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Acid-base reactions in fused alkali borate + TiO_2 mixtures

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The nature of the titanium-containing phases which crystallize from solutions of TiO_2 in fused alkali metal borates, varies with the alkali cation, the mole ratio of alkali oxide to B_2O_3, and the initial concentration of TiO_2. Recrystallization of TiO_2 rather than crystallization of complex titanates, is enhanced by the presence in solution of small cations, by a high proportion of B_2O_3 relative to alkali oxide, and by higher concentrations of TiO_2.

The crystallization of complex titanates is correlated with the formation of borate groups containing non-bridging oxygens whose existence has been suggested by previous workers.

1. Introduction

It is possible that complex titanium-containing molten salt systems, such as molten titaniferous slags, may be refined to systems containing fewer chemical components by the use of a molten salt solvent capable of extracting the titanium phase. Two high-temperature solvents which have been reported to dissolve TiO_2 are cryolite (Na_3AlF_6) and alkali metal borate ($M_2O.xB_2O_3$) melts.

The phase diagram for the TiO_2 + Na_3AlF_6 system, reported by Madhavan *et al* [1], indicates that approximately 4.23 g TiO_2 dissolve per 100 g of solvent at 1000°C. Further, the solubility of TiO_2 in the solvent NaF + AlF_3 (15 wt %) has been investigated by Anikin *et al* [2]. This melt will dissolve 5 g TiO_2 per 100 g of solvent at 960°C. The titanium phase which was crystallized on cooling to room temperature was not identified, but the authors report that TiO_2 is not recrystallized.

Alkali metal borate melts are capable of dissolving greater quantities of TiO_2, than is cryolite, at a given temperature. It has been reported that TiO_2 is soluble in Na_2O + B_2O_3 melts [3] and its solubility is dependent on the Na_2O concentration [4]. More specifically, Anikin *et al* [2, 4] have investigated the solubility of TiO_2 in $Li_2O.2B_2O_3$, $Na_2O.2B_2O_3$, $K_2O.2B_2O_3$, $K_2O.5B_2O_3$ and B_2O_3, and have identified the titanium phase crystallizing beneath the liquidus. These results are summarized in Table I. It appears from these results that when Na is the alkali metal cation in $M_2O.2B_2O_3$ melts, recrystallization of rutile occurs. However, changing the cation to K facilitates the crystallization of potassium hexatitanate $K_2O.6TiO_2$. Thus the melt containing potassium cations is apparently more basic in the sense that it more readily donates O^{2-} to the TiO_2.

TABLE I Results of previous work on solutions of TiO_2 in alkali metal borates

System	g TiO_2/100 g solvent	T(°C)	Titanium phase crystallized
$Li_2O.2B_2O_3$	12	940	TiO_2 [2]
$Na_2O.2B_2O_3$	23	940	TiO_2 [2]
$K_2O.2B_2O_3$	30	940	$K_2O.6TiO_2$ [4]
$K_2O.5B_2O_3$	0.01	900	Not identified [2]
B_2O_3	Nil [2]	—	—

This report describes experiments in which titanium dioxide has been dissolved in various alkali borate melts of the type $M_2O.xB_2O_3$, where x has been chosen such that the melt has the composition of known congruently melting alkali borates. X-ray powder diffraction has been utilized for identification of the titanium phases resulting from slow cooling of the melts to room temperature.

2. Experimental

Analar grade K_2CO_3, Na_2CO_3 and British Drug Houses standard grade Li_2CO_3, Rb_2CO_3,$CsNO_3$ and TiO_2 were used without further purification. The TiO_2 was found by X-ray diffraction to contain only the rutile phase. Boron trioxide was standard grade material supplied by Riedel-De

Haën A.G. To prepare the alkali borates the finely ground starting materials were dried at 200°C and weighed portions of each intimately mixed as slurries in petroleum spirit.

Reaction mixtures of appropriate ratios of B_2O_3:M_2CO_3 (M = Li, Na, K, Rb) were prepared to give on fusion the congruently melting compounds listed in Table II. Caesium triborate ($Cs_2O.3B_2O_3$) was prepared by the fusion of $CsNO_3$ with B_2O_3 in the mole ratio 2:3 according to the reactions [10]

$$2CsNO_3 \xrightarrow{515^\circ C} Cs_2O + 2NO_2 + \tfrac{1}{2}O_2$$
$$Cs_2O + 3B_2O_3 \rightarrow Cs_2O.3B_2O_3.$$

After fusion a sample of each alkali borate was analysed for M_2O and B_2O_3 content.

