Decomposition of Mullite

ROBERT F. DAVIS,[*] İLHAN A. AKSAY, and JOSEPH A. PASK

Inorganic Materials Research Division, Lawrence Berkeley Laboratory, and Department of Materials Science and Engineering,
College of Engineering, University of California, Berkeley, California 94720

Free surfaces of 2:1 mullite ($2Al_2O_3{\cdot}SiO_2$) specimens decomposed with the evolution of SiO and O_2 when they were heated at high temperatures under low partial pressures of O_2; this reaction was analyzed thermodynamically. In addition, bubbles were observed at internal interfaces between mullite and fused-SiO_2 diffusion couples. These bubbles, when formed at 1 atm ambient pressure between 1650° and 1800°C, resulted from reaction of Si particles and residual SiO_2-rich glass in the fused cast mullite.

I. Introduction

During an investigation of diffusion kinetics in the Al_2O_3-SiO_2 system,[1] bubbles were observed at the interfaces in fused SiO_2-2:1 mullite ($2Al_2O_3{\cdot}SiO_2$) couples annealed in static He or in air at high temperatures. Since care had been taken to avoid entrapping He at couple interfaces and since no such phenomenon was observed with sapphire-SiO_2 couples, it was surmised that a reaction which involved the mullite and yielded an insoluble volatile product having a pressure greater than that of the surrounding atmosphere was occurring at the interface of the fused SiO_2-mullite couple.

Several workers have studied the decomposition of mullite. Skola,[2] using X-ray analysis and optical microscopy, reported that pure synthetic mullite decomposed partially when it was heated between graphite plates in a carbon resistance furnace at 1700°C; $\approx$5 wt% corundum was detected after 4 h. Wright and Wolff[3] discovered that mullite bricks were severely attacked by reducing agents above 1370°C in a natural-gas cracking plant; in the zone of greatest attack, the bricks were covered with porous corundum. These workers concluded that SiO_2, free or combined in the mullite, was reduced to SiO by carbon deposited from the cracked methane.

The objective of the present study was to determine the nature of the observed reaction from both experimental and thermodynamic points of view.

II. Experimental Procedure

Specimens were cut from a fused cast ingot of mullite prepared by an arc fusion process,[†] annealed in air at 1200°C for 24 h, polished to optical smoothness, and washed in ethyl alcohol. Ceramographic (reflected light) examination showed crystalline grains surrounded by a continuous glassy phase and some bright spots (Fig. 1). X-ray diffraction analysis using Cu$K\alpha$ radiation identified only mullite; electron microprobe analysis of the crystalline phase showed an average of 75.8±1 wt% Al_2O_3. These analyses and the nature of the mullite formation[1] indicate that the mullite was of the 2:1 type.

A stereo binocular microscope focused below the surface plane clearly revealed that the bright spots were black particles throughout the specimen (Fig. 2) which were reduced considerably in amount by additional heating in air at 1700°C for 48 h. Such particles could be C, SiC, or Si; an electron microprobe examination and their solubility in a solution of HF and HNO_3 indicated that the particles in these specimens were Si.

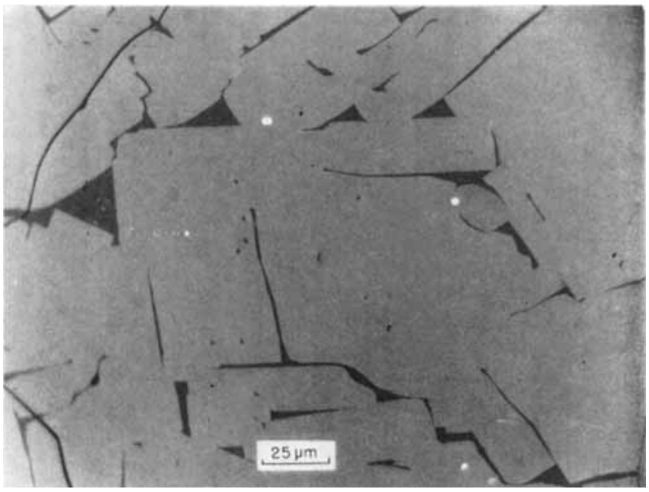

Fig. 1. Microstructure of mullite observed using reflected light. White spots are Si particles intersecting polished surface.

