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Battelle
Pacific Northwest Laboratories
Battelle Boulevard
Richland, Washington 99352

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June 1, 1972

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16. Abstract

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ABSTRACT

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The molten 0.375 Y_2O_3 - 0.625 Al_2O_3 exhibited an apparent supercooling of 270°K. Melting was observed at 2253°K, but solidification occurred at 1983°K. An anomolous change in the liquid properties above 2750°K was also observed.

The techniques for measuring volume change on melting and viscosity can also be used to measure directly the eutectic and liquidus properties of high temperature oxides. Viscosity and volume change on melting appear to be significantly more important for studying the structure of liquids than is the surface tension since these properties are strongly influenced by the addition of other oxides.

INTRODUCTION

Aluminum oxide filaments of long length are being developed for fiber reinforcement of metals for long-time, high-temperature applications. Single crystal α-Al_2O_3 filaments have been successfully used for this purpose; however, these filaments, being difficult and slow to grow, are costly. Processes are being developed to fabricate high-quality polycrystalline continuous fibers that can be utilized economically. These processes involve rapid growth of filaments from liquid Al_2O_3.

The techniques now under development are difficult to control and are complicated by some intrinsic properties of the molten Al_2O_3. The 24 percent volume change on solidification results in the formation of voids in the reinforcing filament, thus reducing its effective strength. Viscosity and surface tension are important in fabricating continuous, long-length filaments because they determine the propensity of liquids to form spheres rather than rods. Altering and controlling these properties could aid significantly in the control of the filament growth processes without adversely affecting the properties of the filament.

The purpose of this work was to study the effects of various oxide additives on the volume change on melting, the surface tension, and the viscosity of liquid Al_2O_3. The goal was to investigate the effects of a variety of oxide additives including those which form solid solutions with Al_2O_3; those which form compounds with Al_2O_3; and those which are multiphase as solids. This report presents a review of the property data available in the literature and describes the property data obtained at this laboratory. Recommendations for further study are discussed.

EXPERIMENTAL TECHNIQUE

The experimental techniques for measuring the volume change on melting, density, surface tension, and viscosity have been described in detail elsewhere(1-3) and are briefly reviewed in this report.

Radiographic Technique

X-radiography of the molten ceramic in an electron-beam sealed, refractory metal capsule was used to observe the volume and surface properties of the liquid. The expansivity, density, and volume change on melting were determined by observing the volume of the sample. The surface tension was determined from the shape of the meniscus.

The sample was radiographed with a 300 kv x-ray source. An x-ray image intensifier and Vidicon camera were used to monitor the sample continuously, and film was exposed for a permanent record. A tungsten-mesh resistance heating element surrounded by split radiation shields allowed x-radiography under effectively isothermal conditions with a minimum of absorbing material in the image-forming x-ray beam. The furnace was operated in vacuum of 1.33×10^{-3} - 1.33×10^{-4} N/m^2 (10^{-5} - 10^{-6} Torr).

Surface Tension

The surface tension was determined from an analysis of the equilibrium meniscus shape using a computer program. The program required a measurement of the coordinates of the meniscus profile. Knowing the density of the liquid, the surface tension could be calculated.

Density and Volume Change on Melting

The density of the molten ceramic material was calculated from the known weight of the sample in the capsule and from the sample volume as a function of temperature. The volume was calculated by measuring the height of the liquid column from the radiographs and using the inside diameter of the refractory metal crucible after correcting for thermal expansion. Corrections also were made for the volume of the material contained in the meniscus.

The volume change on melting was determined by extrapolating the measured volumes of the solid and liquid as a function of temperature to the melting point. The difference between these two volumes was the volume change on melting.

Viscosity

The viscosity of molten oxides was measured with an oscillating cup viscometer. This technique consisted basically of measuring the time rate of decrease in the amplitude of a free-oscillating, closed capsule (containing the liquid) suspended from a torsion wire. The amplitude decrease (or damping) resulted from both the viscous motion of the liquid and the internal friction of the torsion wire.

The amplitude changes were measured by an optical method. The oscillating scale was viewed with a television system,and a video-tape record of the graduated scale was replayed in stop action mode.

Viscosity values were calculated from the measured damping and period, the known values of the moments of inertia of the sample and pendulum, the liquid density, and the crucible geometry.

Temperature Measurements

Temperatures were measured with an optical pyrometer sighted on the capsule. Measurements can be made with a precision of $\pm 10^{\circ}$K. If the melting point of the sample were known, e.g. Al_2O_3, an internal check of temperatures could be obtained.

SAMPLE AND CAPSULE PREPARATION

Fabrication of long cylindrical samples was required for the liquid property measurements. Ideally, the sample should be 100% dense, homogeneous, contain no absorbed gases, and should be compatible with the refractory metal container. Single crystals best fitted this criteria; however, their availability was limited to a few compounds of Al_2O_3, such as the magnesia spinel and yttrium aluminum garnet (YAG).

The fabrication of high density, multiphase samples of Y_2O_3 - Al_2O_3, Sm_2O_3-Al_2O_3, and other oxide mixtures proved to be the most challenging problem of this study. Many of these systems were multiphase as solids with both liquid and solid phases above the eutectic temperature. Cold pressing of the powders and sintering near but below the eutectic temperature was often not sufficient to produce densities above 85% of the theoretical densities. Heating above the eutectic temperature resulted in a high density near 98% but the material flowed plastically and the geometry of the sample was destroyed.

Two methods of preparing the long cylindrical samples were developed:

(1) Cylinders of the admixed powders were pressed and sintered. These cylinders were placed inside an open-refractory metal tube and melted. The melting was initiated at the bottom of the container, and the molten zone was passed from the bottom to the top of the sample. This was successfully used to fabricate the 0.1 Y_2O_3 - 0.9 Al_2O_3 sample. However, the 0.2 Sm_2O_3 - 0.8 Al_2O_3 could not be fabricated by this technique since selective solidification resulted in a separation of the eutectic composition at the top of the casting. This limited the use of this technique for many two-phase, eutectic forming systems. The cast samples often contained a number of large pores which reduced the overall bulk density.

(2) An alternate approach for fabricating the eutectic forming samples at off-eutectic compositions was to cold press and sinter the samples below the eutectic temperature. These cylinders are placed inside a refractory metal container with an inside diameter slightly larger than the desired sample diameter. The sample was heated to a temperature below the liquidus temperature, but slightly above the eutectic temperature. The sample densified and flowed together forming a cylinder with a density greater than 98%. This technique was successfully used to fabricate the 0.2 Sm_2O_3 - 0.8 Al_2O_3 sample.

The single crystals of 0.375 Y_2O_3 - 0.625 Al_2O_3 (YAG) and Al_2O_3, and the Lucalox were obtained from commercial suppliers.*

The cylindrical samples were ground to the desired diameter and length, ultrasonically cleaned, and placed in a molybdenum or tungsten container. The capsule was electron beam welded and leak checked to ensure closure.

