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April 1971

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DECOMPOSITION OF MULLITE

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April 1971

ABSTRACT

A qualitative study has been made of the high temperature surface decomposition of mullite ( $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ) pieces fired in atmospheres of He and air. At low partial pressures of oxygen, mullite decomposes with the evolution of SiO and  $\text{O}_2$ . This reaction becomes favorable with the decrease in  $P_{\text{O}_2}$  because of the correspondingly large increase of the equilibrium partial pressure of SiO. The formation of bubbles at a mullite-fused silica interface is due to a sufficient increase in gaseous product pressure caused by reactions of silica-rich glass and carbonaceous impurities in mullite.

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<sup>\*</sup>Now at Corning Glass Works, Corning, New York

## I. Introduction

During diffusion experiments in the  $\text{Al}_2\text{O}_3\text{-SiO}_2$  system,<sup>1</sup> it was noted that bubbles occurred at the interfaces in fused silica-2:1 mullite ( $2\text{Al}_2\text{O}_3\text{-SiO}_2$ ) couples annealed in He or air at high temperatures. Since care had been taken to avoid entrapped He at a couple interface and as no such phenomenon was observed with the sapphire-silica couples, it was surmised that decomposition was occurring at the interface of the mullite couple with the yielding of an insoluble volatile product.

Literature references concerning the decomposition of mullite are limited. Skola,<sup>2</sup> using X-ray analysis and optical microscopy, reported that pure synthetic mullite was partially decomposed when heated between graphite plates in a carbon resistance furnace at  $1700^\circ\text{C}$  since approximately 5 wt% corundum was detected after 4 h. Wright and Wolff<sup>3</sup> discovered that mullite bricks were severely attacked by reducing agents above  $1370^\circ\text{C}$  in a natural gas cracking plant. In the zone of greatest attack, a covering of porous corundum was found. They concluded that  $\text{SiO}_2$ , free or combined in the mullite, was reduced to  $\text{SiO}$  by carbon deposited from the cracked methane.

The objective of this study was to correlate the results of the observed decomposition reaction from both an experimental and a thermodynamic point of view.

## II. Experimental Procedure

Mullite,\* taken from a large fused cast ingot, was cut and polished

\* Supplied by Carborundum Corp., Niagara Falls, N.Y. Chemical analysis:  $\text{Al}_2\text{O}_3$  78.34,  $\text{SiO}_2$  23.50,  $\text{CaO}$  0.02,  $\text{Fe}_2\text{O}_3$  0.16,  $\text{Na}_2\text{O}$  0.28 wt%. (Approximately 1.0 wt% of the reported  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  is probably present as  $\text{SiC}$  and free alumina, respectively.)

to optical smoothness, washed in ethyl-alcohol, positioned in the center of a tantalum resistance furnace, and heated in He at approximately 0.7 atm ( $10^{-0.16}$  atm) from 1650° to 1800°C at 50°C intervals. Several runs were also made in air at 1650° and 1700°C in a Kanthal Super 33 element furnace. Similar anneals were made with fused silica<sup>\*</sup>-mullite couples as well as with fused silica-sapphire couples. Since none of the heated specimens were in a sealed crucible, the oxygen pressure above them was determined by the tantalum heating element in the helium runs or the normal air atmosphere.

The mullite in the couples was previously annealed in air at 1200°C. An examination of the mullite specimens with a stereo binocular microscope, however, showed particles of carbon or SiC (Fig. 1). It was found that more intensive heating was necessary to remove the black particles, e.g. 1700°C for several days. Additional heatings of fused silica-mullite couples using mullite annealed at 1200°C and 1700°C were then made at 1750°C in helium at 1 atm. Furthermore, under higher magnifications than that of Fig. 1 with a metallographic microscope, the mullite grains were observed to be surrounded by a continuous glassy layer (Fig. 2). An analysis of the original mullite with a Norelco diffractometer, using  $\text{CuK}_\alpha$  radiation filtered through Ni, showed a very small amount of  $\alpha\text{-Al}_2\text{O}_3$  in addition to mullite.