Mullite, fused SiO_2[‡]-mullite couples, and fused SiO_2-sapphire couples were heated in a Ta resistance furnace in static He[§] at $\approx$0.7 atm ($10^{-0.16}$ atm) from 1650° to 1800°C in 50° intervals for 0.5, 1, 3, 6, and 12 h. Several couples were heated in air at 1650° and 1700°C in a furnace with Kanthal Super 33 elements.[¶] Fused SiO_2-mullite couples containing the mullite which had been further annealed at 1700°C were also heated in He at 1 atm at 1750°C for 48 h. Temperature was controlled by thermocouples of W5Re–W26Re in He and Pt6Rh–Pt30Rh in air; the variance was ±3° at 1650°C.

Since all specimens were heated in open crucibles, the equilibrium O_2 pressure above them was determined by the furnace atmosphere. In air, the P_{O_2} was $10^{-0.68}$ atm; in He, it was determined by the Ta heating element. The oxidation of Ta (Ref. 4) is represented by

$$2Ta(s)+{}^5/_2O_2(g)\rightleftarrows Ta_2O_5(s) \qquad (1)$$

Thermodynamic data for the test temperatures are given in Table I.

III. Results and Discussion

(1) Mullite Specimen Surfaces

X-ray diffraction analysis of the surfaces of mullite specimens heated in He showed that increasing amounts of α-Al_2O_3

Received April 12, 1971; revised copy received September 1, 1971.

Work performed under the auspices of the United States Atomic Energy Commission.

[*] Now with Corning Glass Works, Corning, N. Y. 14830.

[†] Carborundum Corp., Niagara Falls, N. Y. Spectrographic analysis by American Spectrographic Laboratories, San Francisco, Calif.: as oxides (wt%) Ca 0.006, Fe 0.02, Na 0.12, Mg 0.01, Zr 0.01, Ti 0.005, Cr 0.003, Mn <0.001, and Cu <0.005; Al and Si principal constituents. Stoichiometric 3:2 mullite ($3Al_2O_3{\cdot}2SiO_2$), Al_2O_3 71.8 wt%; 2:1 mullite, Al_2O_3 77.3 wt%.

[‡] Amersil, Division of Engelhard Industries, Inc., Hillside, N. J.

[§] Analysis showed 2 ppm N_2 and 1 ppm O_2.

[¶] The Kanthal Corp., Bethel, Conn.

Fig. 2. Microstructure of mullite annealed at 1200°C observed with stereo binocular microscope. Black features are Si particles within the specimen.

Table I. Thermodynamic Data for Eq. (1)

Temp. (°C)	$\Delta G°$ (kcal/mol)	Log P_{O_2}
1650	−297.890	−13.59
1700	−293.318	−13.04
1750	−288.769	−12.52
1800	−284.226	−12.03

formed, with a corresponding decrease in mullite, with increasing time at a given temperature and with increasing temperature at a given time. An example of the change in surface appearance with time is shown in Fig. 3; examination of the specimen heated for 12 h at 1750°C in He revealed only α-Al_2O_3 (Fig. 3(*C*)), whereas a specimen heated in air at 1650°C for 11 days (Fig. 3(*D*)) contained no α-Al_2O_3.

Equilibrium constants of possible reactions were evaluated at 1650°C. In agreement with experimental observations, only the reactions with α-Al_2O_3 as a product were favorable. Decomposition of mullite by direct vaporization of molecular SiO_2 was excluded because such a reaction would occur in both He and air. The following step reactions were thus considered to represent the decomposition:

$$3Al_2O_3\cdot 2SiO_2(s) \rightleftarrows 3Al_2O_3(s)+2SiO(g)+O_2(g) \qquad (2)$$

$$2SiO(g)+O_2(g) \rightleftarrows 2SiO_2(g) \qquad (3)$$

The $\Delta G°$ values for Eq. (2) were calculated using thermodynamic data for 3:2 mullite because data for 2:1 mullite are not available. The free energy of formation of thermodynamically metastable 2:1 mullite,[5] however, should be less negative than that of the stable 3:2 compound. The standard

