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Densities of SiO_2-Al_2O_3 Melts

ILHAN A. AKSAY* and JOSEPH A. PASK*

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

ROBERT F. DAVIS*,†

Department of Materials Engineering and The Engineering Research Services Division, North Carolina State University, Raleigh, North Carolina 27607

The densities of binary aluminosilicate melts were measured X-radiographically as a function of Al_2O_3 concentration between 1800° and 2000°C. Within this temperature range, the density curves vary linearly and are parallel from fused SiO_2 to ≈30 to 45 mol% Al_2O_3, depending on the temperature. At higher Al_2O_3 contents, negative deviation from linearity increases with increasing temperature. Recent supplementary research efforts on various aspects of the system SiO_2-Al_2O_3 indicate that the changing coordination and structural role of the aluminum ion may be a primary factor in determining the shapes of the density curves.

I. Introduction

The Boltzmann-Matano analysis of diffusion data derived from SiO_2-Al_2O_3 melts[1] requires accurate measurement of melt densities. These densities were determined for the entire binary system in the range 1700° to 2000°C using an X-radiographic technique developed by Rasmussen and Nelson.[2] The technique involved measuring the volume of a melt at temperature from its radiographed image and relating this volume to its density. This method was especially suitable for the aluminosilicate melts, since the specimens had to be sealed in molybdenum containers to eliminate silica losses during the measurements. The present study describes the density changes observed as a function of Al_2O_3 concentration and temperature and relates this data in terms of possible structural changes of the atomic species, primarily aluminum and oxygen.

II. Experimental Procedure

The binary compositions chosen for this study contained 22.8, 42.2, 60.0, and 80.0 wt% Al_2O_3.‡ These mixtures were weighed, then melted in electron-beam-sealed, He-tight Mo capsules at 1953°C in vacuum for ≈30 to 60 min.

The X-radiographic measurements were made by Rasmussen§ using the system described in Ref. 2. The specimens were heated at a rate of 3°C/min at 1700° to 2000°C. The temperature (International Practical Temperature Scale (IPTS) 68) was monitored continuously with a two-color pyrometer accurate to ± 10°C. The specimen images were obtained at 25°C intervals using a 300 kV X-ray source. Volume of the melt was calculated from the measured height and crucible diameter and corrected for thermal expansion.[3] In most instances, the column length could be measured repetitively to give a density variation of ± 0.004 g/cm^3. A typical set of radiographs used in the measurements is shown in Fig. 1. The amount of molybdenum in the melts was below the detection limit of the electron microprobe.

III. Results and Analysis

Densities of the aluminosilicate melts determined during the

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*Member, the American Ceramic Society.

*Now with the Department of Metallurgical Engineering, Middle East Technical University, Ankara, Turkey.

†A portion of this work was conducted while the author was a Graduate Research Assistant at the University of California.

‡Alcoa XA–16 reactive α-Al_2O_3, chemical analysis (wt%) Na_2O 0.08, SiO_2 0.05, CaO 0.03, MgO 0.05, Fe_2O_3 0.01, MnO 0.0015, B_2O_3 <0.001, Cr_2O_3 0.002, Aluminum Company of America, Pittsburgh, Pa. and Corning 7940 fused silica produced by hydrolysis of $SiCl_4$ when sprayed into an oxy-hydrogen flame; it is practically free from metallic impurities, but contains a high amount of OH (≈1000 ppm) and Cl (≈100 ppm), Corning Glass Works, Corning, N.Y.

§J. J. Rasmussen, Battelle Pacific Northwest Labs, Ceramics and Graphite Section, Richland, Washington. Now with Montana Energy and MHD Research and Development Institute, Butte, Montana 59701.

