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The Density of Titanium(IV) Oxide Liquid

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The density of TiO_2 liquid in equilibrium with air has been measured at 1875° to 1925°C using an Ir double bob Archimedean method. The melt density data have been combined with data extrapolated from the $CaSiO_3$–TiO_2 join at 1600°C. A combined fit to these density data yields the following description of the density of liquid TiO_2: $\rho = 3.7611 - 0.00028T(°C)$, in the temperature range of 1600° to 1925°C. This expansivity value is consistent with those obtained on TiO_2-rich melts using a Pt-based system at lower temperature and with multicomponent oxide data. The similarity between the volume of liquid TiO_2 and that of crystalline rutile implies a dominantly octahedral coordination of Ti in the liquid state. [Key words: titanium oxide, liquids, density, equilibrium, air.]

I. Introduction

THE density of oxide liquids is an important factor controlling their behavior during processes of crystal–liquid fractionation. Such processes occur during geological rock formation and industrial processing involving slags. The liquid compositions in both cases are complex multicomponent systems with respect to the cations present but dominated by oxygen in the anionic component. Measurements of the density of simple end member components of these liquids are useful for the construction of completely general models for the structure and thermodynamics of such systems. Toward the goal of a complete description of such liquid densities, the densities of some simple liquid systems are under investigation. This paper presents the first data from an experimental system allowing the determination of liquid densities in equilibrium with air up to at least 2000°C. The first (to the best of our knowledge) measurements of the density of liquid TiO_2 are presented as an example of the technique.

II. Method

The starting material for the generation of TiO_2 liquid was 2-μm powder of TiO_2 (99.8%, Alfa). The powder was loaded directly into an Ir crucible (2.5-cm inner diameter, 5.1-cm height). The Ir crucible was then wrapped in ZrO_2 felt and placed in a tight-fitting MgO tube. This assembly was bottom loaded into the inner chamber of the high-temperature furnace.

The furnace was a commercially available model (VHT 2100 LINN HighTherm GmbH, Eschenfelden, FRG) (Fig. 1). Its special features are an inner chamber constructed from bubbleform ZrO_2 and two independent sets of heating elements. The outer set are $MoSi_2$ hairpin elements which preheat to 1700°C. These elements sit in wells within the bubbleform ZrO_2 walls. The second set of heating elements are ZrO_2 with $(La,Sr)CrO_3$ end pieces. These elements become sufficiently electrically conducting at 1250°C and are capable of heating to 2150°C in the present configuration.

The furnace was operated via electronic programmable temperature controllers. The preheating was controlled by a type B thermocouple and the main heating was controlled by an infrared pyrometer. The pyrometer was calibrated against a type B thermocouple at 1700°C.

The density measurements were based on the Archimedean buoyancy method. Two Ir bobs were used. The bobs had masses of approximately 14 and 24 g, respectively. Both were suspended from 0.5-mm Ir wire. The measuring balance was a Mettler AE 100. It was interfaced to a personal computer for data gathering using a Mettler 012 Data Interface Module. The datalogging of buoyancy was performed at a 1- to 2-s interval and the results were computer averaged over time.

The procedure for density measurement is to bring the sample to temperature, then load the Ir bob into the furnace from above, wait for thermal equilibrium, tare the balance and submerge the bob to a known depth in the liquid, and computer record the buoyancy. This procedure is repeated for the second bob, and the difference in buoyancy force, divided by the difference in submerged volume of Ir, yields the liquid density, e.g.,

$$\rho = (B_1 - B_2)/(V_1 - V_2) \qquad (1)$$

where ρ is the liquid density, B_1 and B_2 are the buoyancies, and V_1 and V_2 are the submerged volumes of the first and second bobs, respectively. The volume–temperature relationship of Ir was taken from Wimber[1] to be

$$V_t = 4.4601 \times 10^{-4}(100 + 1.994 \times 10^{-3}T - 8.07 \times 10^{-8}T^2 + 4.599 \times 10^{-10}T^3 - 1.052 \times 10^{-13}T^4) \qquad (2)$$

Buoyancy determinations have a precision of ±0.1% at 1σ and the density determinations were repeated with a precision of ±0.3% at 1σ.