TABLE II Alkali metal borates investigated

$Li_2O.B_2O_3$	[5]
$Li_2O.2B_2O_3$	
$Na_2O.B_2O_3$	[6]
$Na_2O.2B_2O_3$	
$K_2O.B_2O_3$	[7]
$K_2O.2B_2O_3$	
$K_2O.4B_2O_3$	
$Rb_2O.2B_2O_3$	[8]
$Cs_2O.3B_2O_3$	[9]

To investigate the titanium phase resulting from the dissolution of TiO_2 in the various alkali borate melts, appropriate quantities of TiO_2 were added to each alkali borate followed by fusion in Pt-5% Au crucibles. A conventional resistance tube furnace was used and the sample temperature was monitored with a calibrated Pt versus 13% Rh/Pt thermocouple. The temperature was raised slowly to approximately 1000°C, and when all the TiO_2 was seen to be dissolved the melt was allowed to cool slowly to room temperature. Each mixture was then examined by X-ray powder diffraction to determine the room temperature phases.

In some mixtures, particularly those containing high proportions of B_2O_3 relative to alkali metal oxide, the room temperature solid mixtures were partially glassy. Crystallization of at least part of the glassy material was induced in most of these mixtures by maintaining the finely ground solids at temperatures of the order 400°C for approximately 4 h. After this treatment, a few weak reflections attributable to B_2O_3 or an alkali metal borate were observed. However, positive identification of the borate phase(s) was not always possible, owing to the paucity of reflections.

Diffraction patterns were obtained with either a 56.6 mm diameter Debye-Scherrer camera or a Guinier focusing camera. Determinations of interplanar spacings were standardized using NaCl for the Debye-Scherrer camera and ThO_2 for the Guinier camera. Intensities of reflections were estimated visually. A modified powder pattern program DEPOD, reported by Langford [11] was used to process the diffraction data.

3. Results

The room-temperature phases identified in mixtures of alkali borate and TiO_2 are listed in Table III. Within the minimum detection limit of X-ray powder diffraction analysis (about 5 wt %), only the system $K_2O.4B_2O_3$ + TiO_2 appears to behave as a simple binary system. In the other systems studied, either an alkali metal titanate was the only titanium phase crystallized (e.g. in the system $K_2O.B_2O_3$ + TiO_2), or a mixture of TiO_2 and alkali metal titanate was formed (e.g. in $Li_2O.B_2O_3$ + TiO_2).

3.1. Lithium borate melts

Lithium metaborate $Li_2O.B_2O_3$ and lithium diborate $Li_2O.2B_2O_3$ solvents were studied in this system. In both solidified melts, rutile was identified as one of the titanium phases. The metaborate also crystallized lithium metatitanate $Li_2O.TiO_2$, the formation of which may be formally represented by the equation

$$2(Li_2O.B_2O_3) + TiO_2 \rightleftharpoons Li_2O.TiO_2 + Li_2O.2B_2O_3.$$

Chemical analysis of the lithium diborate + TiO_2 solidified melt showed that 87 wt % of the dissolved TiO_2 recrystallized as rutile, while 13% crystallized as an unidentified lithium titanate which is soluble in 2M HCl. Jonker [12] reported that the compounds forming in the system Li_2O + TiO_2 are $Li_2O.TiO_2$ (NaCl structure), $2Li_2O.5TiO_2$ (spinel structure) and $Li_2O.3TiO_2$ (orthorhombic [13]). Dmitrevskii *et al* [14] have reported X-ray diffraction data for the lithium tetratitanate $Li_2O.4TiO_2$. However, none of the X-ray reflections recorded for the lithium diborate + TiO_2 mixture were attributable to any of the these reported titanates.

3.2. Sodium borate melts

In contrast to lithium metaborate, sodium

TABLE III

Borate melt	Mol % TiO_2 dissolved	Phases present at room temperature
$Li_2O.B_2O_3$	30	$Li_2O.TiO_2$ TiO_2 $Li_2O.B_2O_3$ $Li_2O.2B_2O_3$
$Li_2O.2B_2O_3$	30	TiO_2 $Li_2O.2B_2O_3$ Unidentified titanate
$Na_2O.B_2O_3$	30	$Na_2O.B_2O_3$ $Na_2O.6TiO_2$
$Na_2O.2B_2O_3$	30	TiO_2 $Na_2O.6TiO_2$ $Na_2O.2B_2O_3$
$K_2O.B_2O_3$	20	$K_2O.6TiO_2$ $K_2O.B_2O_3$ Probably $K_2O.2B_2O_3$
$K_2O.B_2O_3$	65	$K_2O.6TiO_2$ $K_2O.2B_2O_3$ Trace of TiO_2
$K_2O.2B_2O_3$	35	$K_2O.6TiO_2$ $K_2O.2B_2O_3$ Probably B_2O_3
$K_2O.2B_2O_3$	55	Trace TiO_2 $K_2O.6TiO_2$ Probably B_2O_3
$K_2O.4B_2O_3$	30	TiO_2 $K_2O.4B_2O_3$
$Rb_2O.2B_2O_3$	30	$Rb_2O.2B_2O_3$ (vitrified) $Rb_2O.6TiO_2$
$Cs_2O.3B_2O_3$	30	$Cs_2O.3B_2O_3$ $Cs_2O.4TiO_2$

