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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. 3, April 1—July 15, 1978

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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. 3

By:

D. G. Wirth and J. D. Sibold
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ABSTRACT

Microstructural analysis of sessile drop experiments of silicon on mullite indicate reaction at the liquid solid interface which is especially severe after ten hours. Compositional variation including higher purity and elimination of the glass phase did not affect the reaction. The increased surface area of porous samples caused severe structural damage to these substrates. Reaction phases are found away from the interface after long exposure.

Compositional variations have been found to lower the thermal expansion of the mullite to the expansion of silicon. The addition of silica to a standard mullite body is found to increase the amount of glass phase while lowering expansion. It has also been found that a mixture of fused mullite and fused silica fires to a body with thermal expansion very near that of silicon. The thermal expansion of silicon was measured in the 111 crystal direction and found to concur with published data.

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1.0 Introduction

The objective of this study is to develop, evaluate, and fabricate mullite compositions for use as containers for molten silicon and substrates for silicon sheet. Mullite is a good candidate material since it is made from inexpensive raw materials - principally clays, a high temperature material - maintaining its shape above 1650°C, and has a thermal expansion near that of silicon. Mullite is commercially made by blending alumino-silicate clays with aluminum oxide. Upon firing fine needle-like mullite crystals form in a glass matrix. Variables such as purity, amount of glass phase, and density are being evaluated. The development goals are to minimize contamination of molten silicon by mullite, minimize thermal expansion mismatch with silicon and fabricate large crucibles and large substrates with holes and/or slots. Evaluation includes sessile drop experiments, thermal expansion measurements and supplying other contractors such as Honeywell with mullite samples to test in their processes. Fabrication of substrates is by several proprietary ceramic sheet processes. Containers are principally made by isopressing and slipcasting.

2.0 Technical discussion of Results this Quarter

2.1 Sessile Drop Experiments

Silicon Sessile drop experiments have been performed on mullite of eight composition and firing variations. The variations are listed below:

- A. S-1-SI - Coors standard mullite ISO press body
- B. High mullite content - Kyanite substituted for clay
- C. High glass S-1-SI - Excess SiO_2 added to S-1-SI
- D. Glass property modification - Attempt to add B_2O_3 to glass phase
S-1-SI
- E. Open porosity S-1-SI - S-1-SI fired to approximately 10% porosity

F. High purity S-1-SI - E P kaolin substituted for ball clay in S-1-SI

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

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

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

Selected samples were evaluated micrographically as shown in Figures 1 to 8. Figure 1 shows composition A (dense S-1-SI) with a 5 minute soak at 1450°C. Figure 1-a shows the substrate and crystallized sessile drop. The slight shadowing on the substrate results from the sessile drop moving around while molten. It is thought that gas evolution at the interface causes this motion. Figure 1-b and 1-c are polished sections of the interface at 50x and 200x respectively. The dark areas in the mullite (on the left) are pores. In Figure 1-c mullite crystals in the continuous glassy phase can be seen. Figure 2 is the same series of photographs of the same composition with a 10 hour (600 minute) soak. In Figure 2-a we can see that the sessile drop was much more mobile. The drop can also be seen to conform to the edge of the substrate. Figure 2-b shows apparent cracks in the silicon with also a large amount of debris in the silicon. It is also apparent that silicon is now filling some voids in the mullite close to the interface. Closer inspection

1a

FIGURE 1

Composition A - Dense S-1-SI
5 Minute Soak

- 1a - Substrate and Sessile Drop
- 1b - Polish Section 50x, Mullite
Left, Silicon Right
- 1c - Polish Section 200x
Mullite Left, Silicon Right

1b

1c

2a

FIGURE 2

Composition A - Dense S-1-SI 10 Hour
(600 Minute) Soak

- 2a - Substrate and Sessile Drop
- 2b - Polish Section 50x Mullite
Left, Silicon Right
- 2c - Polish Section 200x Mullite
Left, Silicon Right

2b

2c

in 2-c shows a reaction layer of different reflectivity at the interface and in the voids of the mullite body. There is also a reaction zone visible in the mullite, some of which is seen in the silicon. No chemical or phase analysis has been made of these reaction areas.

