International Journal of Thermophysics, Vol. 15, No. 2, 1994

Thermal Properties of Al_2O_3 in the Melting Region

S. V. Stankus[1] and P. V. Tyagelsky[1]

Received October 4, 1993

The density and thermal expansion of alumina (99.99%) were studied in the liquid and solid states in the region of crystallization and melting by irradiating the samples with a narrow beam of gamma quanta. The temperature dependence of the density of strongly supercooled (by 220 K) alumina and the specific volume change on crystallization were determined. The results are compared with the data available in the literature.

KEY WORDS: alumina; crystallization; density; gamma-attenuation technique; melting; supercooling; thermal expansion.

1. INTRODUCTION

The thermal properties of liquid alumina were investigated using a variety of techniques [1-8], but the results are in rather poor agreement. It suffices to say that the data [1, 8] on the melt density at the melting temperature (T_f) differ by 11%, and the data on the thermal expansion coefficient (β) by a factor of 3. It seems likely that direct measurements of the density change of alumina on melting ($\delta\rho_f$) were made only in the work given in Ref. 9. In all other instances, the values of $\delta\rho_f$ were calculated from the density of molten alumina measured above the melting point and the density of solid α-Al_2O_3 at the melting point, as obtained by extrapolation from lower-temperature data. Clearly this procedure leads to substantial errors in the values of density change, since in contrast to direct measurements of $\delta\rho_f$, the systematic errors in the density of both phases are not compensated in that case [10]. The lack of reliable data hampers the solution of both practical and theoretical problems. Among the latter should be mentioned the test of property prediction methods of liquid multicomponent oxides and the question of the structural change existing in melts.

---

[1] Institute of Thermophysics, Siberian Branch of the Russian Academy of Sciences, Novosibirsk 630090, Russia.

0195-928X/94/0300-0309$07.00/0

2. EXPERIMENTS

The aim of the present paper was to obtain new reliable data on the change of α-Al_2O_3 density in the melting region as a function of temperature and phase. Measurements were performed mainly by irradiating the samples with a narrow beam of gamma quanta [11, 12] from a ^{137}Cs source (220 GBq) in the temperature range from 2000 to 2500 K. The samples, having masses of 150–170 g, were cut from single crystals, purity 99.99%, grown by the Czochralski method. Crucibles 40 mm in diameter were made from polycrystalline molybdenum. The temperature was measured with tungsten–rhenium thermocouples embedded in the sample. The measurements were made mainly during continuous heating (cooling) of the furnace at a rate of 2–8 $K \cdot min^{-1}$ in single-phase regions and at a rate of 0.1–0.5 $K \cdot min^{-1}$ in melting-crystallization regions. In addition, at selected points the density was determined after holding the sample at a constant temperature for 10–15 min. The results were unaffected by the rate of temperature change.

The density of liquid alumina ρ_m and the fractional density change on melting $\delta\rho_f = (\rho_S - \rho_L)/\rho_S$ were determined from the expressions

$$\rho_m = \frac{\ln[J_0(T)/J(T)]}{\mu d[1 + \alpha(T)(T - 293)]} \quad (1)$$

$$\delta\rho_f = \frac{\ln(J_L/J_S)}{\ln[J_0(T_f)/J_S]} \quad (2)$$

where T is temperature, μ and d are the mass attenuation coefficient (temperature independent) and the inner diameter of the crucible at 293 K; J and J_0 are the intensities of the radiation after passage through the experimental apparatus with and without the sample, respectively [$J_0(T)$ was measured before the main experiment]; and $\alpha(T)$ is the average linear coefficient of thermal expansion of the crucible material. Subscripts L and S are used to denote the values relative to the liquid and solid states, respectively, at melting temperature. The thermal expansion coefficient $\beta = -[1/\rho(T)][d\rho/dT]$ was defined from the approximate dependencies of density, which were found using the least-squares method. It is easily shown that the thermal expansion coefficients (TECs) measured by the gamma attenuation technique are independent of the absolute value of density and are defined as a whole by the values of the intensities and $\alpha(T)$ (for melts).

Table I. Experimental Data on the Thermal Expansion Coefficient of Liquid Alumina[a]

Sample	Regime	β_L (10^{-5} K^{-1})	Temperature range (K)
1	Heating-1	6.92 ± 3.2	2395–2467
	Heating-2	6.36 ± 2.1	2382–2452
	Cooling-1	6.22 ± 0.26	2119–2472
	Cooling-2	6.81 ± 0.45	2180–2465
2	Cooling-2	6.21 ± 0.34	2108–2462
	Weighted mean	6.38 ± 0.64	

[a] Here and in the following tables a random error is listed for the measured values and a total error for the mean values. All are for a 95% confidence interval.