metaborate melt crystallizes sodium hexatitanate $Na_2O.6TiO_2$ [15] as the principal titanate phase and no lines in the diffraction pattern may be attributed to TiO_2. The formation of $Na_2O.6TiO_2$ may tentatively be represented by the equation

$$2(Na_2O.B_2O_3) + 6TiO_2 \rightleftharpoons Na_2O.6TiO_2 + Na_2O.2B_2O_3.$$

However, the compound $Na_2O.2B_2O_3$ was not positively identified, even in ground and heat-treated solid mixtures.

Decreasing the Na_2O concentration to 33 mol % resulted in the crystallization of TiO_2 and $Na_2O.6TiO_2$ as the titanium phases. This result is in contrast to those of Anikin *et al* [2] which do not indicate crystallization of sodium hexatitanate. Since $Na_2O.4B_2O_3$ is reported as a congruently melting compound in the system $Na_2O + B_2O_3$ [6], two reactions are possible for the production of sodium hexatitanate, namely

$$Na_2O.2B_2O_3 + 6TiO_2 \rightleftharpoons Na_2O.6TiO_2 + 2B_2O_3$$

$$2(Na_2O.2B_2O_3) + 6TiO_2 \rightleftharpoons Na_2O.6TiO_2 + Na_2O.4B_2O_3.$$

However, neither B_2O_3 nor $Na_2O.4B_2O_3$ was detected in the crystallized melts. The powder patterns indicate that TiO_2 is the principal titanium phase crystallized, so that evidently the above equilibria do not favour formation of the hexatitanate.

3.3. Potassium borate melts

Investigations on solid state and melt reactions in $K_2CO_3 + TiO_2$ mixtures have shown that $K_2O.6TiO_2$ is a readily formed stable compound [16]. The present results show that slow cooling of solutions of TiO_2 in potassium metaborate, $K_2O.B_2O_3$ and potassium diborate, $K_2O.2B_2O_3$, result in crystallization of $K_2O.6TiO_2$. This confirms the result of Anikin *et al* [2] for the diborate solvent. When the concentration of TiO_2 was increased to 55 mol % for the $K_2O.2B_2O_3$ solvent small quantities of TiO_2 were found. The TiO_2 needles were extracted and identified separately from the bulk melt. The reactions occurring in the metaborate and diborate melts may be represented by the equations

$$2(K_2O.B_2O_3) + 6TiO_2 \rightleftharpoons K_2O.6TiO_2 + K_2O.2B_2O_3$$

and

$$K_2O.2B_2O_3 + 6TiO_2 \rightleftharpoons K_2O.6TiO_2 + 2B_2O_3.$$

The other possible reaction for the diborate solvent namely

$$2(K_2O.2B_2O_3) + 6TiO_2 \rightleftharpoons K_2O.6TiO_2 + K_2O.4B_2O_3$$

apparently does not occur, because no reflections attributable to $K_2O.4B_2O_3$ were detected, whereas B_2O_3 was detected in the diborate mixture.

At about 1050°C, 30 mol % TiO_2 was dissolved in the solvent $K_2O.4B_2O_3$ and TiO_2 was identified as the sole titanium phase present in the solid.

3.4. Rubidium and caesium borate melts

The congruently melting compounds chosen as solvents for the dissolution of TiO_2 were rubidium diborate, $Rb_2O.2B_2O_3$, [8] and caesium triborate, $Cs_2O.3B_2O_3$ [9]. Titanium dioxide, 30 mol %, was dissolved in the $Rb_2O.2B_2O_3$ melt at about 850°C, and in the $Cs_2O.3B_2O_3$ melt at about 950°C. The reported titanates of rubidium and caesium are $M_2O.TiO_2$, $M_2O.2TiO_2$ and $M_2O.4TiO_2$ [12]). X-ray diffraction data has been reported by Schmitz-Dumont for the dititanates [17] and the tetratitanates [18], and Dmitrevskii *et al* [14] have reported data for the tetratitanates of Li, Na, Rb and Cs obtained as products from the thermal decomposition of their respective alkali hexafluorotitanates at 900°C. $\text{Sin}^2\theta$ values were calculated from the cell parameters of $Cs_2O.3B_2O_3$ [19] and matched with lines occurring in the diffraction pattern of the mixture. The remaining lines could best be attributed to caesium tetratitanate (using the data reported by Dmitrevskii).