The same capsule and sample were used for volume change, surface tension, and viscosity measurements.

Heating of 2 wt% tungsten (particle size less than 0.002 cm in diameter) at 2100°C to 2200°C in tungsten crucibles resulted in the agglomeration and segregation of the tungsten. The particles of tungsten agglomerated into larger bodies and were randomly scattered throughout the molten oxide after 3-5 minutes at temperature. The agglomerates tended to settle to the bottom of the crucible when heated for periods greater than 20 minutes. This agglomeration and segregation of the tungsten precluded any liquid property measurements.

Al_2O_3 samples containing Cr_2O_3 and TiO_2 (10 mole%) were found to react with the molybdenum and tungsten containers at temperatures above their melting points. The reaction of these alloys with the crucibles was severe enough to make liquid property measurements impractical.

---

* Union Carbide Corporation, Crystal Products Division, San Diego, California, and General Electric Company, Schenectady, New York, respectively.

RESULTS

Molten properties were measured for 0.1 Y_2O_3 - 0.9 Al_2O_3, 0.375 Y_2O_3 - 0.625 Al_2O_3 (YAG) single crystal, 0.2 Sm_2O_3 - 0.8 Al_2O_3, and Lucalox (∿ 0.25% MgO in Al_2O_3).

0.1 Y_2O_3 - 0.9 Al_2O_3

The volume change on melting and viscosity were measured. The volume change from the solidus to the liquidus of 0.1 Y_2O_3 - 0.9 Al_2O_3 (19.7 wt% Y_2O_3) was 13.5%.

Since the theoretical density of the 0.1 Y_2O_3 - 0.9 Al_2O_3 sample was not known, it was necessary to measure the density after the property measurements were completed. The density was determined by crushing the sample into particles fine enough to eliminate voids of any substantial size and measuring the density by water displacement. The density of the cylinder was 3.75×10^3 kg/m^3 (3.75 g/cm^3) or 87.2% of the theoretical density calculated from the powders. The low density of the cylinder resulted from large voids which formed during casting. The volume change on melting was calculated to be 13.5 ± 0.5% after correcting for porosity. This volume change is substantially less than the 24% change for pure Al_2O_3. The density data for the liquid and solid are summarized in Table I.

The volume expansion from the eutectic temperature to the liquidus temperature was difficult to determine due to the presence of both liquid and solid. The formation of a liquid phase above the eutectic temperature resulted in densification of the sample and in the release of entrapped gases. However, once above the liquidus, the volume change could be resolved.

The reported phase diagram$^{(4)}$ indicates that the 0.1 Y_2O_3 - 0.9 Al_2O_3 composition should melt at approximately 2223°K. However, the presence of the solid Al_2O_3 phase seen in the radiographs and the sharp discontinuity in the $\Delta V/V$ versus temperature curve (Figure 1) indicate a melting point of 2193 ± 10 K.

TABLE I. Density of 0.1 Y_2O_3 - 0.9 Al_2O_3.

Temperature K ± 10°K	Density kg/m^3 (10^{-3})
Run No. 1	
298	4.30(1,2)
1781	4.12(2)
1965	4.04(2)
2191	3.43
2253	3.42
2192	3.43
2223	3.441
Run No. 2	
2368	3.394
2273	3.433
2228	3.418
2193	3.521

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(1) Measured after tests by crushing sample and water displacement.

(2) Corrected to theoretical density of 4.3 x 10^3 kg/m^3 at 298 K.

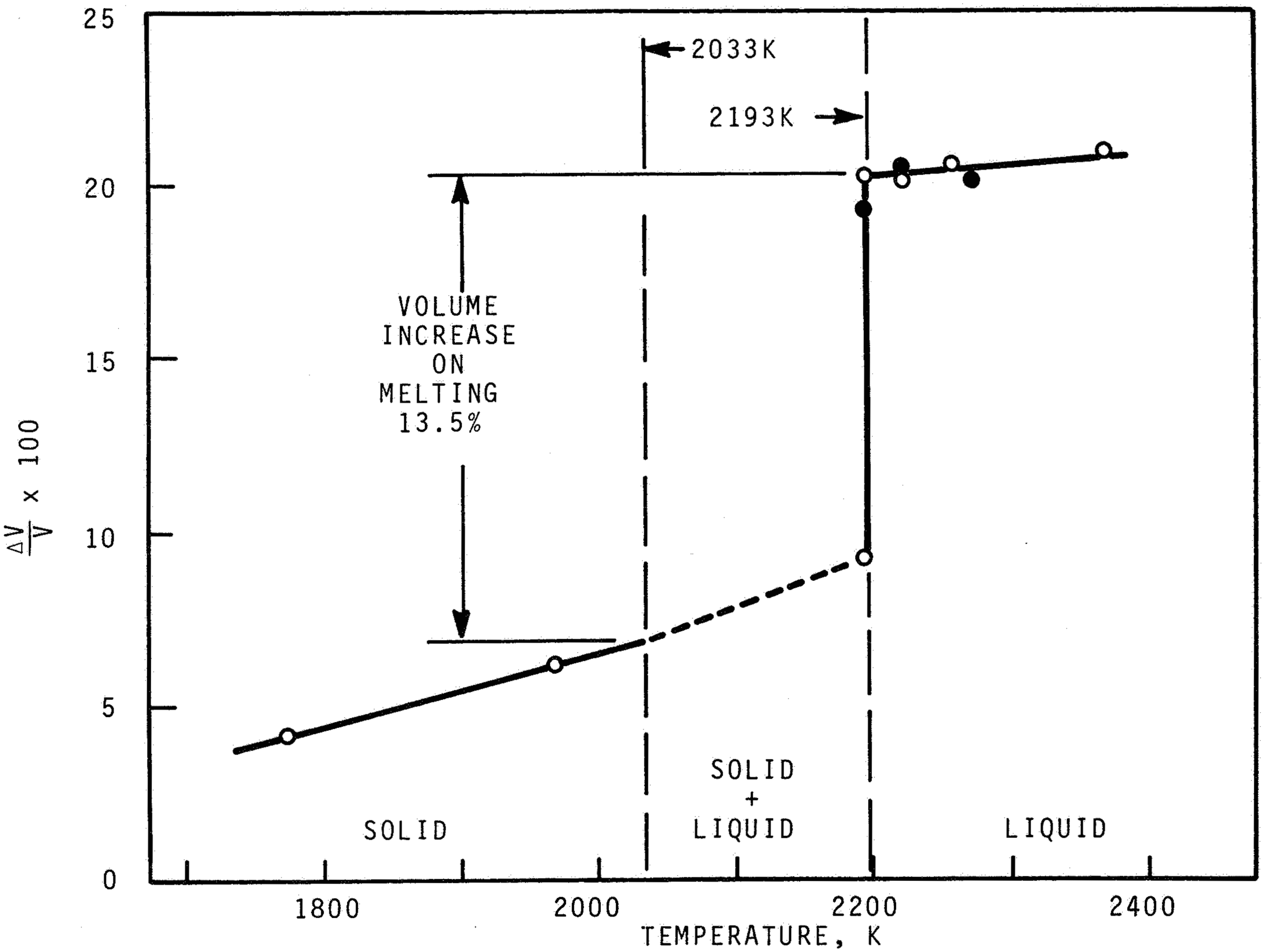

FIGURE 1. Volume Change Between Solidus and Liquidus and Specific Volume of $0.1\ Y_2O_3-0.9\ Al_2O_3$