3. RESULTS

The density of single-crystal samples at room temperature was determined using the indirect Archimedean method. The average of the five measurements is $\rho_r = (3986 \pm 4)$ kg $\cdot$ m^{-3}, which compares well with the density calculated from the lattice parameters of α-Al_2O_3 [13].

Some original high-temperature data are shown in Tables I and II and Figs. 1 and 2. The measurement of the melting-crystallization temperature of alumina was reproduced to within 1 K, with an average value of $T_f = (2325 \pm 5)$ K, which agreed with $T_f = 2327$ K [14] within the estimated error. Supercooling of alumina was detected in all experiments. Its maximum value reached 200–220 K. In each case, the thermal properties were free from anomalies when the melt "intersected" the melting point (Figs. 1 and 2). The density of liquid alumina depends linearly on temperature over the range 2100–2475 K. The values of the thermal expansion coefficient

Table II. Al_2O_3 Melt Density and Its Change on Melting-Crystallization

Sample	Regime	ρ_L (kg $\cdot$ m^{-3})	$\delta\rho_f$ (%)
1	Heating-1	2906 ± 10	—
	Heating-2	2906 ± 6	—
	Cooling-1	2900 ± 2	22.81 ± 0.08
	Coolng-2	2909 ± 2	22.81 ± 0.05
2	Heating-2	2904 ± 5	22.81 ± 0.15
	Cooling-1	2907 ± 1	22.84 ± 0.09
	Weighted mean	2905 ± 14	22.82 ± 0.20

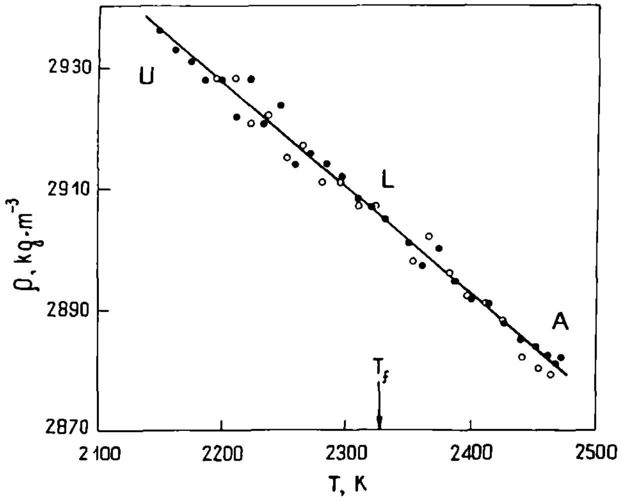

Fig. 1. Temperature dependence of the alumina density (first sample) in the liquid phase. LA and UL, overheating and supercooled states, respectively. Points are experimental values; the line is the linear best fit. (●) First cooling; (○) second cooling.

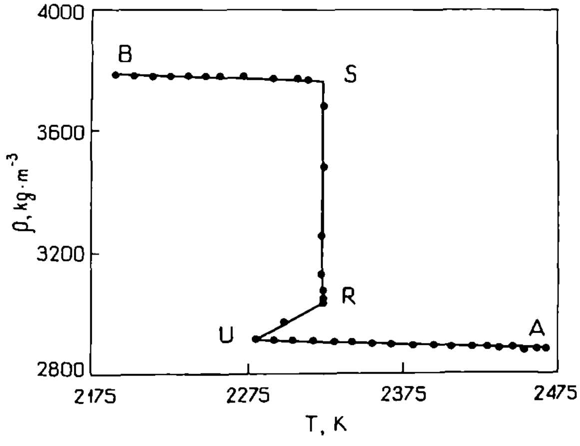

Fig. 2. Change of alumina melt density on crystallization (second sample, first cooling). UA, liquid state; UR, recalescence of the melt; RS, solidification; SB, α-Al_2O_3.

(Table I), the density, and its change on melting (Table II) were reproduced well either in different thermal cycles or in different samples. The equation to describe the temperature dependence of molten alumina over the range studied can be obtained from the weighted average values of ρ_L and β_L:

$$\rho_m(T) = 2905 - 0.18534(T - 2327) \tag{3}$$

where ρ_m is in $kg \cdot m^{-3}$ and T is in K. The data for the density of solid sapphire (ρ_c) in the neighborhood of the melting point (2150–2327 K) are described by

$$\rho_c(T) = 3764 - 0.12873(T - 2327) \tag{4}$$

where ρ_c is in $kg \cdot m^{-3}$ and T is in K. The density of α-Al_2O_3 and its thermal expansion coefficient at 2327 K were defined using the respective average value of ρ_L and $\delta\rho_f$ and the averaging of original data:

$$\rho_S = (3764 \pm 20)\ kg \cdot m^{-3}, \qquad \beta_S = (3.42 \pm 0.26) \times 10^{-5}\ K^{-1} \tag{5}$$