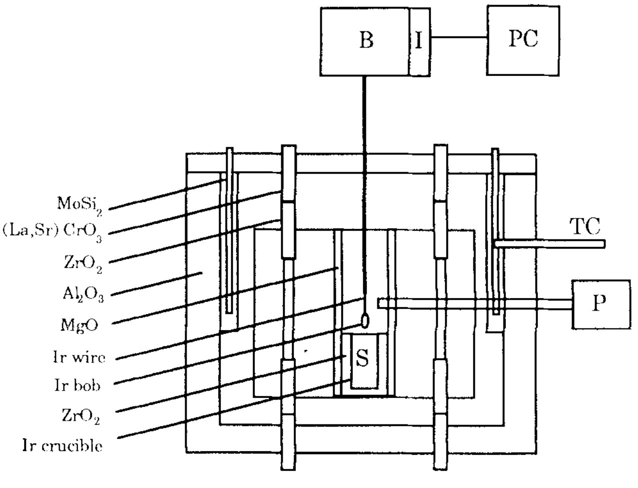

Fig. 1. Schematic of the assembly and furnace used for density measurements: (B) balance, (I) interface, (PC) computer, (TC) thermocouple, (P) pyrometer, (S) sample.

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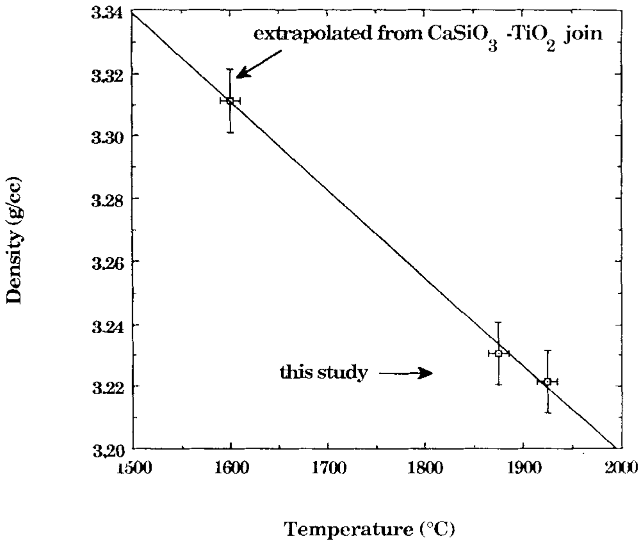

Fig. 2. Data for the temperature dependence of TiO_2 density. Low-temperature data are from Dingwell (1991).

III. Results

The density of TiO_2 liquid was determined at 1875° and 1925°C using the double Ir bob Archimedean method. The densities determined were 3.2308(9) and 3.2215(8) g/cm^3 at 1875° and 1925°C, respectively. Figure 2 compares the results of this study with those of Dingwell[2] obtained at temperatures up to 1600°C using Pt equipment on the $CaSiO_3$–TiO_2 join. The combined fit to the 1600°C extrapolated data point and the data of this study yields a temperature dependence of density given by

$$\rho(T) = 3.7611 - 0.000028T(°C) \tag{3}$$

This value of thermal expansivity is the same as that measured for melts on the $CaSiO_3$–TiO_2 join up to 80 mol% TiO_2. This value corresponds to a molar volume expansivity of 6.70×10^{-3} cm^3/(mol·K) at 1500°C. This value is in agreement with the results of multicomponent modeling of complex silicate melts that yield an end member TiO_2 expansivity of $(7.24 \pm 0.46) \times 10^{-3}$ cm^3/(mol·K) (Lange and Carmichael[3]).

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References

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