Figure 3 is composition E (open porosity S-1-SI) with 5 minute soak at 1450°C. At this length of time the only noted difference between composition A and composition E is the penetration of silicon into the open porosity of E. However, composition E after 10 hours (600 minutes) of soak time is shown in Figure 4 to have severe reaction. The substrate appears to be completely eroded and corroded away. (The smooth material in 4-b and 4-c is the potting material for the mount.) The sections 4-b and 4-c indicate the reacted substrate to be mainly composed of the same two reactants observed in Figure 2, the long soak time dense S-1-SI. It is assumed that the increased surface area of the porous substrate coupled with the lower firing temperature contributed to its poor showing in this test.

Composition F (high purity S-1-SI) soaked at 1450°C for 5 minutes is shown in Figure 5. At this exposure time F appears similar to the dense S-1-SI in Figure 1. In Figure 6 the 10 hour soak again shows the same reaction areas as Figure 2. Figure 6c is a 200x photo of an area away from the interface in the silicon containing the reaction phases. There seems to be no change in reaction due to the increased purity of composition F versus composition A.

Figures 7 and 8 show the electrically fused mullite, composition G. This composition has the highest purity, no apparent glass phase, and approximately 20% open porosity. In Figure 7 we see infiltration into the surface pores after 5 minute duration. We also see a crack extended from the mullite through the interface into the silicon. This crack is also observed in other

3a

FIGURE 3

Composition E - Open Porosity S-1-SI
5 Minute Soak

- 3a - Substrate and Sessile Drop
- 3b - Polish Section 50x Mullite
Left, Silicon Right
- 3c - Polish Section 200x Mullite
Left, Silicon Right

3b

3c

4a

FIGURE 4

Composition E - Open Porosity S-1-SI
10 Hour (600 Minute)
Soak

- 4a - Substrate with reacted area
- 4b - Polish Section 50x - Substrate
reacted Area Right, Potting
Material Left
- 4c - Polish Section 200x - Substrate
Reacted Area Right, Potting
Material Left

4b

4c

FIGURE 5

Composition F - High Purity S-1-SI
5 Minute Soak

- 5a - Substrate and Sessile Drop
- 5b - Polish Section 50x Mullite
Left Silicon Right
- 5c - Polish Section 200x Mullite
Left, Silicon Right

5a

5b

5c

6a

FIGURE 6

Composition F - High Purity S-1-SI
10 Hour (600 Minute)
Soak

- 6a - Substrate and Sessile Drop
- 6b - Polish Section 200x Mullite Left,
Silicon Right
- 6c - Polish Section 200x Reaction Zone
in Silicon

6b

6c

FIGURE 7

Composition G - Electrically Fused Mullite
5 Minute Soak

- 7a - Substrate and Sessile Drop
- 7b - Polish Section 50x Mullite Left,
Silicon Right
- 7c - Polish Section 200x Mullite Left,
Silicon Right

7a

7b

7c

FIGURE 8

Composition G - Electrically Fused
Mullite 10 Hour
(600 Minute) Soak

- 8a - Substrate and Sessile Drop
- 8b - Polish Section 200x Mullite Left,
Silicon Right
- 8c - Polish Section 200x Silicon
Reaction Zone

8a

8b

8c

compositions as well as in figure 8. The increased reaction with longer time is apparent although this reaction is not as severe as the porous S-1-SI composition. In Figure 8-c an area in the silicon away from the interface is observed to have the bright reaction product. In this photograph the reaction material appears to be crystallizing from a nucleation point.