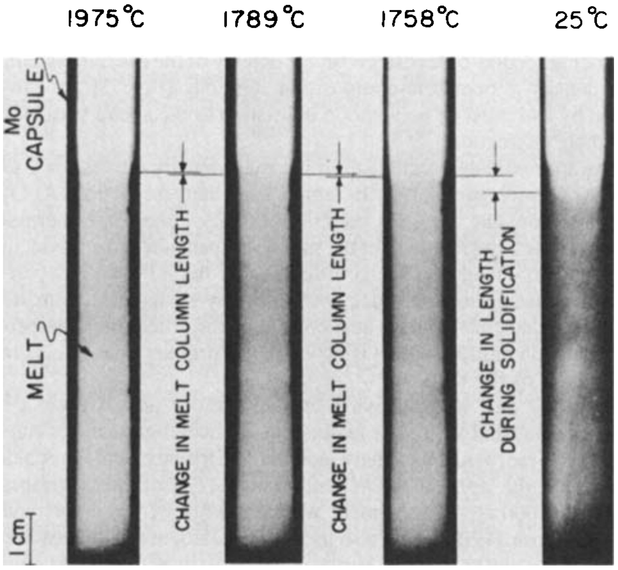

Fig. 1. Radiographs of molten and solidified aluminosilicate columns used in the determination of densities (melt composition 42.2 wt% Al_2O_3 + 57.8 wt% SiO_2).

cooling cycle only are shown in Table I and Fig. 2. The measurements obtained during the initial heating cycle were considered to be erroneous due to the formation of bubbles and the presence of cores in the melts. However, consistent results could be obtained during subsequent reheatings. This phenomenon has also been observed with $MgAl_2O_4$ and Al_2O_3 (Ref. 4) during the formation of initial melts from single crystals usually grown in the presence of H_2 or Ar.

The abrupt volume decrease shown in the 46.9 and 70.2 mol% Al_2O_3 supercooled melts (Fig. 2) was caused by formation of a precipitate. When heated, a volume increase accompanied by complete melting occurred for these compositions at 1913° and 1993°C, respectively, corresponding to alumina liquidus temperatures as determined by Aksay and Pask.[5] The 14.8 and 30.1 mol% Al_2O_3 melts formed glasses; thus, no abrupt volume changes were noted during cooling and reheating.

The density of liquid alumina has been measured by several investigators.[2,4,6-8] Mitin and Nagibin[8] used a hydrostatic technique between the melting point and 2550°C; their results are reproduced in Fig. 2. The density of solid alumina was calculated up to its melting point using the coefficient of expansion data of Wachtman *et al.*[9] and the room temperature density of 3.965 g/cm³ (Ref. 10).

The five density values of liquid silica shown in Fig. 2 are by Bacon *et al.*[11] A straight line is drawn through the data points, excluding the one at 2326°C, since extending a weighted line through all the points gives a density at the melting temperature of cristobalite, which is higher than that of the solid. Thus it is concluded that either the density of liquid silica varies linearly only up to ≈2200° (Fig. 2) and then deviates from linearity or the value reported at 2326°C is erroneous.

Table I. Densities of SiO_2-Al_2O_3 Melts

22.8 wt% Al_2O_3 (14.82 mol%)		42.2 wt% Al_2O_3 (30.08 mol%)		60.0 wt% Al_2O_3 (46.92 mol%)		80.0 wt% Al_2O_3 (70.21 mol%)	
Temp. (°C)	ρ(g/cm³)	Temp. (°C)	ρ(g/cm³)	Temp. (°C)	ρ(g/cm³)	Temp. (°C)	ρ(g/cm³)
1707	2.319	1758	2.475	1755	2.736	1966	2.811
1752	2.319	1789	2.466	1773	2.732	1993	2.799
1813	2.320	1813	2.461	1803	2.724	1995	2.791
1858	2.316	1838	2.465	1808	2.724		
1907	2.313	1858	2.460	1835	2.629		
1909	2.313	1880	2.454	1859	2.627		
1963	2.305	1881	2.455	1882	2.626		
1988	2.302	1909	2.448	1910	2.625		
2008	2.302	1913	2.449	1938	2.615		
		1941	2.445	1959	2.612		
		1975	2.446	1985	2.608		