4. DISCUSSION

Thermal properties of crystalline α-Al_2O_3 were completely investigated because sapphire was used for producing the high-temperature thermal expansion standards. Therefore a comparison between Eq. (5) and literature data makes it possible to define the reliability of our estimated measurement precision. Among recent works, the most reliable data have been reported in Refs. 13 and 15. The temperature dependences of the mean linear expansion coefficient and relative expansion over the range 20–2000 K were recommended in Ref. 15 on the basis of the critical analysis of the available alumina thermal expansion investigations. Precise measurements of the lattice parameters for α-Al_2O_3 from 293 to 2298 K were reported in Ref. 13. The data given in Ref. 15 for the relative expansion and TEC over the range 1100–2000 K were fitted by the least-squares method and were extrapolated to the melting point for ρ_S and β_S determination. The density value was calculated from the fractional volume change from 293 K to T_f and X-ray ρ_r [13]. As shown in Table III, these results are in excellent agreement. This is evidence that our results are free from unaccounted systematic errors.

The thermal properties data of molten alumina (Table IV) are not in such a good agreement. In addition, one can see that the measurement results depend on the technique used. The greatest density values were obtained by the maximum-bubble pressure method [1, 2] and the smallest values were obtained by the drop method [6, 8]. The spread in the ρ_L is

Table III. Comparison of the Data on Thermal Properties of Solid Alumina at Melting Temperature

Ref. No.	Year	ρ_S (kg·m^{-3})	β_S (10^{-5} K^{-1})	Difference from our experimental data (%)	
				ρ_S	β_S
15	1983	3759	3.54	−0.13	3.5
13	1984	3768	3.32	0.11	−3.0
Present work		3764	3.42		

greater than the claimed uncertainty in each work. Application of the Archimedean and dilatometric methods gives close results, but they also differ from the other data. A similar situation is observed for the thermal expansion coefficient of molten alumina. It seems likely that disagreements are not explained by different purities of alumina, because even in the solid state the density and TEC are not affected by the purity of Al_2O_3 within the range 99.5–99.999% [13]. It is more probable that the data spread is due to the presence of gas bubbles in the melt [9], which is capable of distorting the measurement results [10]. All this indicates that the classic methods of the study of thermal properties are difficult to apply to high-temperature oxide melts.

As shown in Table IV, our data on melt density agree with those given in Refs. 4, 6, and 8 to within the total experimental error. A wider spread is noted for the thermal expansion coefficient. Only the results given in

Table IV. Thermal Properties of Al_2O_3 in the Liquid State

Ref. No.	Year	Method[a]	ρ_L (kg·m^{-3})	β_L (10^{-5} K^{-1})	T_{max} (K)
1	1973	MBP	3056 ± 21	31.6	3000
2	1990	MBP	3060 ± 30	—	T_f
3	1960	Arch	3009	37.4	2623
4	1970.	Arch	3012 ± 90	38.2	2823
5	1972	Dil	3005	25.0	2775
6	1959	D	2970	—	T_f
7	1969	D	2700	30.0	2700
8	1983	D	2714 ± 390	10.1 ± 7.1	2959
Present work		G	2905 ± 14	6.38 ± 0.64	2475

[a] MBP, maximum buble pressure; Arch, Archimedean; Dil, dilatometer; D, drop; G, gamma attenuation.

Ref. 8 overlap with our data, but β_L from Refs. 1, 3–5, and 7 exceed it by a factor of 4–6. Nevertheless, there is reason to believe that the results obtained in this work for TEC of molten alumina are more precise. The reason for this is the high reproducibility of the results, the good agreement between the measured and the recommended values of T_f, ρ_S, and β_S, and that the same sources of systematic error of TEC determined by the gamma attenuation technique apply to both condensed states. As shown in Figs. 1 and 2, supercooling of the alumina melt allowed the measurement of the thermal expansion coefficient of solid and liquid Al_2O_3 in the identical temperature range. In that case, systematic errors associated with the mass attenuation coefficient, temperature, crucible diameter, $J_0(T)$ dependence, and $\alpha(T)$ definition make the identical contribution to β_S and β_L. Consequently, excellent agreement of the data for α-Al_2O_3 (Table III) point to the high precision of the results for the liquid state.

