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Investigation of the main structural units in Bi_2O_3-TiO_2 solutions

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To investigate a possible correlation between observed crystal growth phenomena and the structure in the liquid phase of Bi_2O_3–TiO_2 solutions, densities and viscosities have been measured and interpreted by the hard sphere model for liquids. The main flow units are probably BiO_2^- and BiO^+ with some Ti complex formation which increases with increasing TiO_2. A change in the complex formation occurs at 12 mol % TiO_2.

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1. Introduction

In the growth of single crystals of $Bi_4Ti_3O_{12}$ from Bi_2O_3–TiO_2 solution it was observed that the composition range 12 to 15 mol% TiO_2 was particularly good for crystal growth [1]. The purpose of this investigation was to examine the structure of the liquid for a range of TiO_2 concentrations from 0 to 20 mol% and to correlate any structure changes with observations of the phase diagram and with crystal growth experiments. The two compositions of most interest are 15 mol% TiO_2 where there is a change in crystal morphology [1] and 12 mol% TiO_2 where $Bi_{12}TiO_{20}$ is grown in preference to $Bi_4Ti_3O_{12}$ [2].

The structure of the liquid was not observed directly but was deduced from measurements of its physical properties. Density, coefficient of expansion and viscosity were measured as functions of temperature and composition for liquids in the range from 0 to 20 mol% TiO_2. From these properties it is possible to calculate the size of the main structural unit using the hard sphere model for liquid properties. Two formulations of the model were used; one by Reiss *et al.* [3] who predicted the relationship between hard sphere diameter and expansivity and one by Cohen and Turnbull [4] as subsequently modified by Kumar [5] which relates density and viscosity via a hard sphere diameter.

Hard sphere models involve a number of assumptions but have been applied successfully to a range of liquids including molten silicates [6] and phosphates [7], liquid metals [8] and organic liquids [9]. Their relevance to crystal growth system has been demonstrated by Elwell *et al.* [10], who studied yttrium aluminium garnet–barium borate liquids.

2. Experimental

The Archimidean two bob method [11] was used to determine the density and coefficient of expansion of various Bi_2O_3–TiO_2 compositions using the apparatus which was basically similar to that used successfully for measurements in the system PbO–V_2O_3–Ta_2O_5 [12]. The two bobs used weighed 1.0 and 0.5 g, each with 0.2 mm diameter support wires and were fabricated from low rhodium (< 40 ppm) content platinum by Johnson Matthey Metals. The apparent weights were measured using Beckman LM600 microbalance. The liquid temperature was monitored by a thermocouple welded to the base of the crucible and correlated to the actual melt temperature as described in the determination of the phase diagram [2]. The results at 1020° C as a function of TiO_2 composition are given in Fig. 1 and a similar plot of expansion coefficient is given in Fig. 2. The platimum density data used in the calculation of results were taken from the Handbook of Chemistry and Physics 42nd Edition (Chemical Rubber Publishing Co). 1020° C was used because this is above the liquidus temperature of all the compositions measured [2].

The dynamic viscosity of the liquid was measured by an oscillating cylinder technique similar to that used by other workers for measurements of

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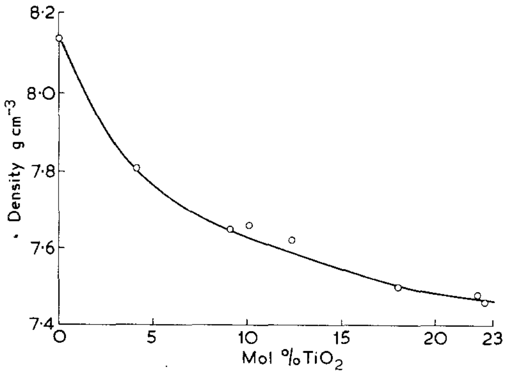

Figure 1 The density of Bi_2O_3–TiO_2 melts at 1020° C as a function of TiO_2 concentration.

liquid metals [13], molten carbonates [14], and molybdates [15]. The liquids studied in this paper presented particular problems in the high temperature required and their highly corrosive Apparatus to meet these constraints was designed and is described elsewhere [16]. The results on dynamic viscosity, η, as a function of temperature are shown as a plot of η versus the reciprocal of the absolute temperature in Fig. 3.