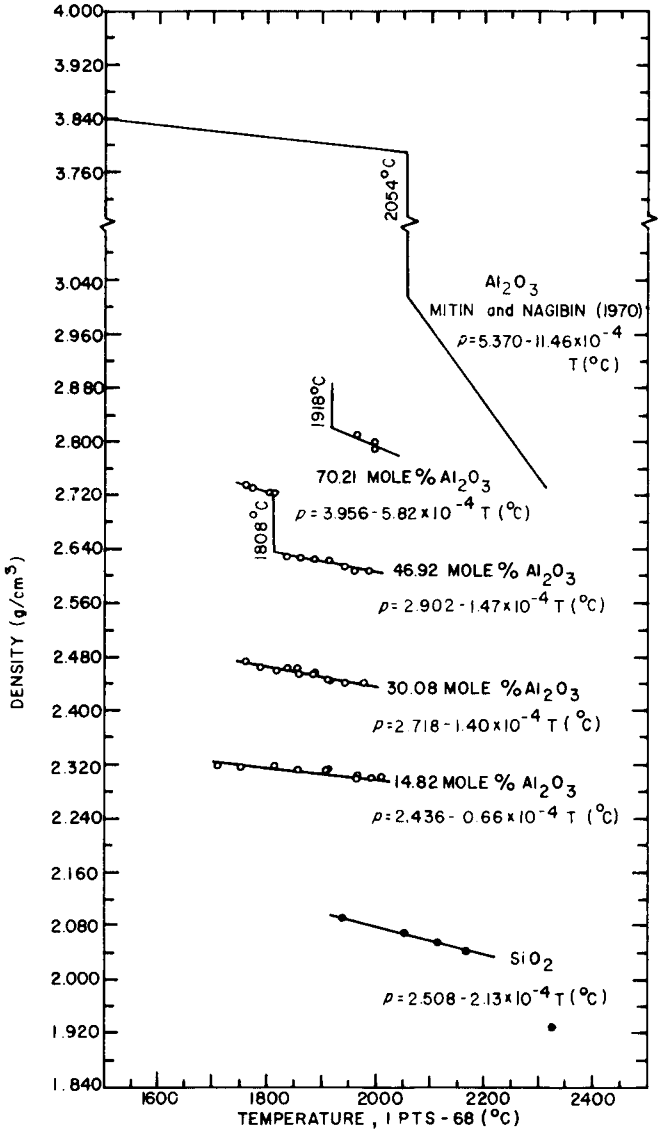

Fig. 2. Variation of aluminosilicate melt densities with temperature; curve for SiO_2 from Ref. 11.

Figure 3 shows the variation of the melt densities with alumina content at 1800° to 2200°C; the densities increase linearly only up to ≈45 mol% Al_2O_3. The negative deviation from linearity at higher alumina contents indicates breakdown of the network structure. The figure also includes room temperature densities of the glasses quenched from 1803°C.[12] On the basis of the data of Fig. 2, these room-temperature densities correspond to a fictive temperature of ≈1200°C.

The partial molar volume of Al_2O_3 and SiO_2 in the melt was not calculated. However, the data compiled by Huggins and Sun,[13] Bottinga and Weill,[14] and others[15] indicate that partial molar volumes are essentially constant in a certain range of silicate compositions and thus may be used to calculate the density of any silicate liquid within that range. The values for ternary alkali and alkaline-earth aluminosilicates reported by Bottinga and Weill were extrapolated to 1900°C and used to calculate the densities of binary aluminosilicate melts containing 20 to 60 mol% Al_2O_3. The agreement between these calculated values and the measured ones is poor, especially at higher alumina contents (Fig. 3). Similar results are obtained if the values compiled by Huggins and Sun[13] are used. It therefore appears that the partial molar volumes obtained from ternary aluminosilicates may be satisfactorily used only to predict