In the rubidium melt, there was a tendency for the borate phase to vitrify and even after the grinding/heat-treatment procedure X-ray analysis revealed only titanate reflections. The reflections did not correlate with data for the meta-, di- or tetratitanates but agreed with data for the rubidium hexatitanate, calculated from the cell parameters reported by Wadsley and Andersson [15]. These authors reported that they were unable to produce $Rb_2O.4TiO_2$ on melting Rb_2CO_3 and TiO_2 in the mole ratio 1:4. $Rb_2O.4TiO_2$ has been reported as a congruently melting compound by Schmitz-Dumont and Reckhard [18].

4. Discussion

4.1. Basicity of the solvent and effect of the alkali metal cation

The results in Table II show that at high concentrations of M_2O, such as in alkali metaborate melts, the solute (TiO_2) will compete for oxygen ions and alkali titanates will crystallize. Further, it is apparent that the alkali metal cation affects the nature of the titanium phase recrystallized, i.e., the alkali cation affects the overall basicity of the borate melt.

In applying the Lewis concept to solvent systems, one envisages the basicity of the solvent as its ability to share its electrons with an acid solute. This tendency to share electrons may be measured on an optical scale for Lewis basicity proposed by Paul [20] and Duffy and Ingram [21], using a Pb(II) probe ion. We have measured optical basicities of $B_2O_3 + M_2O$ glasses containing up to 50 mol % M_2O; details of these measurements will be reported in a separate publication [22]. These values of optical basicity ($\Lambda_{Pb(II)}$) together with previously reported data [20, 21] for Li, Na and K borate glasses at room temperature, are shown in Fig. 1 as a function of M_2O concentration. The higher the value of $\Lambda_{Pb(II)}$ the greater is the electron donation to the Pb(II) probe ion, i.e., the more basic is the solvent. For M_2O contents above 20 mol %, the basicities of the glasses increase in the order

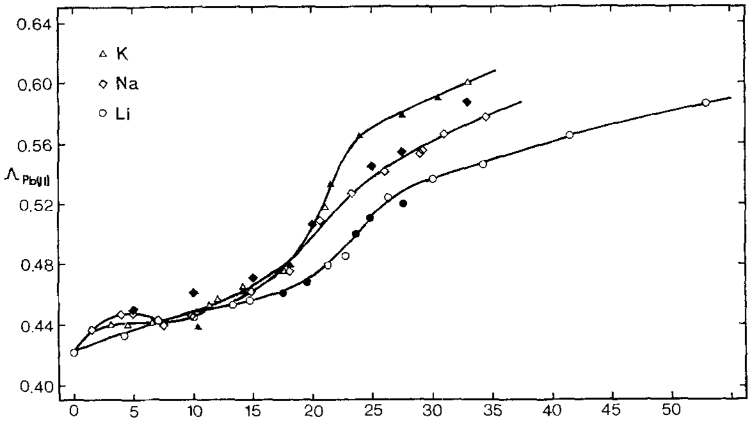

Figure 1 Variation of optical basicity, $\Lambda_{Pb(II)}$, with alkali oxide content of alkali borate glasses. Shaded points from Ref. [20] (Li and K borates), and Ref. [21] (Na borates).

Li < Na < K. This is consistent with the titanium phase recrystallized from the melts $Li_2O.2B_2O_3$, $Na_2O.2B_2O_3$ and $K_2O.2B_2O_3$ listed in Table III, if the crystallization of an alkali titanate as the major titanium phase is taken to indicate a more basic melt than one which recrystallizes rutile as the major titanium phase.

This correlation between basicity of the glass and identity of crystallized phases, depends on the validity of two assumptions. (a) The relative order of optical basicities in alkali metal borate glasses containing a given concentration of alkali metal oxide, is the same, for a series of alkali metal oxides as in the corresponding melts. (b) The components present at room temperature, in crystallized TiO_2 + alkali metal borate melts, and the relative proportions of the components, are as determined by melt equilibria and are not significantly modified by reactions occurring during cooling to room temperature.