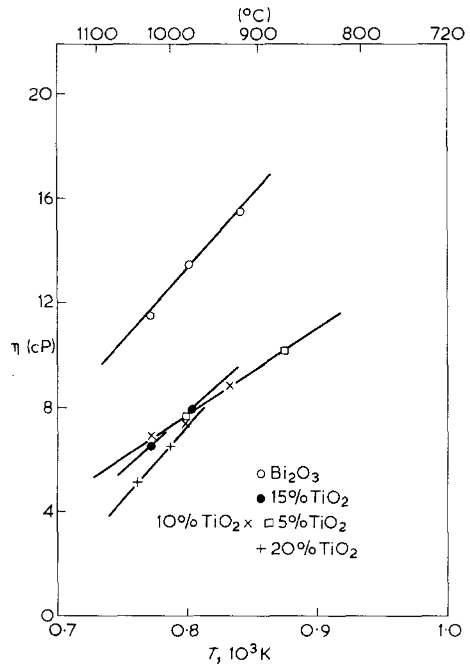

Figure 3 A plot of dynamic viscosity of Bi_2O_3–TiO_2 melts against the reciprocal of absolute temperature.

3. Discussion

The rigid sphere model of Reiss *et al.* [3] relates the expansivity of the liquid α, to a hard sphere

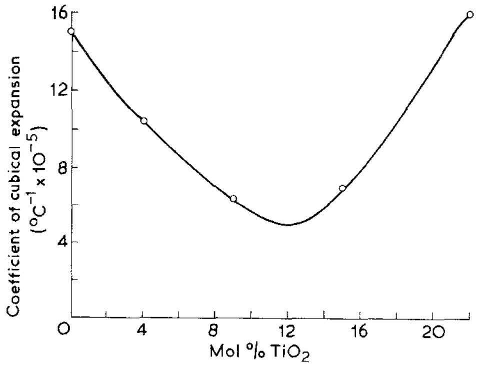

Figure 2 The coefficient of volume expansion of Bi_2O_3–TiO_2 melts at 1020° C as a function of composition.

diameter, a, by the relationship

$$\alpha = \frac{1}{T}\frac{1-y^3}{(1+2y)^3}$$

where T is the absolute temperature and

$$y = \frac{\pi a^3 N}{6V}$$

where N is Avogadro's number and V is the molar volume. The results are shown in Fig. 4. As the expansivity is derived from experimental density

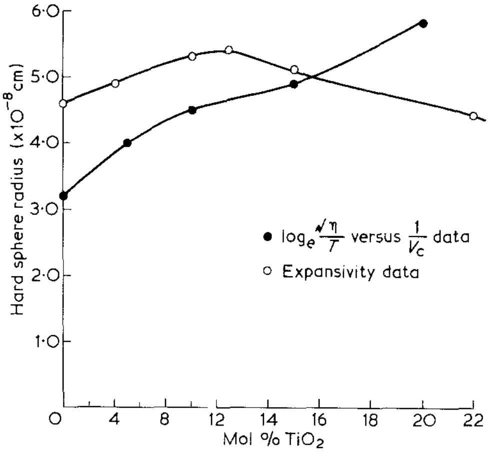

Figure 4 Hard sphere diameters of flow units in BiO_2O_3–TiO_2 melts as a function of TiO_2 content.