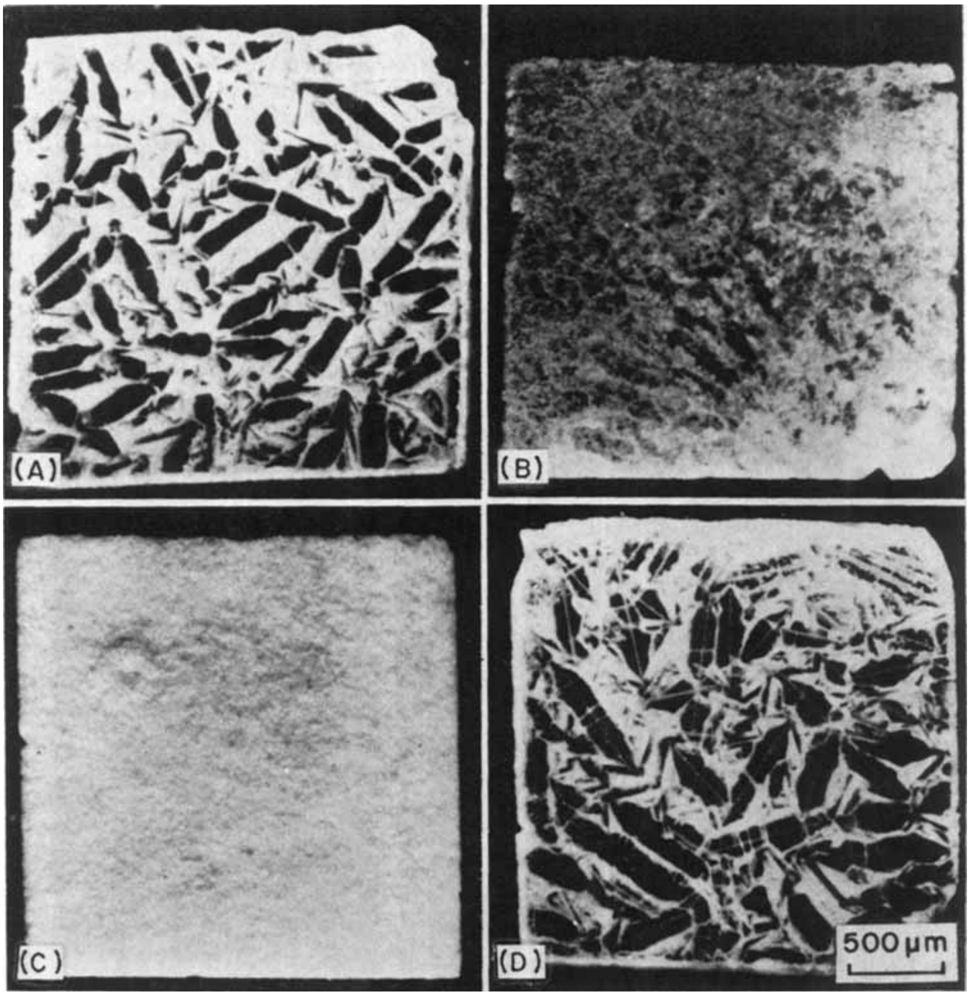

Fig. 3. Microstructure of mullite pieces which were (*A*) unfired, (*B*) fired in He at 1750°C for 30 min, (*C*) fired in He at 1750°C for 12 h, and (*D*) fired in air at 1650°C for 11 days.

Table II. Thermodynamic Data for Eq. (2)

Temp. (°C)	$\Delta G°$ (kcal/mol)	Log $[(P_{SiO})^2 P_{O_2}]$
1650	153.812	−17.50
1700	148.355	−16.50
1750	142.775	−15.45
1800	137.197	−14.55

Table III. Thermodynamic Data for Eq. (3)

Temp. (°C)	$\Delta G°$ (kcal/mol)	Log $[(P_{SiO_2})^2/(P_{SiO})^2(P_{O_2})]$
1650	−29.455	3.36
1700	−27.623	3.08
1750	−25.794	2.79
1800	−23.963	2.53

Gibbs free energies for reactions (2) and (3) are given by Eqs. (4) and (5):

$$\Delta G° = -RT \ln [(P_{SiO})^2 (P_{O_2})] \tag{4}$$

$$\Delta G° = -RT \ln \frac{(P_{SiO_2})^2}{(P_{SiO})^2 (P_{O_2})} \tag{5}$$

and values calculated from available data[6] are listed in Tables II and III.