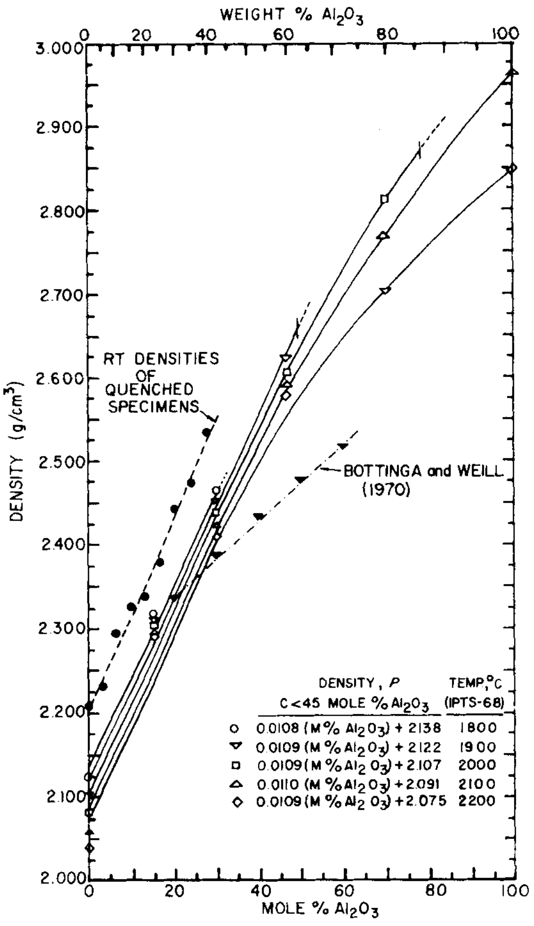

Fig. 3. Variation of aluminosilicate melt densities with Al_2O_3 content. Densities of quenched specimens, pure SiO_2, and pure Al_2O_3 are from Refs. 12, 11, and 8, respectively.

the densities of other ternary or more complex silicates of similar composition.

The experimental density data may also be used to determine the fractional volume change of mullite and alumina on melting or solidification. Tyrolerova and Lu[16] reported a volume decrease of 10.3% during solidification for a fused-cast mullite specimen of 75.1 wt% Al_2O_3. The density of stoichiometric mullite (71.8 wt% Al_2O_3) at its metastable congruent melting temperature, 1890°C,[17] is 3.10 g/cm^3 when calculated from the expansion data of mullite.[18] The density of the corresponding melt at the same temperature is 2.774 g/cm^3, based on the data given in Fig. 3. Thus, the fractional volume decrease of mullite on solidification is 10.52%, which agrees with the value reported by Tyrolerova and Lu.[16]

The fractional volume decrease of alumina on solidification is 20.7%, based on the data of Fig. 2. Similar values were reported by Kingery[19] (20.4%)* and Tyrolerova and Lu[20] (19.9 to 20.1%). Kirshenbaum and Cahill[7] and Bates *et al.*[4] reported values of 22.0 and 24.0%, respectively; however, for comparison, these values should be expressed as fractional volume change on solidification. The new values are 18.2 and 19.4%, respectively, and compare well with those reported by the other workers.

IV. Discussion

The density and any changes in density of a system are a function of the percentages and molecular weights of the components, the structural positions, and the bonding energies of the atomic species as well as the temperature and the resulting thermal expansion of the structure. Furthermore, the particular structural roles of the atomic or molecular components may also be considerably influenced by the concentration of each component and the temperature, thus producing second-order effects on the density of the overall system. The density-temperature-composition relations (Fig. 3) are produced by and must be understood in relation to the above variables and their interaction.

The approximate parallelism of the melt-density curves for 0 to 40% Al_2O_3 indicates that, as the temperature increases at each Al_2O_3 concentration, the densities are controlled by either pure thermal expansion or a combination of the thermal expansion and equivalent proportional changes in the coordination of the Al^{3+} ion. Experimental evidence for the latter postulate may be derived from research conducted on glasses quenched from these high melt temperatures and on mullite, which is in two major primary phase fields in this region of the diagram.[5]

Galakhov and Konovalova[21] and Eipeltauer and Hruschka[22] attributed unusual structural features in quenched glasses containing 12 to 48 mol% Al_2O_3 to phase separation. Eipeltauer and Hruschka found that the crystallization temperature (T_X) of these glasses is 950° to 1000°C, in agreement with the work of Takamori and Roy,[23] whose TEM studies also gave direct evidence of metastable phase separation at 20 to 50 mol% Al_2O_3 (20% was the lowest concentration examined). MacDowell and Beall[24] conducted the most comprehensive study of the microstructure of these glasses and found much evidence for phase separation within a metastable immiscibility gap with limits of 7 to 55 mol% Al_2O_3 and an approximate consolute point of 1650°C. Thermodynamic calculations by Risbud and Pask[25] indicate that this immiscibility gap extends from $\simeq 11$ to 49 mol% Al_2O_3 at 1100° with a consolute temperature of $\simeq 1540$°C at a critical composition of $\simeq 36$ mol% Al_2O_3. Furthermore, their direct TEM and selected-area diffraction studies of the powdered glasses within this gap revealed phase-separated glassy droplets ($\simeq 400$ Å) up to $\simeq 25$ mol% Al_2O_3; beyond this Al_2O_3 concentration the glasses tended to crystallize rapidly. Studies of the underlying structural-chemical reasons for this proposed gap should, in turn, help to explain the density data in this region of the diagram.