The density change of α-Al_2O_3 on melting $\delta\rho_f = 20.0\%$, measured earlier by means of the unfeed casting method [9], is about 3% less than our data. This is not surprising, as this technique is devoid of high precision and always gives low $\delta\rho_f$ values [10]. Compared to other high-temperature oxides, for example, rare-earth garnets ($\delta\rho_f = 7$–10% [16]), alumina has a greater volume change on melting. One can suggest that the large volume increase in α-Al_2O_3 during its transformation to the liquid

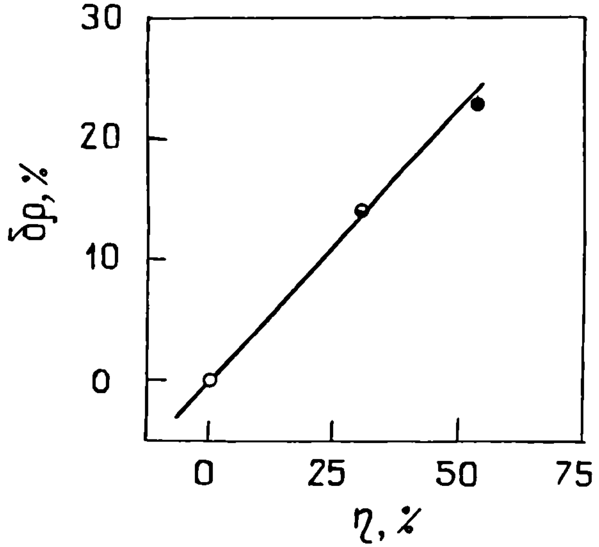

Fig. 3. Fractional density difference of melt (●), γ-Al_2O_3 (◒), and α-Al_2O_3 (○) as a function of cation fraction in tetrahedral surrounding, η. $\delta\rho = [\rho - \rho(\alpha\text{-}Al_2O_3)]/\rho(\alpha\text{-}Al_2O_3)$.

state is associated with radical variation of the short-range order and, primarily, with variation of the coordination number (Z) of aluminum ions. If in the crystalline lattice of α-Al_2O_3 all cations have $Z=6$, then, according to molecular-dynamics simulations [17], 54% of the aluminum atoms are already in a tetrahedral surrounding in the melt. A good correlation between the density and the number of atoms in the four-fold coordination (Fig. 3) is evidence in favor of the above assumption.

In summary, note that the linear dependence of the density and small thermal expansion coefficient value of alumina point to the absence of structural changes in the melt at least up to 2500 K.

REFERENCES

1. E. E. Shpil'rain, K. A. Yakimovich, and A. F. Tsitsarkin, *High Temp. High Press.* **5**:191 (1973).
2. S. Hara, N. Ikemiya, and K. Ogino, *J. Iron Steel Inst. Jap.* **76**:2144 (1990).
3. A. D. Kirshenbaum and J. A. Cahill, *J. Inorg. Nucl. Chem.* **14**:283 (1960).
4. B. S. Mitin and Yu. A. Nagibin, *J. Phys. Chem.* **44**:1325 (1970) (Russian).
5. J. J. Rasmussen, *J. Am. Ceram. Soc.* **55**:326 (1972).
6. W. D. Kingery, *J. Am. Ceram. Soc.* **42**:6 (1959).
7. Yu. V. Zubarev, V. I. Kostikov, B. S. Mitin, Yu. A. Nagibin, and V. V. Nischeta, *Neorgan. Materialy* **5**:1563 (1969).
8. B. Granier and S. Heurtault, *Rev. Int. Hautes Temp. Refract. Fr.* **20**:61 (1983).
9. P. Tyrolerova and W. K. Lu, *J. Am. Ceram. Soc.* **52**:77 (1969).
10. S. V. Stankus, *Density Change of Elements on Melting*, Preprint N 247 (Institute of Thermophysics, Novosibirsk, 1991) (Russian).
11. S. V. Stankus and R. A. Khairulin, *Teplofiz. Vysokikh Temp.* **30**:487 (1992).
12. S. V. Stankus and R. A. Khairulin, *Russ. J. Eng. Thermophys.* **1**:193 (1991).
13. P. Aldebert and J. P. Traverse, *High Temp. High Press.* **16**:127 (1984).
14. H. Preston-Thomas, *Metrologia* **12**:7 (1976).
15. S. K. White and R. B. Roberts, *High Temp. High Press.* **15**:321 (1983).
16. S. V. Stankus, R. A. Khairulin, I. A. Ivanov, Yu. L. Babokin, and A. M. Bul'kanov, in *Thermophysical Properties of Matter, Part 2*, V. E. Nakoryakov, ed. (Novosibirsk, 1989), p. 203 (Russian).
17. D. K. Belastchenko and A. D. Fed'ko, *Neorgan. Materialy* **28**:108 (1992).