### III. Results and Discussion

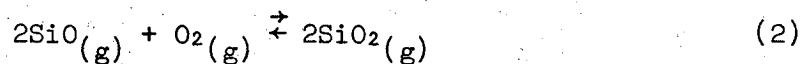
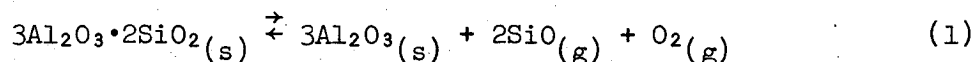
X-ray diffraction analysis revealed that firing at low oxygen pressures, i.e. helium, promoted the formation of  $\alpha\text{-Al}_2\text{O}_3$  on the mullite

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<sup>\*</sup>Amersil (Div. of Engelhard Ind. Inc., Hillside, N.J.).

surfaces in increasing amounts with time at a given temperature and with temperature at a constant time; after 12 h at all temperatures only  $\alpha$ - $\text{Al}_2\text{O}_3$  was detected on the surface. An example of the change in surface appearance with time is shown in Fig. 3. In contrast, heating in air at  $1650^\circ\text{C}$  for as long as 11 days produced almost no decomposition, Fig. 3d.

To explain the mechanism of this decomposition, several reactions were considered and their equilibrium constants evaluated at  $1650^\circ\text{C}$ . Only those reactions which contained  $\text{Al}_2\text{O}_3$  as a solid product had equilibrium constants high enough to be considered as principal decomposition reactions. A simple decomposition of the mullite with vaporization of  $\text{SiO}_2$  was not occurring since it would have had to occur both in air and in He. The vaporizing species must then be  $\text{SiO}$  and  $\text{O}_2$ . The thermodynamic calculations were made on this basis using data for 3:2 mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), as data for the 2:1 composition are not available. The step reactions considered to represent the decomposition process are



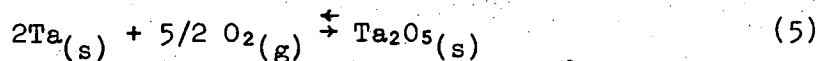
The standard Gibbs free energies for these reactions are given by Eqs. (3) and (4).

$$\Delta G^\circ = -RT \ln[(P_{\text{SiO}})^2(P_{\text{O}_2})] \quad (3)$$

$$\Delta G^{\circ} = - RT \ln \frac{(P_{\text{SiO}_2})^2}{(P_{\text{SiO}})^2 (P_{\text{O}_2})} \quad (4)$$

The values for  $\Delta G^{\circ}$ , calculated from available data,<sup>4</sup> and the resulting values of  $\log [(P_{\text{SiO}})^2 (P_{\text{O}_2})]$  and  $\log [(P_{\text{SiO}_2})^2 / (P_{\text{SiO}})^2 (P_{\text{O}_2})]$  are presented in Tables I and II for the temperature range of 1650-1800°C.

The partial pressure of oxygen is set by the furnace atmosphere. Firing in air, it is  $10^{-0.68}$  atm; however, in helium, it is determined, in these experiments, by the tantalum heating element. The oxidation of tantalum<sup>5</sup> is represented by



The values for  $\Delta G^{\circ}$  and the log of the equilibrium partial pressure of oxygen for the test temperatures are given in Table III.

The conditions for dissociation of mullite can be determined from Eqs. (3) and (4) and Tables I and II. As an example, in air at 1650°C the equilibrium partial pressure of SiO is  $10^{-8.91}$  atm and of SiO<sub>2</sub>,  $10^{-7.07}$  atm. In a helium atmosphere at the same temperature in the presence of tantalum, the equilibrium partial pressures of oxygen and SiO are  $10^{-13.59}$  and  $10^{-1.96}$  atm, respectively, while that of SiO<sub>2</sub> remains  $10^{-7.07}$  atm. Since the equilibrium partial pressure of SiO<sub>2</sub> is the same in both cases and not high enough to cause decomposition, the first step of the reaction represented by Eq. (1), as previously assumed, controls the dissociation of mullite. In the static air