The mullite structure consists of a quasi-ordered distribution for four- and six-coordinated aluminum atoms and four-coordinated silicon atoms[26,27]; however, the ratio of the AlO_4 and AlO_6 polyhedra is variable within this nominal crystal structure. Aramaki and Roy[28] and other investigators† attributed the formation from the melt of the metastable $2Al_2O_3{\cdot}SiO_2$ mullite to a "structural inheritance from the liquid which favors more Al^{3+} ions in four coordination."[28] In addition, heat-treating mullites of fixed composition at 1300° to 1790°C increases the room-temperature unit-cell dimensions, particularly along the *a* axis, again indicating coordination changes in the aluminum ion.[28] Thus the structural position of the aluminum species varies even in the crystalline mullite as a function of Al_2O_3 concentration and temperature. This same effect may also be assumed to exist in aluminosilicate glasses. This prior research leads to at least three explanations which may act separately or in combination to produce the parallelism of the melt density curves in the 0 to 40 mol% range.

(1) At high temperatures (above the liquidus and therefore above the consolute point) the ratio of AlO_4 to AlO_6 becomes relatively constant for each concentration, and the decrease in density as temperature increases is only a function of the increase in the thermal vibrations of the structure.

(2) The pure thermal expansion of the structure is accompanied by small decreases in the number of oxygens surrounding the normally octahedrally coordinated aluminum ions as well as, to a lesser extent, the more strongly bonded tetrahedrally coordinated aluminum and silicon ions. This common high-temperature structural-chemical effect maintains the structural role of the ions, e.g. a modifying position, but decreases their average oxygen coordination.

(3) The pure thermal expansion of the structure is accompanied by slight increases in the AlO_4 to AlO_6 ratio which are proportional to the Al_2O_3 concentration up to 30 to 45 mol%, depending on the temperature.

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*This value was erroneously reported by Kingery (Ref. 19) as fractional volume change on melting instead of solidification.

†For a discussion of this phenomenon, see Ref. 29.

It is impossible, from the current status of research, to differentiate between these effects and their contribution, if any, to the formation of parallel density curves; however, all of the preceding structural changes have occurred in this binary system. Also, the apparent linearity of these melt density curves can be explained as a result of the additive volume relations between Al_2O_3 and SiO_2; however, what combination of the above mechanisms produces this phenomenon is not known.

As the melts cool, the aluminum ions have an increasing tendency to transform into six coordination and exert an increasing force on the surrounding oxygen ions, eventually causing phase separation (within certain compositional limits) into alumina-rich and silica-rich glasses. MacDowell and Beall[24] showed that the alumina-rich glasses crystallize to mullite when heated. It is reasonable that this microphase separation would tend to produce a slight increase in the density of the system and would explain the somewhat higher slope of the room-temperature density curve (Fig. 3) as compared to those of the melts.

