JOURNAL OF MATERIALS SCIENCE 10 (1975) 422–426

Activity of nickel oxide in alkali borate melts

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The activity/concentration relationships of NiO in R_2O–B_2O_3 melts (R = Li, Na or K) have been studied by saturating glass melts contained in a nickel crucible under different partial pressures of oxygen. A pure boric oxide melt dissolves very little NiO (solubility less than 0.001 wt %); on adding R_2O the solubility increases and reaches a maximum around 20 mol % for Li_2O and Na_2O, and 30 mol % for K_2O; thereafter the solubility of NiO decreases with increasing R_2O content of the melt, the maximum decrease being in K_2O–B_2O_3 melts. It is suggested that the low solubility of NiO in low- and high-alkali borate melts is due to poor donor capacity of $B\phi_{3/2}$ groups and high activity of oxide ions respectively. NiO in alkali borate melts produces a non-ideal solution.

1. Introduction

Transition metal oxides are often used to make coloured glasses where the final colour is determined by the concentration of different oxidation states of the transition metal ion and their site symmetry. The distribution into different oxidation states in the glass melt when equilibrated with known partial pressures of oxygen at a particular temperature, can be calculated if the standard free energy change and activity coefficients of the involved redox oxides in the melt at that temperature are known. A knowledge of the activity coefficient of any component oxide and its variation with temperature in a melt can also be used in determining the equilibrium solubility and vice versa, which is of considerable importance in producing precipitation colours, for example in copper ruby or chrome aventurine glasses. Anionic substitution around transition metal ions in glass is possible [1] (for example, iron-sulphur amber glass) where the equilibrium concentration of the substituted chromophore depends critically not only on the activity of the ligands but also equally on the activity coefficient of the redox oxide concerned. Some base metal alloys on heat-treatment are oxidized on the surface; the surface oxidation can be substantially reduced, and the oxide layer, if any, removed if a layer of non-durable glass is applied prior to heat-treatment. After heat-treatment the glassy layer can be removed by pickling in a suitable acid bath. To determine the suitable glass composition for removing the oxide layer, the activity coefficient of the respective oxide in the glass may be used, at least, as a guide line. A knowledge of the activity coefficient of component oxides is desirable in understanding glass-to-metal bonding [2], wetting of refractories by glass melts [3], solid-liquid phase equilibria; even the kinetics of reactions in glass melts may also be controlled by the activities of the components. For example, the rates of those processes which are diffusion controlled, such as dissolution of many pure oxides by glass melts, will be dictated not by composition gradients but also by activity gradients, which, in the case of non-ideal solutions, may be quite different from the former.

Redox equilibrium in coloured glasses with transition metal ions has been studied extensively but relatively very few attempts have been made to determine the activity concentration relationship of different transition metal oxides in molten glass as functions of composition and temperature [4]. When a pure metal is equilibrated with a known partial pressure of oxygen $2M(s) + O_2(g) \overset{\Delta G^\circ}{\rightleftharpoons} 2MO(s)$, at a particular temperature, T, the activity of the metal oxide, a_{MO} can be calculated if ΔG_T^0 of the oxidation reaction is known:

$$\log a_{MO} = \tfrac{1}{2}[\log p_{O_2} - \Delta G_T^0/(4.575 \times T)] .$$

TABLE I Composition, temperature of melting and oxygen potential of glasses

Glass number	Composition (mol %)				Temperature (°C)	Oxygen pressure (atm)
	Li_2O	Na_2O	K_2O	B_2O_3		
L1	7			93	1000	air
L2	10			90	1000	air
L3	15			85	1000	air
L4	20			80	1000	air
L5	30			70	1000	air
L6	42			58	1000	air
L7	55			45	1000	air
N1		8		92	1000	air
N2		12		88	1000	air
N3		16		84	1000	air
N4		20		80	850 to 1100	10^{-9} to 10^{-14}
N5		22		78	1000	air
N6		26		74	1000	air
N7		35		65	1000	air
N8		53		47	1000	air
K1			6	94	1000	air
K2			13	87	1000	air
K3			17	83	1000	air
K4			20	80	850 to 1100	air
K5			23	77	1000	air
K6			25	75	1000	air
K7			27	73	1000	air
K8			30	70	1000	air
K9			32	68	1000	air
K10			36	64	1000	air
K11			45	55	1000	air
K12			51	49	1000	air