data, the value obtained is very sensitive to experimental error. An alternative formulation of a hard sphere liquid relates density and viscosity, which are directly measured properties, to a hard sphere diameter [4, 5]. The relationship used by Fray [6] and Boyer *et al.* [7] is

$$\eta = \frac{(mkT)^{\frac{1}{2}}}{3\sqrt{3}\pi b a^2}\exp\left(\frac{\gamma V^*}{V_f}\right) \qquad (1)$$

where η is the dynamic viscosity, m the mass and V^* the volume of the diffusing unit, k = Boltzmanns constant, b a geometric factor, T the absolute temperature and γ is a constant such that γV^* is the size of the void into which the diffusing unit migrates. V_f is the free volume of the liquid and is defined as the difference between the molar volume of the liquid and the molar volume of the solid at its melting point (or decomposition temperature) [15]. Hence a plot of $\log_e \eta/\sqrt{T}$ against $1/V_f$ is a straight line with slope γV^*. Kumar [5], assuming γ to be unity and that the void was spherical, obtained a hard sphere diameter

$$a = \left(\frac{6V^*}{\pi N}\right)^{\frac{1}{3}}.$$

A departure from linearity would indicate a dependence of hard sphere diameter on temperature but this was not observed. Wittenberg and De Witt [8] review a number of models and confirm the usefulness of this type of relationship and quote alternative formulations of the model which give straight line relationship between $\log_e \eta/\sqrt{T}$ against $1/V_f^{-2/3}$ which gives a better correlation for liquid metals whereas Equation 1 gives the better correlation for oxide based materials. $\text{Log}_e\, \eta T^{-1/2}$ against V_f^{-1} is plotted in Fig. 5 for the five compositions measured. Straight line plots were obtained and the hard sphere diameters calculated from the slopes are presented in Fig. 4.

The expansivity-derived diameters are higher at low TiO_2 content than the free volume data and show a maximum at 12% TiO_2 where the latter shows a point of inflexion. The numerical difference between the hard sphere diameters is probably an indication of the degree to which these liquids fit the hard sphere model but a much better correlation has been obtained than for borate based liquids [10]. The different shapes of the curves could be due either to experimental error in the expansivity result at 20 mol % TiO_2 or to a break down in the hard sphere model above 12 mol % TiO_2. It is significant that both formulations show a liquid structural change at 12 mol % TiO_2 which corresponds to the change from the growth of $Bi_{12}TiO_{20}$ to $Bi_4Ti_3O_{12}$ [2]. No change was observed at 12 mol % TiO_2, the other composition of special interest. The magnitude of the hard sphere diameter is consistent with assuming that molten Bi_2O_3 is composed of $(BiO)^+$ and $(BiO_2)^-$ pairs as BiO_2 would have a diameter 3.54 Å (Bi^{3+} = 0.74 Å, O^{2-} = 1.4 Å) by straight addition. In the γBi_2O_3 structure the Bi–O bond length lies between 2.1 and 3.2 Å [17]. Thus an average value of 4.5 Å in the liquid is consistent with the observed values in the solid for a O–Bi–O grouping. The addition of TiO_2 increases the hard sphere diameter presumably because an unstable Bi–Ti–O complex forms and the hard sphere diameter represents some time-averaged value of the size of this complex. Fig. 4 indicates that the nature of this complex changes for compositions above 12 mol % TiO_2.

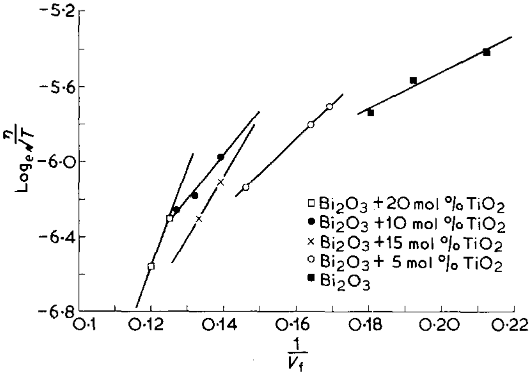

Figure 5 The graph of $\log_e \eta T^{-1/2}$ against the reciprocal of free volume in Bi_2O_3–TiO_2 melts for 0, 5, 10, 15 and 20 mol % TiO_2.

4. Conclusion

The hard sphere model reveals a marked transition in liquid structure at around 12 mol % TiO_2 corresponding to an observed change in the crystalline phase precipitated from the solution. The liquid is probably dissociated into BiO_2^- and BiO^+ ionic groups and a complex forms with the additional TiO_2. Further studies are necessary to deduce the structure of this complex and to detect any change in liquid structure in the 12 to 15 mol % TiO_2 range.

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