The viscosity of 0.1 Y_2O_3 - 0.9 Al_2O_3 was measured at 2223, 2243, and 2293 K (Table II). Attempts to measure the viscosity at 2273 K were unsuccessful because of capsule distortion. The viscosity decreases rapidly above the liquidus temperature of 2193 K and at 2293 K is significantly more fluid than Al_2O_3 at its melting point (2323 K). The viscosity for 0.1 Y_2O_3 - 0.9 Al_2O_3 at 2293 K and for Al_2O_3 at 2443 K is 0.27 and 0.74 poise, respectively.

TABLE II. Viscosity of 0.1 Y_2O_3 - 0.9 Al_2O_3

Temperature K	Viscosity Poise
2223	2.95
2243	2.60
2293	0.27

The surface tension measurements were complicated by the lack of convergence of the computer program used to calculate the surface tension values. The cause of this is not known but is probably related to the poor resolution of the radiographs in the area where the meniscus approaches the capsule wall.

The 0.1 Y_2O_3 - 0.9 Al_2O_3 was a two-phase solid after the measurements.

0.2 Sm_2O_3 - 0.8 Al_2O_3

The capsule containing a cast 0.2 Sm_2O_3 - 0.8 Al_2O_3 sample failed during heating when the top half of the capsule split longitudinally, allowing part of the liquid sample to leak from the capsule. This precluded measurement of the viscosity. However, the volume change on melting was calculated to be 10 ± 2% by analyzing the sample remaining in the capsule. This value is substantially smaller than for pure Al_2O_3 (24%) and is close to the value for 0.1 Y_2O_3 - 0.9 Al_2O_3 (13.5%).

The solidified solid contained a large central void. The originally yellowish-tan sample had become a multi-phase solid containing large areas of red, orange, grey, and yellow.

Lucalox

The viscosity, surface tension, and volume change on melting of Lucalox ($< 0.25\%$ MgO in Al_2O_3) were measured. No significant differences were observed between the single crystal Al_2O_3 and Lucalox samples for the surface tension, volume change on melting, or liquid density. The surface tension was determined to be 0.248 Newtons/m (248 dynes/cm) in Mo (compared to 0.360 Newtons/m for Al_2O_3 single crystals), and the temperature dependence relationship from 2323 to 2673°K for the liquid density (ρ) was calculated as $\rho = 3.58 \times 10^{-3} - 2.77 \times 10^{-7}$ T (kg/m^3) [$\rho = 3.58 - 2.77 \times 10^{-4}$ T K (g/cm^3)]. The change in volume on melting was 22%, very close to the value for pure Al_2O_3 (24%).

The viscosity for Lucalox was significantly lower than that for pure Al_2O_3 (0.74 and 0.30 poise at 2443 K for Al_2O_3 and Lucalox, respectively).(1) The results are illustrated in Table III.

TABLE III. Viscosity of Lucalox.

Temperature K	Viscosity, poise	Activation Energy, Kcal/mole
2353	0.358	
2393	0.331	21.7 (< 2473 K)
2453	0.297	
2493	0.287	
2543	0.280	5.7 (> 2473 K)

0.375 Y_2O_3 - 0.625 Al_2O_3

The viscosity and volume change on melting were measured for a 0.375 Y_2O_3 - 0.625 Al_2O_3 (YAG) single crystal.* The molten 0.375 Y_2O_3 - 0.625 Al_2O_3 exhibited some unusual and unexpected properties:

- The apparent supercooling of the molten oxide from 2253 to 1983 K.
- An anomalous change in liquid properties above 2350 K.
- The absence of a large central void generally associated with the solidification of a solid.

The sample, when heated rapidly the first time, appeared to melt at 2293 K. However, subsequent tests at slower heating rates consistently indicated melting at 2253 ± 10 K. This was higher than the 2203 K reported in the published phase diagram.(4) On cooling, solidification did not occur until the temperature was approximately 1983 K, indicating extensive supercooling of the sample. This result was substantiated by both the viscosity data and the x-ray radiographs. Cycling tests also confirmed the supercooling of the YAG.

The volume change on melting was 7.8% (Figure 2), significantly less than the 24% observed for Al_2O_3.

There was an anomalous change in the ΔV/V for the liquid at 2423 K. The ΔV/V exhibited a higher rate of increase above this temperature than between 2253 and 2423 K. The reason for this behavior is not known.

The viscosity data for the 0.375 Y_2O_3 - 0.625 Al_2O_3 are tabulated in Table IV and illustrated in Figure 3.

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* Supplied by Union Carbide Corporation, Crystal Products Division, San Diego, CA.