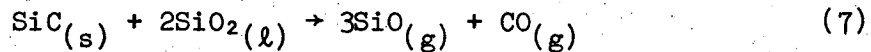
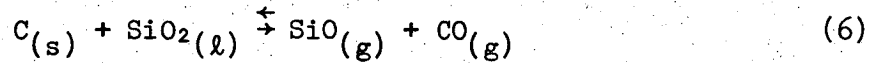


atmosphere, the  $P_{\text{SiO}}$  in the vicinity of the specimen must have reached  $10^{-8.91}$  atm immediately thus preventing dissociation. In helium, however, the  $P_{\text{SiO}}$  equilibrium pressure of  $10^{-1.96}$  was not attained, and the mullite continued to decompose.

This analytical approach can now be applied to explain the formation of bubbles at the interfaces of the fused silica-mullite diffusion couples. A minimum gas pressure of 0.7 or 1 atm was required to nucleate the bubbles at the interface. The total equilibrium pressure of the gaseous products of the mullite decomposition (Eq. (1)) varies from  $8 \times 10^{-3}$  to  $11.4 \times 10^{-3}$  atm in the temperature range of  $1650^\circ$  to  $1800^\circ\text{C}$ . Thus, even at  $1800^\circ\text{C}$ , the decomposition of mullite, alone, cannot be the cause of the observed bubbles. The actual SiO and  $\text{O}_2$  equilibrium pressures are probably somewhat higher than those calculated since the free energy of formation of thermodynamically metastable 2:1 mullite should be less negative than that of stable 3:2 mullite, thus making the  $(P_{\text{SiO}})^2(P_{\text{O}_2})$  values of Table I larger. There is also the possibility that the  $P_{\text{O}_2}$  in the helium atmosphere may be lower if the tantalum heating element is not saturated with oxygen. Nevertheless, it is quite unlikely that these corrections would be enough to raise the total SiO and  $\text{O}_2$  pressure to 0.7 or 1 atm.

The presence of C or SiC impurities in the mullite result in gas forming reactions that contribute to raising the gas pressure at the interfaces of fused silica-mullite diffusion couples: the couple heated in 1 atm of helium at  $1750^\circ\text{C}$  using mullite annealed in air at  $1700^\circ\text{C}$  showed considerably smaller bubbles at the interface than the one using  $1200^\circ\text{C}$ -annealed mullite. The impurities are reacting either with mullite

or with the glassy layer surrounding the mullite grains (Fig. 2). This latter possibility is represented by Eqs. (6) and (7).



The total equilibrium pressure of the gaseous products of the reaction described in Eq. (6) varies from 0.74 to 3.40 atm in the temperature range of 1650 to 1800°C. Similarly, the total equilibrium pressure of the products of the reaction described in Eq. (7) varies from 0.32 to 1.06 atm. Thus, either of these reactions can provide the needed pressure to nucleate bubbles at the fused silica-mullite interfaces. Similar calculations of gaseous product pressures for the reactions of C or SiC with mullite in the same temperature range indicate that these reactions are unfavorable.

#### IV. Conclusions

At low partial pressures of oxygen, mullite decomposes with the evolution of SiO and O<sub>2</sub>. This reaction becomes favorable with the decrease in P<sub>O<sub>2</sub></sub> as a result of the correspondingly large increase of the equilibrium partial pressure of SiO. The formation of bubbles at the mullite-fused silica (glass) interface, however, requires the additional factor of a gaseous product pressure greater than that of the furnace atmosphere. This is achieved by the formation of gaseous CO and additional SiO from the reactions of silica-rich glass with carbonaceous

impurities.

#### Acknowledgments

Grateful acknowledgment is extended to John Chipman, Leo Brewer, and John J. Margrave for helpful discussions. This work was done under the auspices of the United States Atomic Energy Commission.

