materials are inexpensive, they are not high purity and result in impurity levels in the fired mullite of 0.5% Fe_2O_3 , 0.5-1.5% TiO_2 , 0.1% CaO , 0.15% Na_2O , and 0.1-1.0% K_2O . These impurities can be lowered by judicious selection of clays. Therefore, the approach is to vary impurity levels, alumina-clay ratio, and firing schedules and determine the effect of these variations in silicon impurity pick up and mechanical performance.

Fabrication development will adapt several proprietary processes to generate large sheets of mullite for silicon-on-ceramic process. Further fabrication development will be required in forming containers for silicon for crystal growing and ribbon growing.

2.0 Technical Discussion of Results this Quarter

2.1 Compositional and Thermal Expansion Experiments

One of the most favorable properties of mullite for use in contact with silicon is the good match of mullite's thermal expansion with that of silicon. This thermal expansion match is very important in the silicon-on-ceramic process to minimize bowing of the substrate and possibly spalling off of the silicon from the ceramic. Furthermore, mismatch can also affect the electrical characteristics of silicon. For crucibles, the better the thermal expansion match the more likely the crucible will be reusable. As a result, compositional variations have been evaluated to better match the expansion.

The mullite compositions commercially available have thermal expansion coefficients from room temperature to 700°C of $4.1 - 4.7 \times 10^{-6}$ in/in/°C. Liter-

ature data for silicon is 3.92×10^{-6} in/in/°C in this temperature range. Fused mullite has a coefficient of thermal expansion in this temperature range of 4.96×10^{-6} in/in/°C, therefore, to lower the expansion in the body, the glass phase apparently must be increased and its expansion kept low. Initial attempts at higher silica content composition increased the apparent glass phase and gave a perceptable decrease in thermal expansion (Figure 1). Another attempt involved trying to form a low expansion bond borosilicate glass by adding boric acid to the composition. This composition had, in fact, a higher thermal expansion. (Figure 2) Based on these results, more compositions have been made to try to increase the glass phase and control the glass phase composition. Unfortunately, due to problems, the thermal expansion dilatometer, these experiments are not complete.

2.2 Sessile Drop Experiments

In order to evaluate these various compositions of mullite in contact with silicon, sessile drop experiments have been used. The procedure has been to melt high resistance, undoped silicon nuggets on mullite substrates for various times under 10^{-4} micron vacuum. Soak temperature for these experiments was 1450°C. The timing of the exposure was begun when the silicon nugget was completely molten. The exposure times so far used have been five minutes, twenty minutes, and ten hours. The five minute and twenty minute exposures produced no discernible gross difference among the compositions and firing variations. However, after ten hours the porous parts were badly attacked by the silicon. Figure 3 demonstrates this attack on the porous S-1-SI composition. It is speculated that the increased surface area of these porous parts leads to this increased chemical attack. Another run of this ten hour duration is planned so that the parts may be observed during this attack.

Figure 1 Thermal Expansion Curve High Silica S-1-SI

Figure 2 Thermal Expansion Curve B_2O_3 Dopeo S-1-SI

FIGURE 3

1450° C 10 minutes

1450° C 10 hours

Electrical four point resistance measurements are underway as are photo micro-graphic work and chemical analysis to evaluate these tests. Compositions of optimized thermal expansion will also be tested as they become identified.

2.3 Substrate Fabrication

2.3.1 Large Sheet - One of the requirements for Honeywell's silicon-on-ceramic process is for large sheets of mullite. The present requirement is for 100 CM x 10 CM x 0.1 CM substrates. These substrates have been delivered to Honeywell. The substrates were fired from a tape made by a proprietary roll compaction process. Two thicknesses were fired: .023 inches and .037 inches. It was quickly determined that the 0.23 inch thick material was too weak to handle except by the most careful methods. Therefore, all of the substrates delivered to Honeywell were of the .037 inch thickness. The fabricated tape was cut to the appropriate size to shrink to the desired length and width dimensions and fired on refractory setters to 1650 C for approximately 2 hours. The resultant parts were dense and conformed to the surface they were lying on. Figure 4 is a photograph of one of these substrates.

2.3.2 Substrates with slots and holes. - A further requirement of the Honeywell process is substrates with slots and holes for electrical back contacts to the silicon sheet. At present holes and slots .020 to .060 inches spaced .040 to .080 inches are being studied. Currently holes are being drilled or punched into green or bisqued tape while slots are cut into bisqued tape. Figure 5 shows some typical substrates being manufactured. All slots and holes are being cut into the small 1.5 x 2.0 substrates. As the slot design becomes finalized and the large substrates are required, larger samples with slots will be made.

2.4 Crucible Fabrication

Crucibles of mullite composition S-1-SI were fabricated this quarter. These

FIGURE 4
PHOTO LARGE SUBSTRATE

FIGURE 5

PHOTO SLOTTED SUBSTRATES

crucibles were approximately 2 inches diameter by 2 inches long. Half of these parts were fired to full density while the other half were fired to about 10% porosity. These crucibles were fabricated by ISO pressing and green forming. All samples will be manufactured in this manner to minimize body development which would be required to slip cast each composition. As the best composition for crucibles is determined a manufacturing process will be selected based on cost, material properties, and configuration.

2.5 Cost Analysis

2.5.1 Substrate Cost Analysis - An initial cost project has been made for large substrates (100 CM x 10 CM x 0.1 CM) without slots or holes. No consideration for potential specifications on size tolerance, flatness, smoothness, etc. All of these factors of course would increase the cost.

3.0 Plans for next Quarter

Next quarter will include more thermal expansion work including a thermal expansion measurement of silicon on our unit to allow better matching. More analysis of the sessile drop tests are planned along with another sessile drop test at ten hours with observation during the exposure. Substrate fabrication will center on slotted substrates and improved methods of manufacture. If lower expansion compositions are forth coming these will be made into slotted substrates for Honeywell's testing. Cost projections for various shaped crucibles should be ready next quarter.

4.0 New Technology

No significant new technology was developed this quarter.

FIGURE 6

COST ANALYSIS - MULLITE SUBSTRATESQuantity - $5 \times 10^6 \text{ m}^2/\text{year}$.

Size - 1m. x 10cm. x 1mm.

Breakdown\$/m² at 1mm thk.

Raw Material Cost	\$1.21
Body Preparation	\$0.02
Roll Compaction	\$1.25
Forming	\$0.25
Firing	\$7.21
Refractory	<u>\$1.25</u>
	\$11.19

Above costs based upon:

- a.) \$25/hr. labor rate with overhead
- b.) 80% process yield

For other compositions the RMC is as follows:

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

Sensitivity on above factors:

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

	<u>FIRING COST</u>
Standard Condition	\$8.46
10X Improvement	.845
20X Improvement	.423