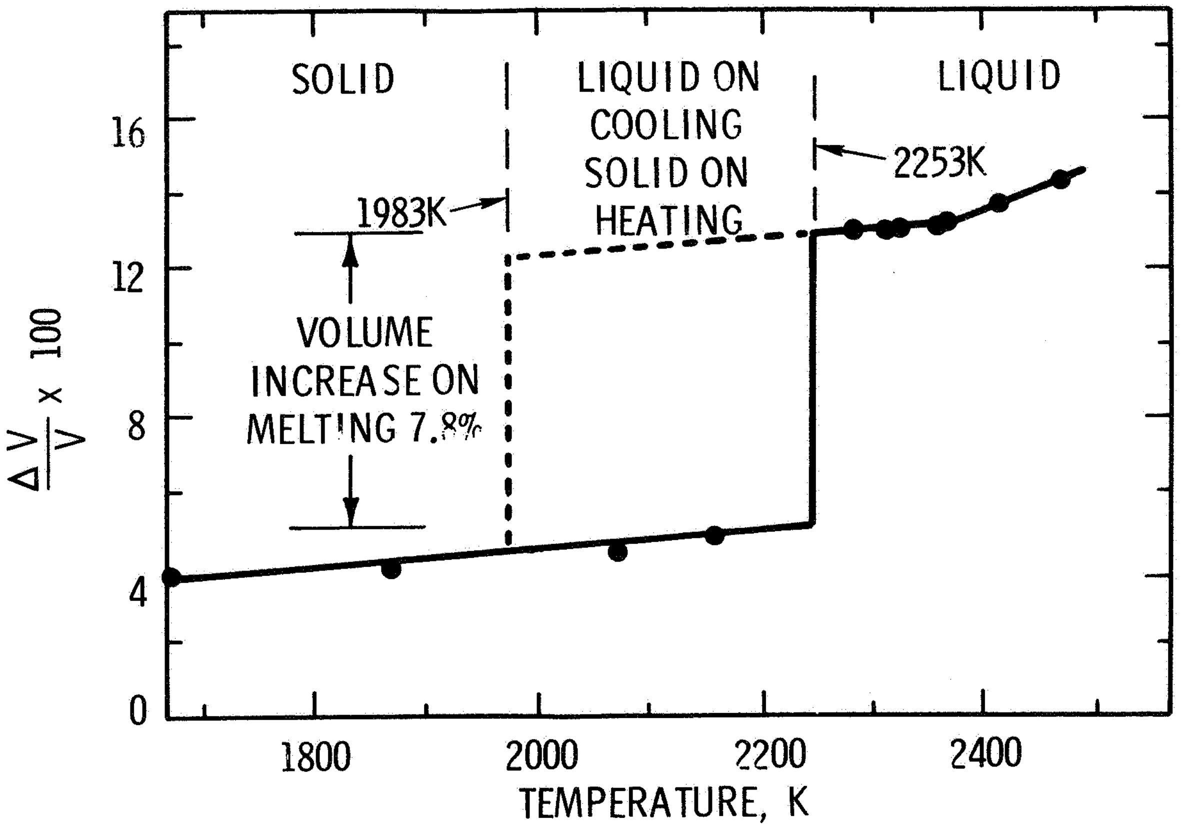

Figure 2. Volume Change On Melting and Solidification Of Single Crystal 0.375 Y_2O_3-0.625 Al_2O_3

TABLE IV. Viscosity of 0.375 Y_2O_3 - 0.625 Al_2O_3*

Temperature K	Viscosity poise
2326	0.301
2394	0.248
2445	0.245
2473	0.254
2318	0.281
2218	0.310
2173	0.354
2117	0.394
2273	0.292
2373	0.267
2433	0.268

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*Measurements above 2253 K or on cooling.

The data were reproducible only above 2253 K and during cooling below 2253 K after melting. The observed scatter in data after solidifying at 1953 K and remelting immediately was possibly related to changes in composition during supercooling of the liquid.

The viscosity appeared to deviate from the expected linear log versus 1/T relationship above 2423 K and was more viscous than predicted by the linear relationship. Although this deviation was close to the experimental error, this change, if real, was probably caused by the same phenomenon which increased the rate of change in $\Delta V/V$ at this same temperature. If the density of the liquid had not experienced a sharp decrease above 2423 K (Figure 1), this apparent deviation in viscosity above 2423 K would be more pronounced since the absolute viscosity is proportional to the density. This measured decrease in density was used to calculate the viscosity values in Figure 2. The estimated activation energy for the viscosity was approximately 10 Kcal/mole.

A cross section of the sample after measurements showed no large central void. The central core was milky-white and contained a high concentration of very small pores. The sample near the capsule wall was translucent white and very dense with a grey zone present between the core and the translucent oxide. The absence of a central void may be a consequence of the supercooling of the liquid.

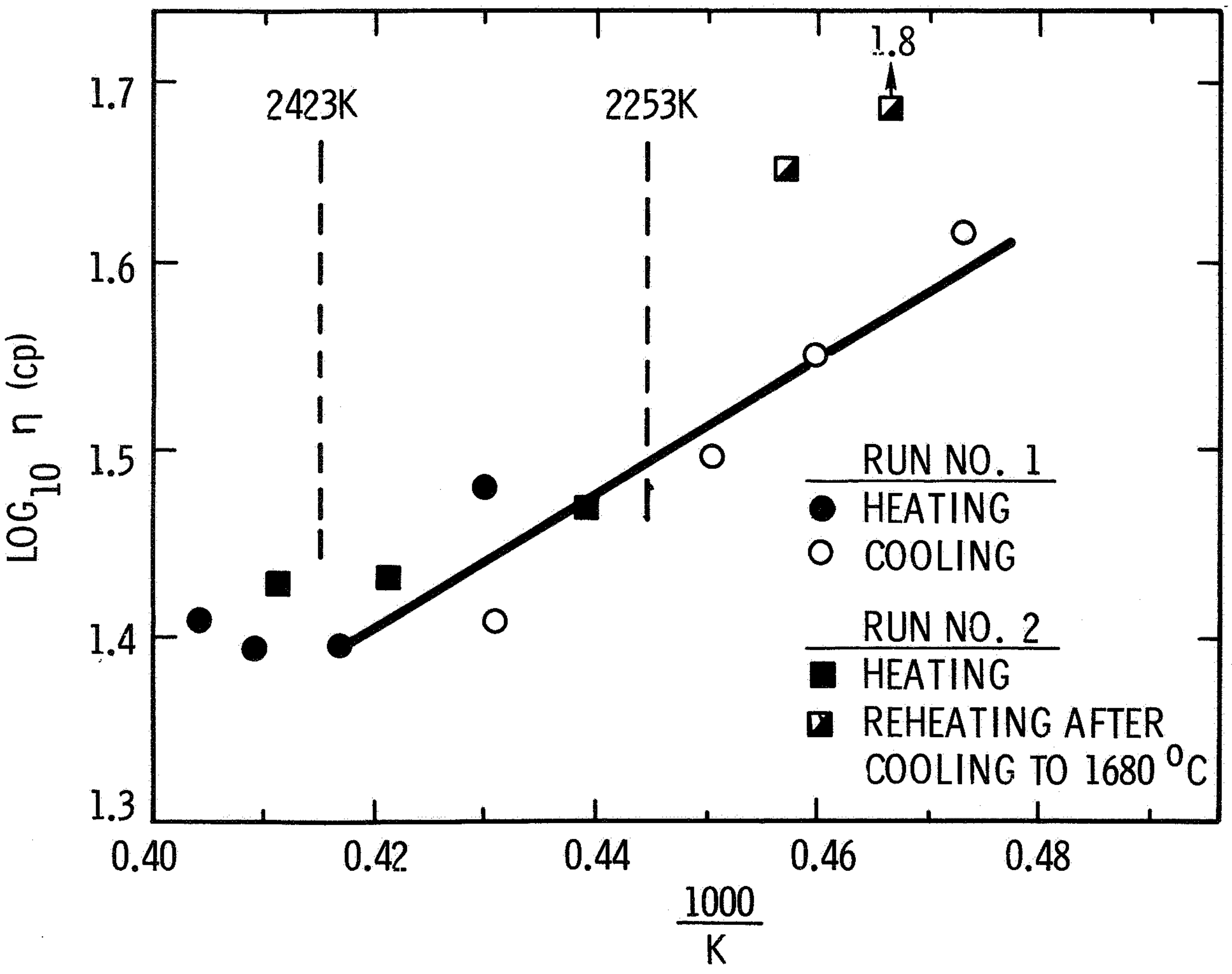

FIGURE 3. Viscosity of Single Crystal 0.375 Y_2O_3-0.625 Al_2O_3

DISCUSSION

Oxide additions to Al_2O_3 reduce the volume change on melting, decrease the viscosity (with the exception of SiO_2) and can both increase and decrease the surface tension. A review of all the data for Al_2O_3 and Al_2O_3 containing additives reported previously by other investigators and the data obtained in this study are summarized in Tables V and VI.* These data form the basis for the following discussion on the effects of additives on the surface tension, viscosity, volume change on melting, and density of Al_2O_3.