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Table I. Thermodynamic data for Eq. (1)

Temperature (°C)	$\Delta G^\circ$ (Kcal/mole)	Log $[(P_{\text{SiO}})^2 P_{\text{O}_2}]$
1650	153.812	-17.50
1700	148.355	-16.50
1750	142.775	-15.45
1800	137.197	-14.55

Table II. Thermodynamic data for Eq. (2)

Temperature (°C)	$\Delta G^\circ$ (Kcal/mole)	$\text{Log} [(P_{\text{SiO}_2})^2 / (P_{\text{SiO}})^2 (P_{\text{O}_2})]$
1650	-29.455	3.36
1700	-27.623	3.08
1750	-25.794	2.79
1800	-23.963	2.53

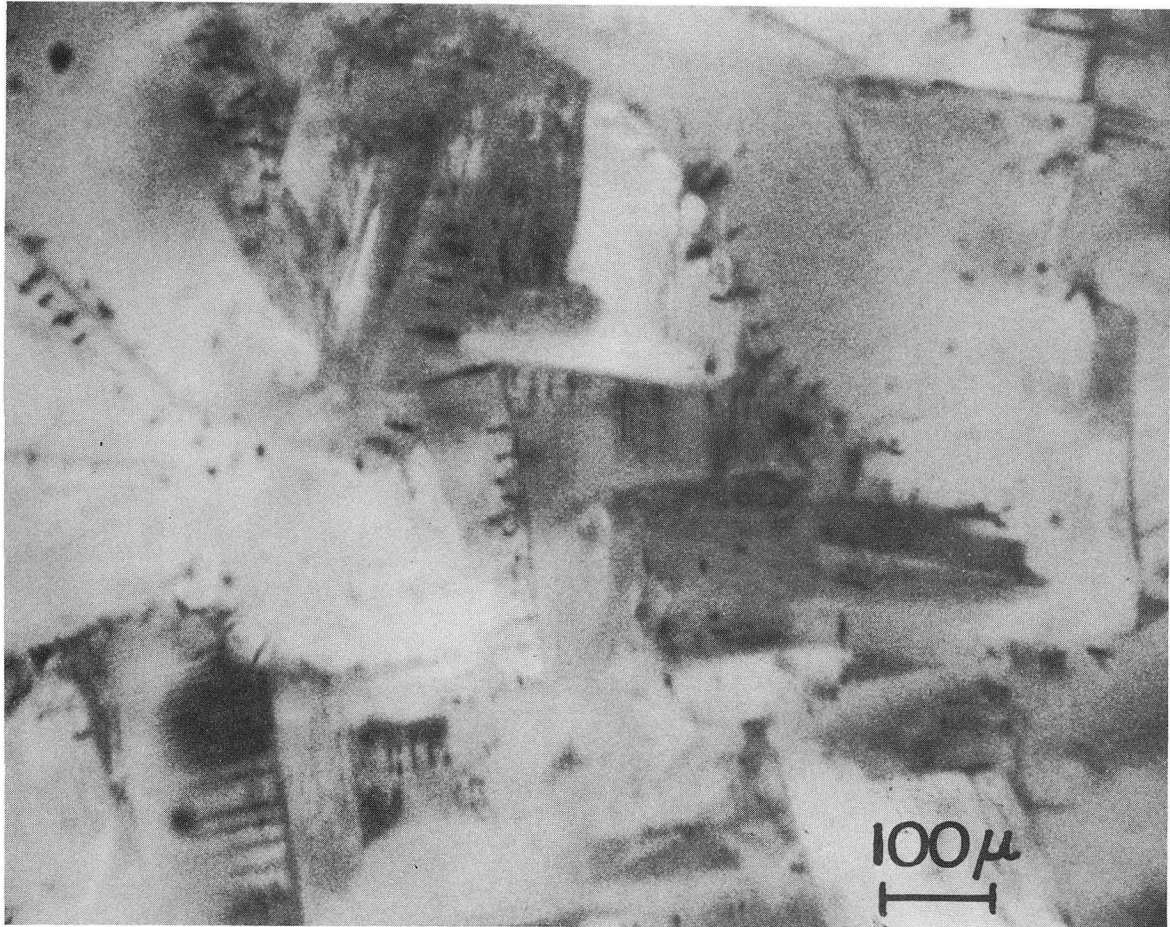
Table III. Thermodynamic data for Eq. (5)