The conditions for dissociation of mullite can be determined from Eqs. (4) and (5) and Tables II and III. As an example, in air at 1650°C at equilibrium, P_{SiO} is $10^{-8.91}$ atm and P_{SiO_2} $10^{-7.07}$ atm. In He at 1650°C in the presence of Ta at equilibrium, P_{O_2} and P_{SiO} are $10^{-13.59}$ and $10^{-1.90}$ atm, respectively, whereas P_{SiO_2} remains $10^{-7.07}$ atm. The first step of the reaction, represented by Eq. (2), thus controls the dissociation of mullite. In air, P_{SiO} near the specimen must reach $10^{-8.91}$ atm immediately to prevent dissociation. In He, however, the equilibrium SiO partial pressure, $10^{-1.90}$ atm, was not *attained, and the mullite continued to decompose.*

(2) *Fused SiO_2-Mullite Interfaces*

The formation of bubbles at the interfaces of the fused SiO_2-mullite couples depended on the generation of a pressure of gaseous products greater than the atmospheric pressure, i.e. 0.7 or 1 atm. *The decomposition of mullite just described* thus cannot cause the observed bubbles since the total calculated equilibrium pressure of the gaseous products of the decomposition (Eq. (2)) varied from 8×10^{-3} to 11.4×10^{-3} atm at 1650° to 1800°C. Although the actual equilibrium P_{SiO} and P_{O_2} were probably somewhat higher than the calculated values because of the presence of 2:1 mullite instead of the 3:2 compound, it is unlikely that the total SiO and O_2 pressure exceeded 0.7 or 1 atm.

The Si particles in these mullite specimens must then participate in gas-forming reactions that result in high gas pressures at the interfaces of the couples. This premise is supported by the appearance of smaller bubbles at the interface of a couple containing mullite annealed at 1700°C compared with those in a couple containing mullite annealed at 1200°C (Fig. 4). The Si particles would be expected to react with either the SiO_2 in the mullite or that in the glassy layer surrounding the mullite grains. Reaction with the glassy layer is more favorable; the reaction with a glass containing only SiO_2 is represented by:

$$Si(l) + SiO_2(l) \rightleftharpoons 2SiO(g) \tag{6}$$

The equilibrium pressure of the gaseous product increases from 0.37 to 1.29 atm at 1650° to 1800°C. A similar calculation of the pressure of the gaseous products for the corresponding reaction of Si with mullite indicates an increase from 3.24×10^{-9} to 6.02×10^{-8} atm. Since Al_2O_3 is in solution in the liquid phase of the mullite specimen and since this phase is in equilibrium with the mullite,[1] continued reaction with the Si particles should cause precipitation of mullite; the $\Delta G°$ for the reaction would then be expected to be smaller and the gaseous-product pressure greater at a given temperature. *Thus, this reaction provides the needed pressure to nucleate* bubbles at the fused SiO_2-mullite diffusion-couple interfaces.

If the particles had consisted of C or SiC and if the reaction had proceeded fast enough, the total pressure of the gaseous products of their reaction with SiO_2 glass would have increased from 0.74 to 3.40 atm and from 0.32 to 1.06 atm, respectively, at 1650° to 1800°C. Thus, these reactions could also have provided the needed pressure to nucleate the bubbles observed at the couple interface.