Surface Tension

The reported values for the surface tension of liquid Al_2O_3 vary over a wide range from 0.360 to 0.690 Newtons/m. Kingery(5) and Wartenberg et al.(6) used the pendant-drop technique to determine surface tension values of 0.690 and 0.577 Newtons/m, respectively. Bartlett and Hall(7) used the sessile-drop technique and found a lower value of 0.551 Newtons/m. Sokolov(8) calculated a theoretical value of 0.700 Newtons/m.

Studies, however, have shown that the technique for measuring surface tension (pendant drop versus meniscus method) and the container material can influence the surface tension values. Rasmussen and Nelson(2) found the surface tension to be dependent upon the measurement technique and container material. Using a meniscus measurement, the surface tension for liquid Al_2O_3 in molybdenum and tungsten was 0.360 ± 0.040 and 0.638 Newtons/m, respectively. In contrast, the pendant drop measurements where the Al_2O_3 did not contact the container indicated a value of 0.574 ± 0.068 Newtons/m. The surface tension, thus, was significantly dependent upon the container material, undoubtedly affected by the reactions and impurities at the liquid - container interface.

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* Located at end of report.

The addition of oxides to Al_2O_3 appears to influence the surface tension, although the effects were inconsistent, small, and no systematic changes could be recognized. The surface tension of $MgAl_2O_4$ was independent of measurement method.(3) Values obtained using the pendant drop technique or the meniscus measurement technique in tungsten or molybdenum were 0.490, 0.491 ± 0.113, and 0.471 ± 0.101 Newtons/m, respectively.(3) The close agreement between the surface tension values from the pendant drop and meniscus techniques for $MgAl_2O_4$ suggests little reaction between the oxide and the tungsten or molybdenum.

Density and Volume Change

The density of molten Al_2O_3 at the melting point was found to be 3.01×10^3 kg/m^3.(3) Kingery's value for the density was 2.97×10^3 kg/m^3,(5) while Kirshenbaum and Cahill(9) reported a value of 3.05×10^3 kg/m^3 (2) at the melting point.

The specific volume of the liquid oxides increases with temperature. However, the temperature dependence is generally small. For Al_2O_3, $\Delta V/V$ does not appear to be strongly influenced by additives. However, the 0.375 Y_2O_3 - 0.625 Al_2O_3 (YAG) which melted at 2253 K exhibited an unusual increase in $\Delta V/V$ at 2423 K. Between 2253 K and 2423 K, there was only a slight increase in $\Delta V/V$ with temperature. At 2423 K, the $\Delta V/V$ began to increase more rapidly with temperature. The reason for this increase is not known. However, as will be discussed later, the viscosity also appears to change at this same temperature.

Kirshenbaum and Cahill(7) reported a volume change on melting of 22% for Al_2O_3. Kingery's(5) value was 20.4%, Tyrolerova and Lee(10) found values of 19.9 and 20.1%, compared to the 24% reported by Rasmussen and Nelson.(3)

Oxide additions to Al_2O_3 resulted in significant decreases in the volume change on melting and solidification. The largest reductions in volume change (to 8-10%) were observed in those additive systems of Sm_2O_3 and Y_2O_3 which form an eutectic composition and are two-phase as solids. Reductions (to 14-17%) were also observed for the compounds MgO - Al_2O_3(3) and 0.375 Y_2O_3 - 0.625 Al_2O_3.

Even small additions of MgO resulted in a measurable decrease in $\Delta V/V$. The <0.25 wt% MgO in Lucalox reduced the $\Delta V/V$ from 24 to 22%. From the volume changes measured, 24% for Al_2O_3, 13.5% for $MgAl_2O_4$, and 22% for Lucalox, there is an approximately linear decrease in $\Delta V/V$ with mole percent MgO added.

Rasmussen et al.(3) also found that the initial volume change on melting of single crystals of sapphire and spinel was greater than the subsequent volume changes on melting and the volume change on solidification. For Al_2O_3, this was 33% and 24%, respectively. Upon heating, the decrease in liquid density was not linear with increasing temperature from 2408 K to 2673 K. The density then increased linearly as the temperature was lowered. Upon reheating, the density decreased linearly with an increase in temperature. The larger volume observed on melting was reportedly due to the presence of gases entrapped in the liquid during the initial melting and released after prolonged heating.

From the limited data, it appears that most additives tend to significantly reduce the $\Delta V/V$ for Al_2O_3. The smaller decrease in the volume change on melting for the yttrium aluminum garnet and the magnesia alumina spinel compared to the Al_2O_3 is consistent with the relatively large open structures of these crystals compared to the more closely packed structure of the Al_2O_3. For spinel $\rho = 3.58$ compared to $\rho = 4$ for Al_2O_3 and $\rho = 3.6$ for MgO.

Viscosity

The viscosity of Al_2O_3 has been measured by a number of other investigators(1,11-15) with values for viscosity near 2373 K varying from 0.6 poise(11-13) to 10 poise.(14) The very large values of viscosity for Al_2O_3 (1 to 10 poise) reported by Hasapis et al.(14) were impossible to analyze and evaluate since no details of results and procedures were described. However, an evaluation of the other data suggest that the viscosity of Al_2O_3 near its melting point is less than 1 poise. The results of Elyuten et al.(13) and Kozakevitch(11-12) agree (approximately 0.6 poise at 2375 K). These data are lower than the values (approximately 0.9 poise) obtained by Bates et al.(1) using the same equipment used in this study. Larger variations were observed at the higher temperatures. For example, the viscosities reported by Bates et al.(1) and Elyuten et al.(13) at 2633 K were 0.64 and 0.24 poise, respectively. The reason for this difference is not understood. Experimental errors could be the cause for this variation since different techniques were used, although each used acceptable standardization techniques. It should be noted that the higher viscosity values(1) involve high purity, single crystal Al_2O_3, while the lower values are related to starting samples which were polycrystalline and of unknown purity and gas content. It is difficult to rationalize why the structure difference should carry over into the liquid, unless it involves impurity effects. However, as seen in the data for Lucalox, the less than 0.25% MgO lowered the viscosity by one half.