4.2. The structure of borate melts in relation to basicity

Nuclear magnetic resonance investigations [23] have indicated that when alkali metal oxides are added to molten boric oxide the probable sequence of reactions occurring can be represented by

$$B\phi_3 \rightarrow B\phi_4^- \rightarrow B\phi_2O^-$$

where ϕ indicates an oxygen shared by two boron atoms. The first product is a $B\phi_4^-$ tetrahedron which may be termed mildly basic. When further alkali oxide is added the more basic $B\phi_2O^-$ group with a non-bridging oxygen is formed. The n.m.r. studies were made on borate glasses; the inference that the glass structure reflects that of the liquid from which it is derived is reasonable, albeit not proven.

Paul and Douglas [24] have determined the critical concentration of M_2O at which $B\phi_2O^-$ groups in alkali borate glasses appear, by utilizing the absorption spectrum of Chromium (VI). The optical absorption spectra of CrO_4^{2-} and $HCrO_4^-$ complex groups are distinctly different. The conversion of one form to the other is governed by the basicity of the solvent and it is suggested that Cr (VI) may be present in the borate glasses as either CrO_4^{2-} or $O_3Cr\text{-}O\text{-}B\phi_2^-$. The equilibria expected to occur may be represented as

$$CrO_3 + B\phi_4^- \rightleftharpoons O_3Cr\text{-}O\text{-}B\phi_2^- \qquad (1)$$
$$O_3Cr\text{-}O\text{-}B\phi_2^- + B\phi_2O^- \rightleftharpoons CrO_4^{2-} + 2B\phi_3.$$

As more CrO_4^{2-} species are formed the specific absorbence of chromium (VI) at the absorption maximum 370 nm increases very rapidly until conversion is virtually complete. The specific absorbences of Cr(VI) were determined as a function of the alkali oxide concentration. The absorbence at 370 nm increases rapidly with concentration of M_2O at about 19, 22 and 26 mol % K_2O, Na_2O and Li_2O, respectively. The specific absorbence of the alkali glasses remains in the order K > Na > Li up to 30 mol % M_2O. This indicates that the alkali metal cation affects the equilibria represented in Equation 1 such that for a given concentration of M_2O (> 20 mol %), the concentration of $B\phi_2O^-$ groups is greatest for the glass containing K ions and smallest for the lithium glass.

There is a close correlation between the results obtained from Cr(VI) absorption spectra and the identity of the titanium phase crystallized from solution of TiO_2 in borate melts. If the non-bridging oxygens in $B\phi_2O^-$ groups are assumed to be the source of O^{2-} ions, then the absorption spectra indicate that for TiO_2 + potassium borate solutions, only TiO_2 should crystallize from solvent melts containing less than about 20 mol % K_2O. Moreover, titanates should crystallize almost exclusively from solvent melts containing more than about 28 mol % K_2O. These predictions are in agreement with the results presented in Table III, for TiO_2 concentrations less than 40 mol %. Likewise, our results for the lithium and sodium borate solutions of TiO_2 are in at least qualitative agreement with similar predictions based on the Cr(VI) absorption spectra.

5. Conclusions

The nature of the titanium phase crystallized from solutions of TiO_2 in fused alkali metal borates, is dependent upon the basicity of the solvent melt. TiO_2 can thus be used as an "indicator", to establish a qualitative basicity scale for borate melts. The basicity of the fused borates is consistent with the hypothesis that basicity is determined primarily by the concentration of $B\phi_2O^-$ groups, containing one non-bridging oxygen per group. The alkali metal cation has a marked effect on the nature of the titanium phase which is crystallized. Paul and Douglas has suggested [24] that the basicity of alkali metal borate glasses is determined by an ionization equilibrium of the form

$$B\phi_2OM \rightleftharpoons B\phi_2O^- + M^+.$$

The equilibrium constant for such a reaction would depend to some extent on the field strength (and hence the size) of the alkali metal cation. If such equilibria exist in TiO_2 + alkali borate melts, then the basicity of the solvent, for a given alkali metal oxide content, should be different for different alkali metal cations. This may be at least in part the origin of the effect of the alkali metal cation on the nature of the titanium phase crystallized from these melts.

The proposed role for the cation is consistent with the observations that TiO_2 is crystallized from melts containing as much as 50 mol % Li_2O, but not from sodium or potassium metaborates. Moreover if the TiO_2 concentration is maintained at 30 to 35 mol %, then less than 50 mol % Na_2O, and less than 33 mol % K_2O are required to prevent crystallization of TiO_2.

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