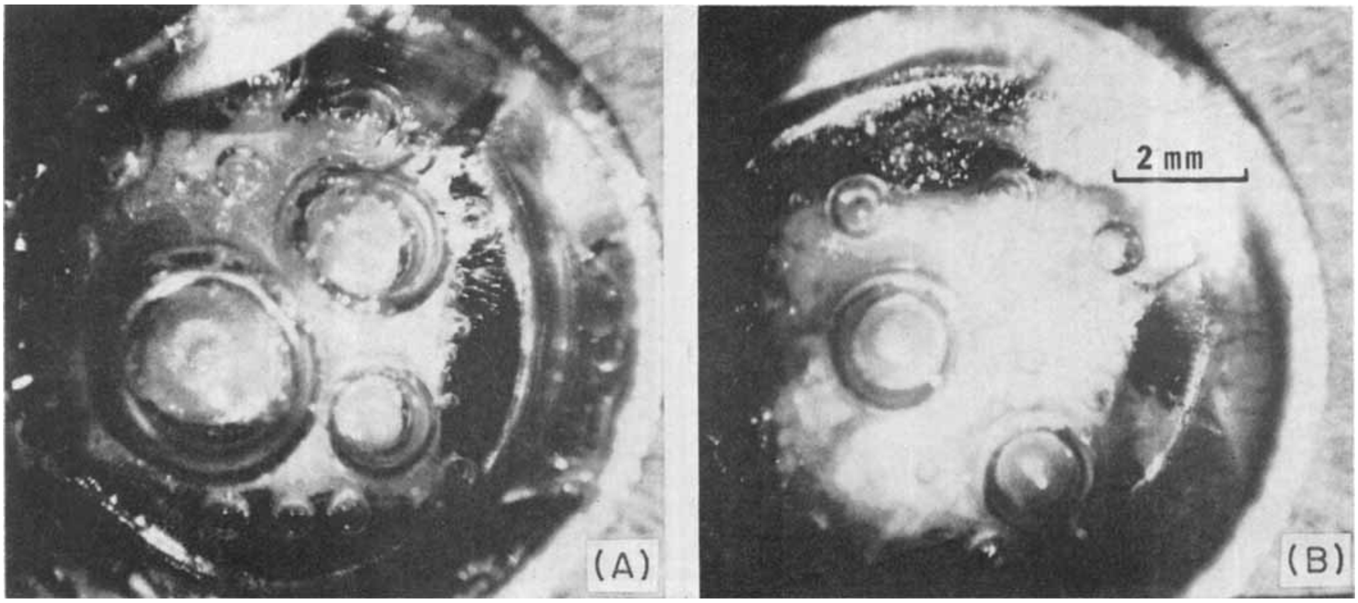

Fig. 4. Bubbles at fused SiO_2-mullite interface at 1750°C in 1 atm He, using mullite (*A*) annealed at 1200°C for 24 h and (*B*) annealed further at 1700°C for 48 h.

IV. Conclusions

At low partial pressures of O_2 and at high temperatures, 2:1 mullite ($2Al_2O_3 \cdot SiO_2$) decomposes with the evolution of SiO and O_2. Bubbles form at a mullite-fused SiO_2 interface because the pressure of the gaseous products of reaction of SiO_2-rich glass and Si particles present in this mullite specimen exceeds the ambient pressure. The additional presence of C or SiC would also contribute to the increase in gaseous products and pressures. At $\approx$1 atm ambient pressure, the decomposition of mullite alone cannot provide sufficient gaseous-product pressure to nucleate bubbles.

Acknowledgments
Grateful acknowledgment is extended to John Chipman, Leo Brewer, John J. Margrave, and Paul Cichy for helpful discussions and to Neal W. Houlding for assistance in the laboratory work.

References

[1] R. F. Davis and J. A. Pask, "Diffusion and Reaction Studies in the Alumina-Silica System"; submitted to the *Journal of the American Ceramic Society.*
[2] Vladimir Skcla, "Thermal Decomposition of the Mullite Phase," *Keram. Rundsch. Kunst-Keram.*, **45**, 188–215 (1937).
[3] R. E. Wright and H. I. Wolff, "Refractory Problems in Production of Hydrogen by Pyrolysis of Natural Gas," *J. Amer. Ceram. Soc.*, **31** [2] 31–38 (1948).
[4] O. Kubaschewski, E. L. Evans, and C. B. Alcock, Metallurgical Thermochemistry, 4th ed. Pergamon Press, Oxford, 1967.
[5] Shigeo Aramaki and Rustum Roy, "Revised Phase Diagram for the System Al_2O_3-SiO_2," *J. Amer. Ceram. Soc.*, **45** [5] 229–42 (1962).
[6] JANAF Thermochemical Tables. Thermal Research Laboratory, Dow Chemical Co., Midland, Mich., August 1967.