Additions of SiO_2, CaO, MgO, Sm_2O_3, and Y_2O_3 altered the viscosity of molten Al_2O_3. SiO_2 additions increased the viscosity while the other additives decreased the viscosity (Figure 4). Small increases in viscosity were reported for compositions containing less than 20 mole% SiO_2, while larger increases resulted for larger additions.(11-12) For example, at 2353 K, the viscosity at 0, 20 mole%, 40 mole% (mullite), and 50 mole%, SiO_2 was 0.54, 0.64, 1.25, and 2.0 poise, respectively. There was also a corresponding reduction in melting point.

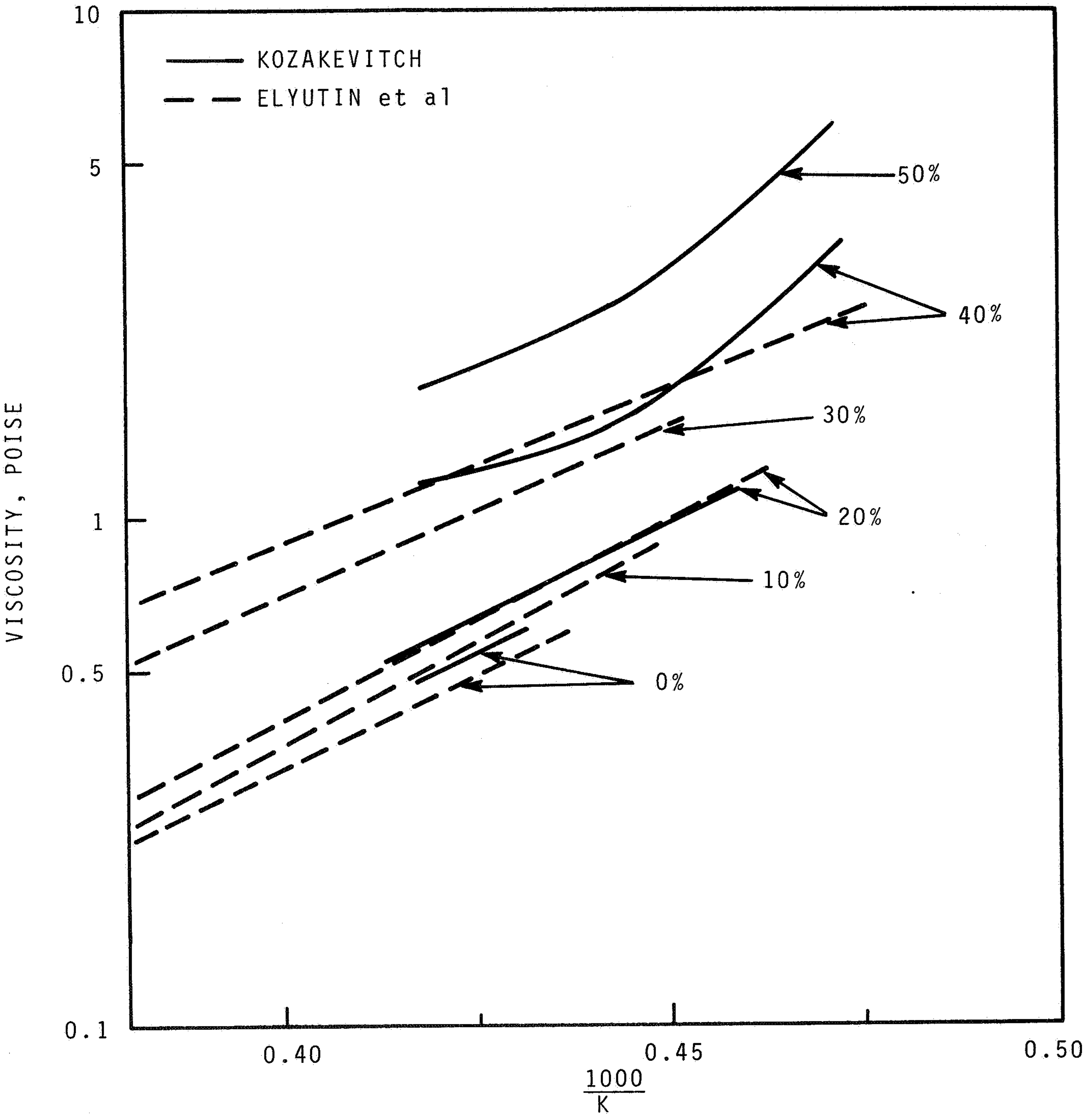

FIGURE 4. Effects Of SiO_2 On The Viscosity Of Al_2O_3 (Additions Expressed In Weight Percent)

CaO added to Al_2O_3 lowered the viscosity of Al_2O_3, but the size of the effects was less than that for SiO_2.(11-12) (Figure 5) The additions of CaO decreased the melting point with a resulting decrease in viscosity, η.

In both the SiO_2 - Al_2O_3 and CaO - Al_2O_3 systems, there exist large regions of wide compositional ranges below the liquidus temperature where both solid and liquid phases exist. However, there is complete solubility in the liquid state.

In the more complex liquid systems containing CaO, Al_2O_3, and SiO_2, additives also altered the viscosity.(15-16) The melts containing higher SiO_2 contents generally had a higher viscosity. Above approximately 35 mole% of SiO_2, the viscosity depended primarily on the SiO_2 content. Below this value, other additions became important. FeO, MgO, CaO, and MnO decreased the viscosity of these systems. CaF_2 was much more effective in lowering the viscosity than CaO, with larger changes occurring at the lower temperatures. Although these effects relate to complex oxide systems which are primarily silicates, they do indicate possible avenues for altering the properties of molten Al_2O_3.

The viscosity of spinel, $MgAl_2O_4$, was significantly less than that for Al_2O_3 and was associated with a smaller activation energy, 2.9 Kcal/mole. The data fit a reciprocal temperature relationship of η. $\log_{10} \eta = 0.811 + 636.9\ T^{-1}$ where T is temperature in K and η is the viscosity in centipoise.