Studies of the direct determination of aluminum ion coordination in silicate glasses and melts have been primarily limited to alkali aluminosilicates.[31] Both tetrahedral (the tricluster* and network-forming types) and octahedral coordinations of aluminum have been proposed under certain conditions. The presence of the aluminum ion in tetrahedral and octahedral coordination in binary SiO_2-Al_2O_3 glasses was shown by Davis,[12] who used Al$K\alpha$ X-ray fluorescence derived from electron-beam microprobe measurements on 5 to 40 wt% (3 to 28 mol%) Al_2O_3 glasses with a fictive temperature of ≈1200°C (Fig. 2). The Al$K\alpha$ wavelength of these aluminosilicate glasses, when compared to the X-ray emission of metallic aluminum, $AlPO_4$, and α-Al_2O_3 (Table II), corresponded to that of a tetrahedrally coordinated aluminum at 5 wt% (3 mol%) Al_2O_3 and octahedrally coordinated aluminum ≥10 wt% (6 mol%) Al_2O_3. Similar, more refined research was conducted by Aksay[32] on 10.9 wt% (7 mol%) and 22.8 wt% (15 mol%) Al_2O_3 binary glasses, using similar standards plus kyanite and mullite. In both samples, the deconvoluted curves† revealed the presence of six- and four-coordinated aluminum ions as well as an increase in the former in the higher Al_2O_3 composition. Wardle and Brindley[33] pointed out that, although the X-ray fluorescence technique provides a means for determining coordination numbers, when more than one coordination state occurs simultaneously the results reflect the weighted average of the two coordinations. Thus, Davis's findings do not necessarily indicate a sudden change from fourfold to sixfold coordination at 10 wt% Al_2O_3 but could also indicate a gradual change from a predominantly fourfold-coordinated structure to a predominantly sixfold-coordinated one, as demonstrated by Aksay. This gradual change is also substantiated by the density data.

As the Al_2O_3 concentration increases (>40 mol%), the resulting compositions represent melts above the primary phase field of Al_2O_3; thus, it is feasible that the percentage of aluminum in octahedral positions structurally similar to that occupied in the oxide will increase with increasing concentrations of Al_2O_3. The viscosities of these melts also decrease dramatically from that of the high-silica liquids,[34] indicating that the structural network is becoming increasingly broken down and that bond energies between the atomic species are decreasing. These two premises would allow for a continual decrease in the average coordination of oxygen around the quasi-octahedrally coordinated aluminum atoms as the temperature increased at each Al_2O_3 concentration. Such an effect, coupled with static or increased coefficients of thermal expansion, could explain the increasing deviation from linearity as a function of temperature and composition in the high Al_2O_3 range (Fig. 3). Much research and the development of presently unknown techniques are necessary to achieve a complete understanding of the density-temperature-composition phenomena.

Table II. Aluminum Coordination Data Determined from Al$K\alpha$ X-Ray Emission Spectra*

Material	Peak position half height (Å)	Displacement Å from Al metal
Al	8.3390	0.0000
$AlPO_4$	8.3357	.0033
Al_2O_3	8.3339	.0051
5 wt% Al_2O_3	8.3353	.0037
10 wt% Al_2O_3	8.3340	.0050
15 wt% Al_2O_3	8.3339	.0051
20 wt% Al_2O_3	8.3337	.0053
25 wt % Al_2O_3	8.3339	.0051
30 wt% Al_2O_3	8.3337	.0053
35 wt% Al_2O_3	8.3336	.0054
40 wt% Al_2O_3	8.3336	.0054

*$AlPO_4$ and Al_2O_3 were the 4-fold and 6-fold coordinated standards (from Ref. 12).

V. Conclusions

(1) The X-radiographic technique represents an accurate method for measuring homogeneous single-phase melt densities and fractional volume changes in single- and multicomponent ceramic systems.

(2) Extrapolating available partial molar volume data of ternary aluminosilicates to the temperatures of the present research does not give accurate calculated values of density for the binary system.

(3) Melt density curves in the system SiO_2-Al_2O_3 are parallel and linear to ≈30 to 45 mol% Al_2O_3, depending on the temperature. At high Al_2O_3 concentrations, increasing negative deviation from linearity is noted as a function of increasing temperature and Al_2O_3 content.

(4) A review of recent research on glasses in the system SiO_2-Al_2O_3 strongly indicates the existence of changing structural roles of the aluminum ion from AlO_4 to AlO_6 polyhedra with increasing Al_2O_3 content and decreasing temperature. This effect, coupled with normal structural-chemical decreases in the coordination number of all cations with increasing temperature, and pure thermal expansion of the structure have roles that cannot now be differentiated in determining the absolute and relative values of densities in melts and quenched glasses of the system SiO_2-Al_2O_3.