If a glass melt is now brought into contact with this M–MO–O_2 system, MO will dissolve in the glass, and ultimately a saturated solution will result where,

$$a_{\mathrm{MO}}(\text{in contact with the crucible}) = a_{\mathrm{MO}}(\text{in the glass solution})\,.$$

The concentration of MO in the saturated solution can be experimentally determined; thus the activity coefficient of MO, γ_{MO}, in the glass melt at any temperature can be calculated from the relationship:

$$\gamma_{\mathrm{MO}} = \frac{a_{\mathrm{MO}}\ (\text{in glass})}{N_{\mathrm{MO}}\ (\text{in glass})} = \frac{a_{\mathrm{MO}}\ (\text{in contact with the metal})}{N_{\mathrm{MO}}\ (\text{in glass})}\,.$$

In the present investigation the activity coefficient of NiO in different R_2O–B_2O_3 glasses has been determined by the saturation technique.

2. Experimental details and results

10 g portions of premelted R_2O–B_2O_3 glass powder were placed in a 30 ml capacity pure nickel crucible and equilibrated with various oxygen potentials at different temperatures. The different glass compositions, temperatures and oxygen potentials are given in Table I. Different oxygen potentials were obtained by mixing appropriate volumes of dry CO, CO_2, N_2 and H_2 gases. The sealed vertical furnace tube, with one inlet and one outlet tube, was flushed with 95 ml of the gas mixture per minute while 5 ml of the same gas mixture was bubbled through the melt per minute to increase the rate of solution. At 1000°C with $p_{O_2} \geqslant 10^{-9}$ atm, the crucible, including the inner bottom portion which was covered with molten glass, was covered with a thick and unbroken layer of green NiO. After different lengths of time, about 1 g portions of the sample were drawn and chemically analysed for NiO concentration [5]; the melting was continued until the melt became saturated with

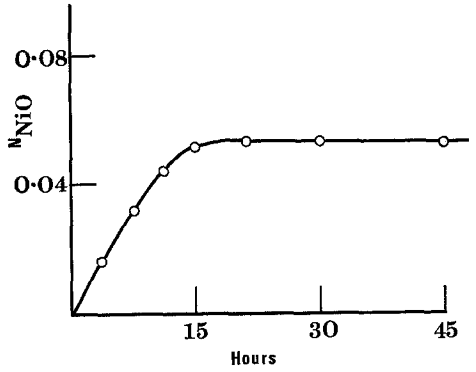

Figure 1 Rate of solution of NiO in $Na_2O,4B_2O_3$ melt at 1000°C.

TABLE II Equilibrium solubility of NiO in Na_2O, $4B_2O_3$ melt at 1000°C with various partial pressures of oxygen

$-\log p_{O_2}$	a_{NiO}	N_{NiO} (in saturated glass)
9.0	1	0.0671
10.0	0.7738	0.0520
10.5	0.4351	0.0262
11.0	0.2446	0.0132
11.5	0.1376	0.0061
12.0	0.0774	0.0030
12.5	0.0435	0.0017
13.0	0.0245	0.0010
13.5	0.0138	0.0005
14.0	0.0077	0.0003

NiO. Some typical results for an $Na_2O,4B_2O_3$ melt at 1000°C in air are shown in Fig. 1. The equilibrium solubility of NiO in $Na_2O,4B_2O_3$ melt with various activities of NiO on the crucible is given in Table II. Fig. 2 shows the equilibrium solubility of NiO in different R_2O–B_2O_3 melts at 1000°C. The solubility of NiO ($a_{NiO} = 1$) in two glasses of molar compositions $20Na_2O$, $80B_2O_3$ and $20K_2O,80B_2O_3$ was also studied as a function of temperature in thetemperature range 800 to 1100°C, and the results are shown in Fig. 3 plotted as log N_{NiO} versus $1/T$; the heat of solution calculated from the slopes of the experimental linear plots are 35 and 21 kcal mol^{-1} for $20Na_2O,80B_2O_3$ and $20K_2O,80B_2O_3$ melts respectively.

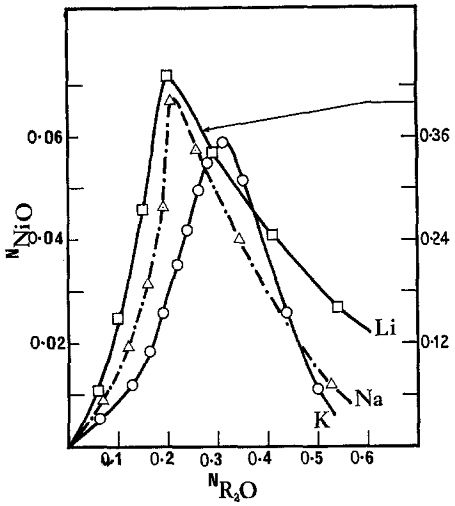

Figure 2 Equilibrium solubility of NiO in different R_2O–B_2O_3 melts at 1000°C.