The above values for the viscosity of $MgAl_2O_3$ were significantly smaller than the data reported by Ermolaeva et al.(17) (0.11-0.12 poise compared to 2.3 poise near 2373 K). This large difference may be due to differences in the experimental techniques. The method used by Ermolaeva et al. was based on the flow rate of a liquid through a capillary. The flow rate was dependent on the hydrostatic pressures above the capillary

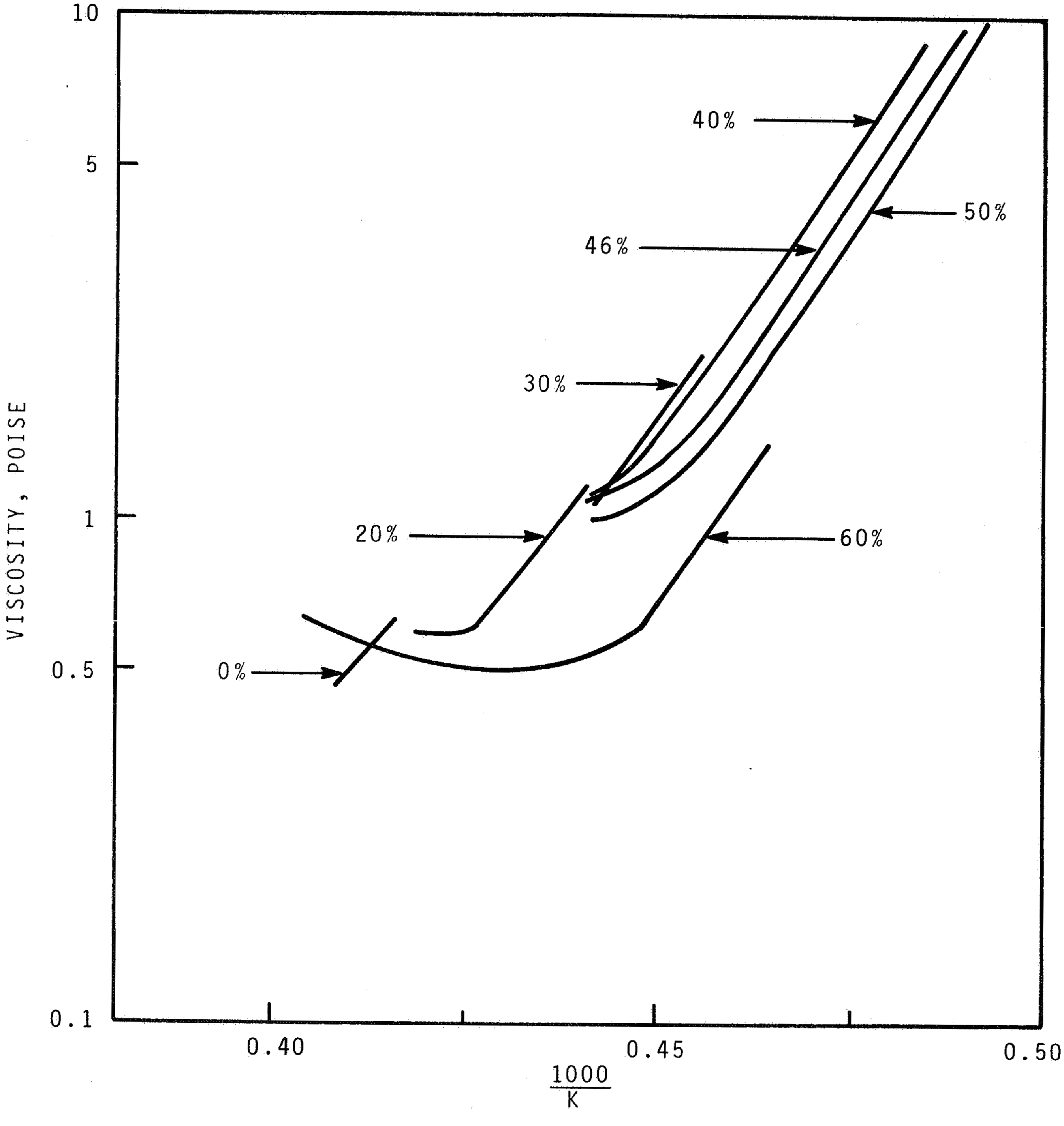

FIGURE 5. Effects Of CaO On The Viscosity Of Al_2O_3.(12)
(Additions Expressed In Weight Percent)

and the viscosity of the liquid. The method was not an absolute measurement but required the direct comparison of fluids with known viscosities. The author failed to mention the viscosity standard used and did not consider the significant effects of the high surface tension of these oxides on capillary flow. Such effects would tend to restrict the flow through the capillary. If the surface tension of the standard was substantially different from that of the spinel, no direct comparison could be made.

In addition, the spinels used by Ermolaeva et al.(17) were not pure $MgAl_2O_4$ but contained SiO_2 (∿3%), Fe_2O_3 (∿1%), Cr_2O_3 (∿1%), and CaO (∿1%). The addition of SiO_2 would tend to increase the viscosity.(11-12) Thus, there is some doubt concerning the data of Ermolaeva et al.

The data for the non-eutectic compositions of 0.2 Y_2O_3 - 0.8 Al_2O_3 indicated a very high activation energy resulting from the high viscosity near the liquid temperature. This contrasts to a low activation for Al_2O_3 and the other single phase compounds. However, at the melting temperature of Al_2O_3, the viscosity of the 0.2 Y_2O_3 - 0.8 Al_2O_3 was less than that for pure Al_2O_3 and was the same magnitude as that for the yttrium - aluminum garnet. The high viscosity at temperatures slightly above the liquidus temperature suggests that a relatively high degree of order exists that is not generally found in the single phase solids such as Al_2O_3 and $MgAl_2O_3$ (spinel). This order appeared to persist until the temperature was raised significantly above the liquidus temperature. Such order would exist even though the large volume expansion had occurred.

It would be beneficial if sufficient information were available to relate the viscosity results to the structure of the additive.

Melting and Supercooling

Some mention should be made concerning the potential use of these techniques for determining the melting points, liquidus temperatures, eutectic temperatures, and supercooling of oxides. Large voids and second phase were easily resolved by radiography. Melting was indicated by the formation of a meniscus and the formation of a homogeneous liquid (for the two-phase oxide systems). Viscosity measurements were very sensitive to the formation of a liquid.

Melting inside the crucible was readily observed: (1) from the radiographs, (2) from sharp discontinuities in ΔV/V, and (3) from the viscosity measurements. Prior to melting, damping of the rotating capsule during measurements was negligible. However, on melting or partial melting, damping effects were easily observed. Since the measurements are observed simultaneously with the changes and measurements of temperature, melting and solidification temperatures were readily determined. For example, the reported melting point for 0.375 Y_2O_3 - 0.625 Al_2O_3 is 2203 K(4). However, from the x-ray radiographs and viscosity evaluations, the oxide consistently melted at 2233 ± 10 K.

Similarly the reported phase diagram indicated that the liquidus temperature of the 0.1 Y_2O_3 - 0.9 Al_2O_3 should be 2223 K. However, the presence of the solid Al_2O_3 phase seen in the radiographs and the sharp discontinuity in the ΔV/V versus temperature curve indicated a liquid temperature of 2193 K.

The presence of two separate phases could be determined if the densities of the two phases were sufficiently different. When studying the 0.1 Y_2O_3 - 0.9 Al_2O_3 sample, the formation of a meniscus at the eutectic temperature (2033 K) and the separation of the sample into a liquid and solid phase was resolved from the radiographs providing a measure of the eutectic temperature. The disappearance of the second phase and the sharp changes in damping provided a measure of the liquidus temperature.