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*Lacy (Ref. 30) argued that in low concentrations of Al_2O_3, AlO_6 octahedra cannot exist. He postulated the existence of triclusters of AlO_4 tetrahedra accompanied by tribridging oxygen. The aluminum species in these triclusters is four-coordinated to oxygen but only bonded to three to maintain charge balance. No phase separation is detected in this low Al_2O_3 range even on slow cooling (Ref. 22).

†Work conducted at Walter C. McCrone Associates, Chicago, Illinois, using a Model 310 curve resolver, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

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Delayed Failure in Chemically Vapor Deposited ZnSe

K. R. McKINNEY, J. J. MECHOLSKY,[*,*] and S. W. FREIMAN[*,‡]

Naval Research Laboratory, Washington D.C. 20375

Room-temperature delayed failure of CVD ZnSe was tested in 4-point flexure. Fracture surfaces of specimens exhibiting delayed failure, i.e. failing after some time under a fixed load, showed an intergranular region of fracture, surrounding a mechanically induced flaw. This intergranular region was attributed to slow crack growth and the remaining transgranular fracture to high-velocity crack propagation. This behavior contrasts with that of specimens failing during loading, i.e. with little or no slow crack growth, which typically exhibited only transgranular failure, as was also observed in bend tests of specimens loaded to failure. Actual times to failure fell between failure-time predictions based on single-crystal and polycrystalline slow crack growth data, but were much closer to that for the single crystal.

I. Introduction

Moisture-assisted subcritical crack growth occurs in chemically vapor deposited (CVD) ZnSe.[1,2] The primary objective of the present work was to experimentally measure times to failure of CVD ZnSe as a function of stress in deadweight loading and to compare these times to those predicted from slow crack growth data and fracture mechanics principles. A second objective was to investigate possible correlations of failure behavior with microstructure.

II. Experimental Technique

Thirty-two 4-point bend specimens (1.9 by 4.4 by 25.4 mm) were cut from a plate of CVD ZnSe,[‡] finished with 1-μm diamond paste, and the corners rounded. Specimens were deadweight-loaded in 4-point flexure (outer span 22.9, inner span 7.5 mm) in air at 21°C and 50% rh, using eight test fixtures (Fig. 1). When a specimen fractured, a microswitch located at the pivot point of the loading bar opened, stopping a timer. Two stress levels, 46.9 and 55.8 MPa, were chosen based on statistical analysis of the strength distribution of bars previously tested in 4-point bending.[3]

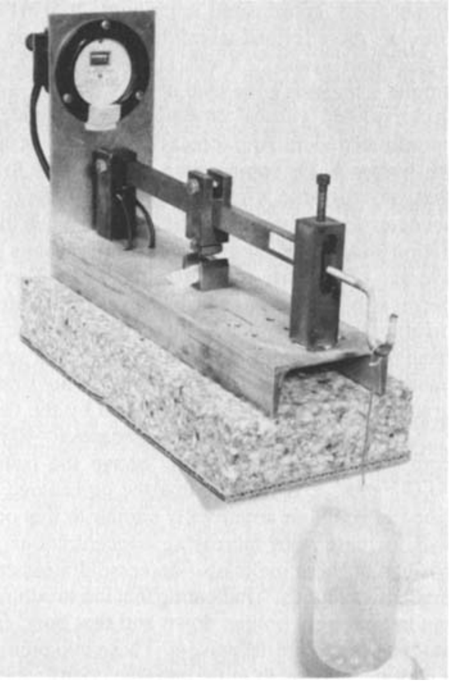

Fig. 1. Test fixture used to apply constant stress in 4-point flexure, showing weights and timer.

Scanning electron micrographs of the fracture surfaces were used to determine the type, size, and geometry of failure origins.[4]

III. Results and Discussion

(1) Fracture Surface Analysis

Fracture origins were identified in the 27 bars which failed in 300

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[*] Member, the American Ceramic Society.

[*] Now with Sandia Laboratories, Albuquerque, New Mexico 87185.

[†] Now with the National Bureau of Standards, Fracture and Deformation Division, Washington, D.C. 20234.

[‡] Plate MT–11A, supplied by the University of Dayton Research Institute, Dayton, Ohio.