Temperature (°C)	$\Delta G^\circ$ (Kcal/mole)	Log $P_{O_2}$
1650	-297.890	-13.59
1700	-293.318	-13.04
1750	-288.769	-12.52
1800	-284.226	-12.03

Figure Captions

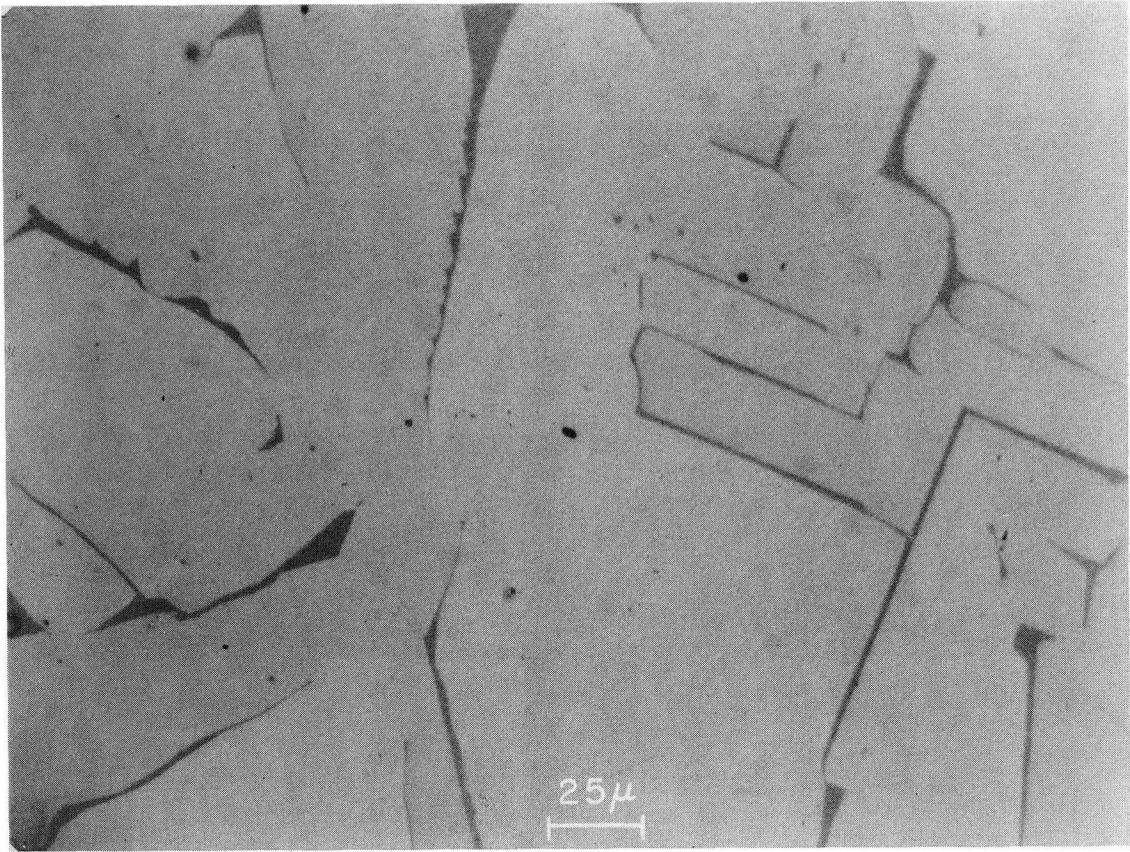
- Figure 1. Microstructure of mullite, annealed at 1200°C, as observed with a stereo binocular microscope. The dark spots are C or SiC particles within the specimen.
- Figure 2. Microstructure of mullite as observed with a metallographic microscope using reflected light. The white spots are C or SiC particles intersecting the polished surface.
- Figure 3. Microstructure of mullite pieces; (a) unfired; fired in helium at 1750°C for (b) 30 min, and (c) 12 h, and (d) fired in air at 1650°C for 11 days.