The supercooling of the molten 0.375 Y_2O_3 - 0.625 Al_2O_3 (yttrium - aluminum garnet) was totally unexpected and may be the first direct evidence of such a phenomena in high temperature oxide systems. The presence of supercooling appeared to affect the final state of the sample cooled in the capsule. On cooling, the nucleation of crystals was initiated at the walls of the capsule with rapid growth occurring. However, once the lower solidification point was reached, the melt solidified very rapidly leaving a center containing very fine pores. Whereas, if supercooling were small or non-existent, the center would have contained large central voids. similar to Al_2O_3, etc. Such supercooling may be very important and even essential to the growth from the melt of single crystals of these oxides. It would appear that many other oxides might exhibit supercooling phenomena, especially those where single crystals can be grown from the melt.

CONCLUSIONS

1. Additions of oxides to Al_2O_3 reduced the volume change on melting when compared to Al_2O_3.

2. With the exception of SiO_2, which forms a glass, all other oxides reduced the viscosity of Al_2O_3.

3. Surface tensions changed with oxide additions, but changes depended upon the capsule material.

4. Supercooling of 270 K for yttrium aluminum garnet (0.375 Y_2O_3 - 0.625 Al_2O_3) was observed on cooling.

5. Techniques for measuring the liquid properties can be used to determine eutectic and liquid temperatures of high temperature oxides.

6. Viscosity and volume change on melting appeared to be significantly more important for studying the structure of liquids than was surface tension. This was easily seen since the viscosity and volume change of Al_2O_3 appeared to be strongly affected by the addition of other oxides.

TABLE V. Property Data of Molten Al_2O_3.

	Volume Change		Surface Tension		Viscosity	
Investigator	Melting (%)	Density kg/m^2 (2323°K) (10^3)	Container	Newtons/m (10^{-3})	Temperature (°K)	Poise
Kingery (5)		2.97		690		
Van Wartenberg (6)		2.55		577 (695)*		
Bartlett and Hall (7)				551		
Solokov (8)				700**		
Kozakevitch (11,12)		3.05			2323	0.6
					2300	0.5
Rasmussen and Nelson (2)	24***	$\rho = 4.755 \times 10^3 - 7.52 \times 10^{-1}\ T$ (2323 - 2673°K)	Mo	360 $\pm$ 40	2473	0.70
Bates et al. (1)			W	574 $\pm$ 68	2573	0.64
					2673	0.54
					2773	0.50
Elyuten (13)					2323	0.584
					2373	0.457
					2473	0.335
					2573	0.265

---

* 0.695 Newton/m calculated on $\rho = 3.01 \times 10^3\ kg/m^2$ at 2323°K.

** Calculated.

*** On Cooling.

TABLE VI. Property Data of Molten Al_2O_3 Containing Additives.

Sample Composition	Investigator	Volume Change		Surface Tension		Viscosity		Activation Energy
		Melting %	Density kg/m^2	Container	Newtons/m (10^{-3})	Temperature K	Poise	
Al_2O_3	Rasmussen and Nelson (BNW)(2)	24 ± 1.5	3.00×10^3 at 2323 K.	Mo	360 ± 40	2473	0.70	11.8
	Bates et al.(1)		$\rho = 4.755 \times 10^3 - 7.52 \times 10^{-1}\ T$	W	574 ± 68	2573	0.64	
			(2323 - 2673 K)			2673	0.54	
						2773	0.50	
Lucalox <0.25% MgO	This study	22	Same as Al_2O_3		Same as Al_2O_3	2353	0.36	5.7 (>2473 K)
						2393	0.33	
						2453	0.30	21.7 (<2473 K)
						2493	0.29	
						2593	0.28	
$MgAl_2O_4$	Rasmussen et al.(2,3)	14.1 ± 1.3	$\rho = 5.263 \times 10^3 - 9.63 \times 10^{-1}\ T$	Mo	491 ± 113	2458	0.117	
				Mo	471 ± 91	2563	0.115	2.9
			(2413 - 2673 K)		490 ± 98	2658	0.112	
1.5 Al_2O_3 - 1.0 MgO	Rasmussen et al.(3)	17.4 ± 0.3	$\rho = 3.22 \times 10^3 - 0.16\ T$	Mo	360			
			(2413 - 2673 K)					
SiO_2 - Al_2O_3 10 wt% SiO_2	Elyuten(13) et al.					2273	0.775	
						2373	0.54	
						2473	0.385	
						2573	0.29	
20 wt% SiO_2						2173	1.10	
						2273	0.81	
						2373	0.59	
						2473	0.43	
						2573	0.32	

TABLE VI (Cont'd)

Sample Composition	Investigator	Volume Change		Surface Tension		Viscosity		Activation Energy
		Melting %	Density kg/m^2	Container	Newtons/m (10^{-3})	Temperature K	Poise	
30 wt% SiO_2						2273	1.26	
						2373	0.96	
						2473	0.74	
						2573	0.59	
40 wt% SiO_2						2173	2.10	
						2273	1.51	
						2373	1.18	
						2473	0.94	
						2573	0.78	
Al_2O_3-SiO_2	Kozakevitch (11,12)							
20 wt% SiO_2						2273	0.80	
						2373	0.60	
40 wt% SiO_2						2173	2.40	
						2273	1.50	
						2373	1.20	
50 wt% SiO_2						2173	4.10	
						2273	2.50	
						2373	1.90	

TABLE VI (Cont'd)

Sample Composition	Investigator	Volume Change		Surface Tension		Viscosity		Activation Energy
		Melting %	Density kg/m^2	Container	Newtons/m (10^{-3})	Temperature K	Poise	
CaO-Al_2O_3	Elyuten et al.(13)							
20 wt% CaO						2073	1.1	
						2173	0.7	
						2273	0.6	
30 wt% CaO						1973	1.8	
						2073	1.1	
40 wt% CaO						1873	3.3	
						1973	1.7	
						2073	1.1	
50 wt% CaO						1773	5.70	
						1873	2.3	
						1973	1.2	
						2073	1.0	
60 wt% CaO						1973	0.8	
						2073	0.6	
						2173	0.5	
0.2 Sm_2O_3- 0.8 Al_2O_3	This study	10 ± 2						

TABLE VI. (Cont'd)

Sample Composition	Investigator	Volume Change		Surface Tension		Viscosity		Activation Energy
		Melting %	Density kg/m^2	Container	Newtons/m (10^{-3})	Temperature K	Poise	
0.1 Y_2O_3- 0.9 Al_2O_3	This study	13.5 ± 0.5	3.521 x 10^3 at 2193 K			2223	2.95	
						2243	2.60	
						2293	0.27	
0.375 Y_2O_3- 0.625 Al_2O_3 (YAG)	This study	7.8				2117	0.394	
						2173	0.354	
						2218	0.310	
						2273	0.292	
						2318	0.281	
						2373	0.267	
						2394	0.248	
						2433	0.268	
						2443	0.245	
						2473	0.254	

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