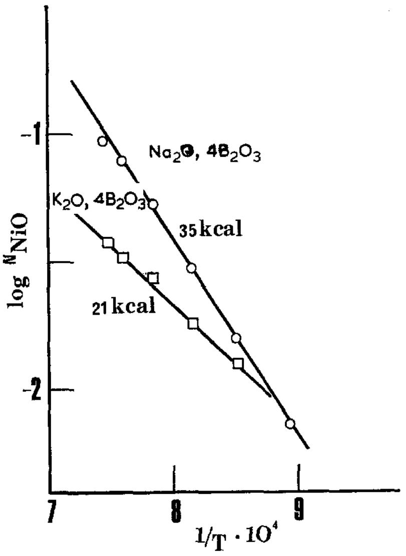

Figure 3 Solubility of NiO in $Na_2O,4B_2O_3$ and K_2O, $4B_2O_3$ melts at different temperatures.

3. Discussion

A pure B_2O_3 melt does not dissolve any significant amount of NiO (solubility $\leqslant$ 0.001 wt % or $N_{NiO} \leqslant 0.000\,009$). During the initial stages of this work it was found that if orthoboric acid is used in the nickel crucible instead of using anhydrous boric oxide, then up to 0.01 wt % NiO could be dissolved in the B_2O_3 melt at 1000°C in air. However, with "anhydrous" B_2O_3, the solubility reduced drastically to less than 0.001 wt % and the enhanced solubility was thought to be due to chemically dissolved water in the melt. Subsequently, in all other saturation experiments, alkali borate glasses were premelted in a platinum crucible at 1100°C for 6 h and dry nitrogen gas was bubbled through the melt to reduce the water content. The melt was cast and crushed to a coarse powder and used for subsequent saturation experiments in a nickel crucible.

In low alkali borate glasses ($R_2O \leqslant 20$ mol %) NiO dissolves forming an octahedral nickel(II) complex [5]. This process may be visualized as consisting of the following steps:

$$NiO \rightleftharpoons Ni^{2+} + O^{2-} \qquad (1)$$

$$2\,B\phi_{3/2} + O^{2-} \rightleftharpoons 2\,B\phi_{4/2}^{-} \qquad (2)$$

$$Ni^{2+} + 6L \rightleftharpoons [NiL_6]^{n-} \qquad (3)$$

where L corresponds to $B\phi_{3/2}$ or $B\phi_{4/2}^{-}$ ligands. The dielectric constant of alkali borate melts is much smaller than that of aqueous solutions, thus precise local charge neutralization is a stringent requirement for the formation of this nickel(II) complex in glass. In pure B_2O_3 melt, all the ligands are $B\phi_{3/2}$ having poor donor capacity [6], thus effective charge neutralization of Ni^{2+} centres cannot take place. NiO does not, therefore, dissolve in a pure B_2O_3 melt. When R_2O is added to the B_2O_3 melt, (say up to 30 mol % R_2O) the predominant reaction is [6]:

$$B_2O_3 + R_2O \rightleftharpoons 2\,B\phi_{4/2}^{-},\ R^{+}.$$

As the R_2O/B_2O_3 ratio in the melt increases, the concentration of tetrahedral boron increases and, therefore, also the number of tetrahedral boron ligands in the first co-ordination sphere of nickel(II) complex. Since tetrahedral boron has more donor capacity (due to higher electron density on oxygen) than $B\phi_{3/2}$ group, the $[NiL_6]^{n-}$ complex becomes more stable and correspondingly more NiO dissolves in the melt.

When more than about 20 mol % R_2O is added to B_2O_3 melt, in addition to tetrahedral boron, triangular boron with non-bridging oxygen is also formed [7]. All these species are in equilibrium, at least in principle, with free O^{2-} in the melt. Thus with more than 20 mol % R_2O, $a_{O^{2-}}$ in the melt increases sharply and reaction 1 (the dissociation of NiO to the ionic form) is hindered. The solubility of NiO therefore decreases again. In the case of K_2O–B_2O_3 melts, this increase of oxide activity is manifested in the formation of purple tetrahedral nickel(II) complexes, whereas in Na_2O–B_2O_3 and Li_2O–B_2O_3 series, four co-ordinated square planar complexes are formed [5]. The ligand field stabilization energy of Ni^{2+}, a $3d^8$ system, is in the order:

octahedral > square planar > tetrahedral.