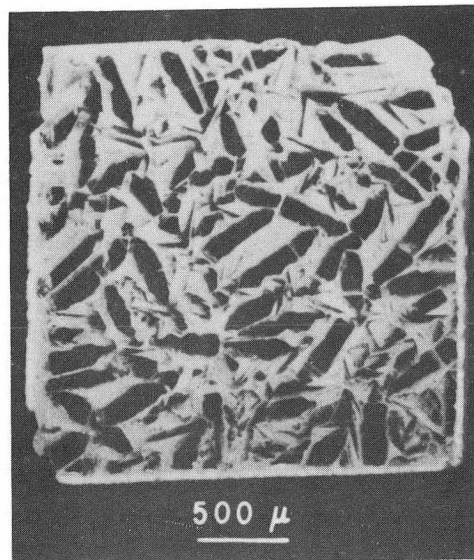
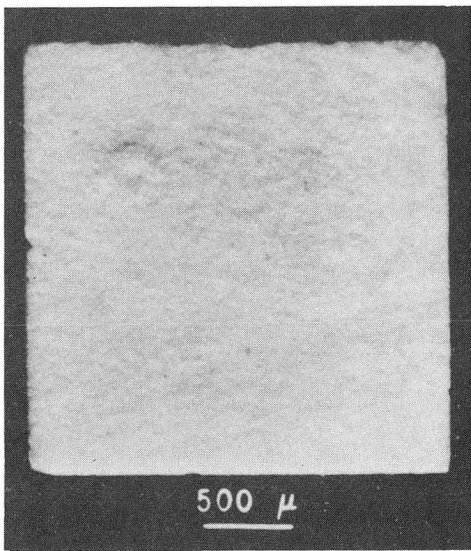
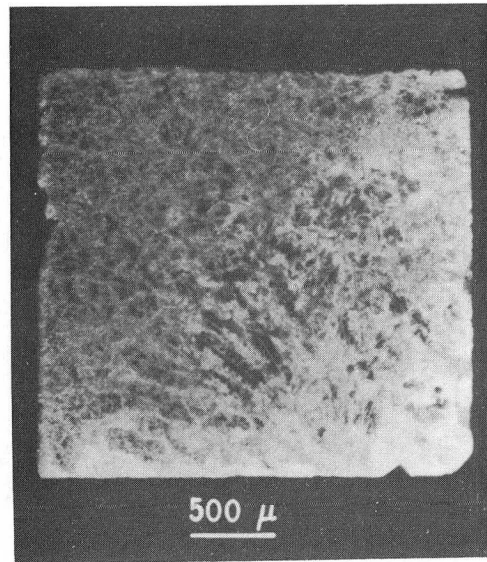
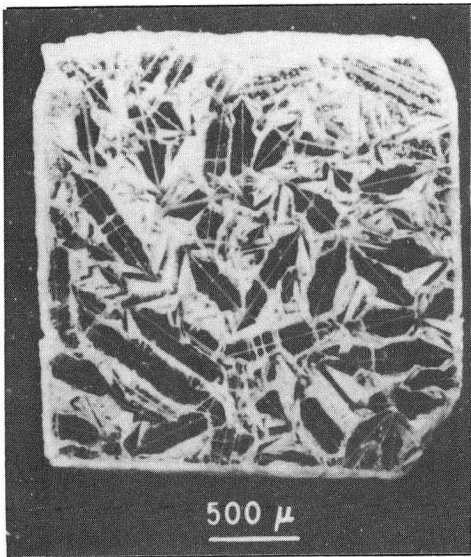
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Fig. 1.



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Fig. 2.



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Fig. 3.

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