From these sessile drop experiments we conclude that mullite is not stable in contact with molten silicon for extended periods of time. It appears that the mullite is dissolving in the silicon and subsequently precipitating. Higher purities and the lack of glass phase do not seem to improve the situation. Some analysis of these reaction phases are expected to be done shortly. Also four point resistivity should also be available. An additional experiment is anticipated with fused quartz being used as a standard.

2.2 Thermal Expansion Experiments

Mismatch in thermal expansion between silicon and mullite has become an area of concern for Honeywell's Silicon-On-Ceramic process. As Honeywell moves into coating thin slotted substrates the expansion mismatch is deteriorating the ceramic with time. For this reason and others enumerated earlier, composition and firing experiments have been under way to lower the thermal expansion of S-1-SI (Figure 9) towards that of silicon (Figure 10). (This may not be the absolute value for silicon, but is intended for comparing mullite compositions since both are measured on the same instrument.) As indicated in earlier reports, of the first eight compositions studied, the composition with the highest silica content had the lowest expansion. Based on this, experiments were designed to test the effect of silica on thermal expansion.

One of the first experiments was to make some mixtures of fused mullite and fused quartz. Of these mixtures a dry milled 60% electrically fused mullite

Figure 9 - Thermal Expansion S-1-SI

Figure 10
111 Silicon

and 40% crushed fused quartz crucible fired to a reasonable ceramic body. Thermal expansion proved to be quite low. (Room temperature to 800°C coefficient 3.74×10^{-6} in/in/°C Figure 11.) When this composition is fired at low temperature (1150°C) a discontinuous expansion curve results, Figure 12. Since this body would not be a low cost body, attempts were made to duplicate these results with clay derived mullite bodies.

The approach taken for these experiments was to add excess silica to a standard mullite composition. A standard body was blended with a fine naturally occurring amorphous silica. Figure 13 is a plot of the percent linear expansion at 800°C versus percent excess silica blended into the standard mullite body. The horizontal line at .29% linear expansion is the expansion recorded for 111 silicon. The asterisk is the expansion of a 60% fused mullite 40% fused quartz body plotted at its equivalent silica content. This plot indicates that thermal expansion can be varied with composition within the same body system. The fused mullite fused quartz system would appear to have a different plot. Other fused mullite-fused quartz mixtures have not been tried, since the goal was to closely match silicon. The excess silica in the standard mullite body seems to increase the amount of glass phase. X-ray diffraction analysis reveals mullite as the only crystalline phase. Cool down curves on the thermal expansion measurement do not show hysteresis that would be expected if another crystalline phase such as cristobalite or tridymite were precipitating during heating and cooling. Sample substrates for Honeywell are being fabricated from two of the lower expansion compositions. The compositions are the lowest expansion and an intermediate expansion. These are being made in the two thicknesses with and without slots.

2.3 Substrate Fabrication

Substrates 18 inches x 2 inches x .035 inches were fabricated and sent to

Figure 11

*60% Fused Mullite 40% Fused Quartz

Figure 12

60% Fused Mullite 40% Fused Quartz

Figure 13 Percent Linear Expansion at 800°C
vs % Excess Silica In Standard Mullite Body

Honeywell for SCIM coating experiments. These were of standard S-1-ST composition and were made from the normal tape process. Additionally, slotted substrates 1.7 x 2.7 x .035 inches were made from the same composition for dip coating experiments. Fabrication problems for both sides were minimal and yields of 85% were observed.

3.0 Plans for Next Quarter

During next quarter chemical analysis and 4 point resistivity tests will be concluded on the sessile drop tests. Since alumina is added to clay in standard mullite bodies to raise alumina content and silica is being added to this body to lower the expansion in this development work, elimination of alumina will be tried to lower the expansion without these offsetting additions to the formulation. Substrate fabrication is planned for dip coating specimens with and without slots using the lower thermal expansion compositions.

4.0 New Technology

Description - Lowering of thermal expansion of mullite through compositional variations

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