Computation of Residual Stresses in Quenched Al_2O_3

W. R. BUESSEM[*] **and R. M. GRUVER**
Ceramic Finishing Company, State College, Pennsylvania 16801

A method of computing the residual stress profile in quenched Al_2O_3 rods was developed. For these calculations, certain material parameters must be determined. Thus, strain rate was measured as a function of stress for 96% Al_2O_3 at 1300° to 1500°C, and the heat-transfer rates of cylindrical samples quenched in several media were determined. Using calculated temperature distributions and measured strain rates, plastic strains were computed for the entire quenching period, and these strains were converted to a profile of residual room-temperature stresses. The substantial increases in flexural strength observed in Al_2O_3 after it is quenched (thermally conditioned) are considered to originate in the residual compressive surface layers.

I. Introduction

Several workers[1] have strengthened polycrystalline Al_2O_3 considerably by quenching it in fluid media. The resulting increases in tensile and flexural strength can be ascribed in most cases to residual compressive stresses in the surface. In the present work, computation of these stresses was attempted to determine if they are of the correct order of magnitude and to correlate their magnitude and distribution with the material properties and the parameters of the quenching process.

Basically, strengthening of Al_2O_3 by quenching is analogous to strengthening of glass by tempering. It appears that tempering of Al_2O_3 should be the simpler process, since Al_2O_3 is crystalline and does not change structurally during the critical period, as glass does. However, "transient plastic creep," which will be discussed in Section II(1), introduces an element of structural change which is neither completely understood nor easily accounted for.

II. Procedure

(1) Plasticity

At high temperatures, small-grained polycrystalline Al_2O_3 exhibits a linear plasticity (vacancy creep) which is described by the Nabarro-Herring[2] equation. Under a uniaxial normal stress, σ, the normal strain rate, $\dot{\epsilon}$, is given by

$$\dot{\epsilon} = \frac{1}{3\eta}\sigma \qquad (1)$$

where η is the viscosity.[3]

For the 96% Al_2O_3[†] used in the present investigation, the proportionality factor, $1/(3\eta)$, was determined by (1) compressive-strain-rate measurements on cylinders ½ in. in diameter and ¼ in. high, (2) deflection-rate measurements using three-point bending of rods ⅛ in. in diameter, and (3) tensile-strain-rate measurements on rods ⅛ in. in diameter. The deflection and tensile tests gave consistent values, but the compression measurements gave lower results which were ascribed to the friction between the graphite cylinders transmitting the pressure and the sample; the latter measurements were thus discarded.

The steady-state strain rate measured in the present experiments agrees well with that determined by Warshaw and Norton[4] for Al_2O_3 of the same grain size (10 μm) in the temperature range ($\approx$1500°C) covered in both investigations. Present measurements were extended to 1400° and 1300°C, but the slope of the plot of $\ln \dot{\epsilon}$ vs $1/T$ was unchanged.

When the linear part of the creep-rate-vs-time curve (steady-state creep) is extrapolated to zero time, a positive strain is obtained.[5] This strain is quite large; it exceeds the elastic strain by several orders of magnitude and must be considered plastic. This "transient creep" is important because it prevents crazing of the surface up to severe quenching rates and increases the deformation rate by a factor. As a first ap-

---

Presented at the 72nd Annual Meeting, The American Ceramic Society, Philadelphia, Pa., May 6, 1970 (Joint Session IV, No. 6–JIV–70). Received April 2, 1971; revised copy received September 18, 1971.
Supported by the Naval Air Systems Command under Contract No. N00019–67–C–0489.

[*] Professor emeritus of ceramic science, The Pennsylvania State University, University Park, Pa. 16802.

[†] American Lava Corp., Chattanooga, Tenn.