These stabilization energies make a significant contribution towards the total free energy of the different complexes of nickel(II) [8]. Thus it is expected that the excess free energy of mixing of NiO and R_2O–B_2O_3 melts will be less negative if Ni^{2+} enters the melt in the tetrahedral configuration relative to square planar or octahedral symmetry. Indeed from Fig. 2 it can be seen that above 30 mol % R_2O, the solubility of NiO drops sharply for the K_2O–B_2O_3 series, whereas the corresponding decrease in Na_2O–B_2O_3 and particularly Li_2O–B_2O_3 melts is much less relative to the K_2O–B_2O_3 series. From Fig. 2 marked differences in solubility of NiO at R_2O concentrations below the maximum may also be noted. The maximum solubility of NiO in Li_2O–B_2O_3 melt is about seven times more than that in either Na_2O–B_2O_3 or K_2O–B_2O_3 melts. This strongly suggests formation of mixed species of R_2O, B_2O_3 and NiO in the melt, and the free energy of formation of the lithium compound(s) is much more negative than that of either Na_2O or K_2O compounds.

It may be noted at this point that Freiling [9], while studying distribution equilibrium of different metal salts between binary alkali borate melts and NaCl, has observed a similar maximum around 20 to 25 mol % R_2O; some of his results are shown in Fig. 4.

It may be shown that, for any system, if Nx_1 and Nx_2 are the equilibrium solubilities at temperatures T_1 and T_2 respectively, then

$$\ln \frac{Nx_2}{Nx_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} = \frac{1}{T_2}\right)$$

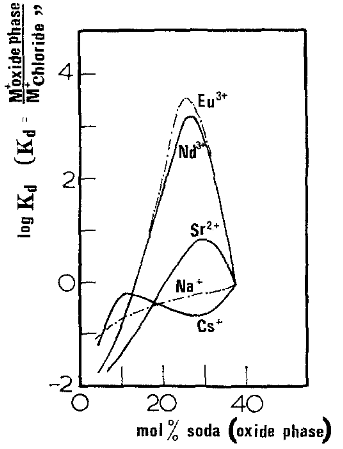

Figure 4 Distribution coefficients of different metal ions in the system Na_2O–B_2O_3–NaCl at 830°C (after [9]).

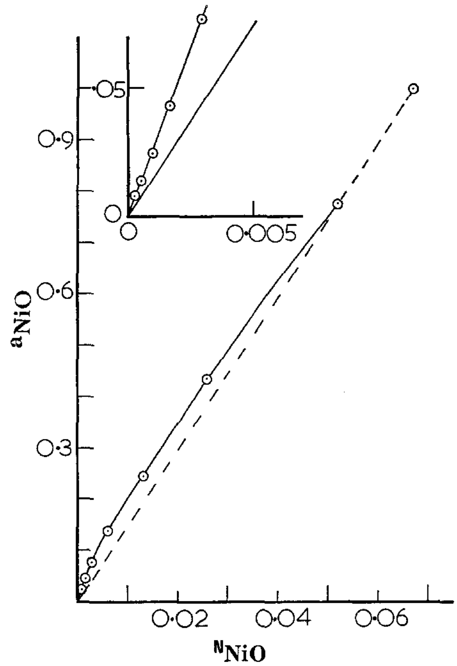

Figure 5 Activity/concentration relationship of NiO in $Na_2O,4B_2O_3$ melts at 1000°C.

where ΔH is the partial molar heat of mixing. Derivation of the above equation is based on the assumptions that ΔH remains constant over the temperature range T_1 to T_2 and the solutions are dilute and obey Henry's law.

The plots of log N_{NiO} versus $1/T$ are shown in Fig. 3 where linear relationships are seen. The values of ΔH, calculated from the slope of these lines, change significantly with composition of the melt. These very high ΔH values (about 30 kcal mol^{-1}) indicate that significant structural changes should take place when NiO dissolves in the melt, and the solutions should not behave as ideal solutions. Indeed the non-ideal behaviour of NiO in alkali borate melts can be seen from Fig. 5 where a_{NiO} is plotted against N_{NiO} in an $Na_2O,4B_2O_3$ melt at 1000°C.

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Received 29 July and accepted 11 September 1974.