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Ferrous-ferric equilibrium in BaO-B_2O_3 melts

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The ferrous–ferric equilibrium in different BaO–B_2O_3 melts containing iron oxides have been studied as functions of temperature and total iron concentration. On equilibrating the melts at 1200° C with air, 3 to 6% of the total iron was reduced to the ferrous state. The equilibrium ferric/ferrous ratio in the melt decreased with increasing temperature and with decreasing BaO content of the melt. Total iron content (in the concentration range of 0.6 to 11.5 wt % Fe) had no significant effect on the equilibrium ferric/ferrous ratio of the melts.

1. Introduction

In fabricating barium hexaferrite magnet, liquid phase sintering with barium borate as an additive has been found beneficial [1, 2]. Barium borate, the liquid phase, is thought to produce a favourable combination of density and grain size in this material on firing even at some 250 to 300° C lower than employed commercially. This is due to the fact that barium borates (containing less than 50 mol % BaO) melt at about 900° C producing a viscous liquid which spreads over the surfaces of the barium hexaferrite particles to minimize interfacial free energy. The unattached particles are then drawn together by the surface tension of the liquid. A large fraction of densification occurs during this rearrangement stage. The grain growth takes place by solution of the solid into the liquid phase from grain surfaces of high curvature, followed by diffusion through the liquid and precipitation on to grains with surfaces of lower curvature.

Although barium hexaferrite magnets are conventionally believed to be of stoichiometric BaO, $6Fe_2O_3$ composition, existence of a better magnetic phase having an oxygen deficiency in the barium hexaferrite magnet has recently been suggested [3].

Pure Fe_2O_3 when heated in air, does not loose any detectable amount of oxygen below 1150° C [4]. A mixture of BaO and Fe_2O_3 having BaO:Fe_2O_3 ratio $\geqslant 2$ when heated in air, is known to gain weight by oxygen absorption, and formation of ferrate Fe(IV) in the matrix has been suggested [5, 6]. However, the behaviour of Fe_2O_3 dissolved in barium borate melt may be different. If any FeO is formed in the melt, this being in contact with Fe_2O_3 of barium hexaferrite crystal, it will produce Fe_3O_4 during precipitation from the melt, because in the presence of FeO or any liquid phase containing FeO dissolved in it, magnetite is thermodynamically more stable than barium hexaferrite [7] at all conceivable temperature and partial pressures of oxygen. Thus formation of barium hexaferrite with an oxygen deficiency, particularly in samples fabricated by the liquid phase sintering, is expected.

To study the amount of oxygen loss from Fe_2O_3 dissolved in barium borate, we have studied the ferrous–ferric equilibrium in a series of barium borate glasses containing different BaO:B_2O_3 ratios. Effects of temperature and total iron concentration on the ferrous–ferric equilibrium in the melt have also been studied.

2. Experimental

Three series of glasses were melted:

(A) glasses containing different BaO/B_2O_3 ratios but a constant amount of iron (~ 2 wt % Fe) and equilibrated at 1200° C with air as the furnace atmosphere;

TABLE I Composition of glasses (after chemical analysis)

Glass	Composition (mol %)		Iron Content (wt % Fe)			log (Fe^{3+}/Fe^{2+})	Melting temp (°C)
no.	BaO	B_2O_3	Total	Fe^{2+}	Fe^{3+}		
A_1	10	90	1.924	0.165	1.759	1.028	1200
A_2	20	80	1.766	0.154	1.612	1.020	1200
A_3	30	70	1.735	0.113	1.622	1.157	1200
A_4	40	60	1.728	0.082	1.646	1.303	1200
A_5	50	50	–	–	–	–	1200
B_1	30	70	0.618	0.038	0.580	1.184	1200
B_2	30	70	1.735	0.113	1.622	1.157	1200
B_3	30	70	2.694	0.157	2.537	1.208	1200
B_4	30	70	3.148	0.186	2.962	1.202	1200
B_5	30	70	4.811	0.295	4.516	1.185	1200
B_6	30	70	7.337	0.450	6.887	1.185	1200
B_7	30	70	9.532	0.622	8.910	1.156	1200
B_8	30	70	11.544	0.751	10.793	1.158	1200
C_1	30	70	2.099	0.064	2.035	1.502	1100
C_2	30	70	1.735	0.113	1.622	1.157	1200
C_3	30	70	1.819	0.222	1.597	0.857	1300
C_4	30	70	1.819	0.381	1.438	0.577	1400

(B) glasses containing a constant BaO/B_2O_3 ratio (BaO–70 mol% B_2O_3), doped with different amounts of iron oxides (total iron contents ranged from 0.62 to 11.54 wt% Fe) and equilibrated as above;

(C) glasses containing a constant BaO/B_2O_3 ratio (BaO–70 mol% B_2O_3), and a constant total iron content (~ 2 wt% Fe) but equilibrated at different temperatures ranging from 1100 to 1400° C with air as the furnace atmosphere.

Analar barium carbonate and orthoboric acid, and laboratory prepared Fe_2O_3 were used as batch material. Batch materials to produce 10 g glass were melted at a time in a Pt + 2% Rh crucible in an electric furnace with air as the furnace atmosphere. Temperature of the furnace was controlled within ± 2° C over 24 h. All the melts were founded for progressively longer times until a constant chemical analysis indicated that a ferrous–ferric equilibrium in the melt had been attained. After the desired period of founding, the melt was air-quenched, crushed to a fine powder under benzene in an agate mortar and used for chemical analysis. All the glass samples, except A_5 containing 50 mol% BaO, dissolved easily in 6 N HCl in the cold. Sample A_5 crystallized on cooling and could not be dissolved in the cold, thus estimation of ferrous and ferric content of this sample was not possible. BaO was estimated with atomic absorption, B_2O_3 by the standard alkalimetric titration after separation by distillation, ferrous iron with ICl [8], and total iron with the thioglycollic acid method. Ferric ion was calculated from the difference of total and ferrous iron. Composition of all the glasses, after chemical analysis, is shown in Table I along with their melting history.

3. Discussion

The Ellingham diagram (standard free energy of formation) for the Fe–O system is shown in Fig. 1. From this diagram it is clear that in the case of a pure iron and oxygen system, at 1200° C and $p_{O_2} = 0.21$ atm (air), the predominant phase is Fe_2O_3 with a small amount of Fe_3O_4 activity in it; this is expected to be solid solution of Fe_3O_4 in Fe_2O_3. In fact, under these equilibration conditions, $a_{Fe_3O_4}$ will be about 0.265; the activities of FeO and Fe will be much smaller than that of Fe_3O_4 and will not be considered for the present purpose. Thus the overall iron equilibrium in glass can be written as

$$4Fe_3O_{4(glass)} + O_{2(glass)} \rightleftharpoons 6Fe_2O_{3(glass)}. \tag{1}$$

It should be pointed out that in the solution of glass, Fe_3O_4 and Fe_2O_3 may not be present as molecular species as written in the above equation; it is only a convenient means of expressing the chemical stoichiometry, and from this to calculate the activity of individual oxides. In principle, the

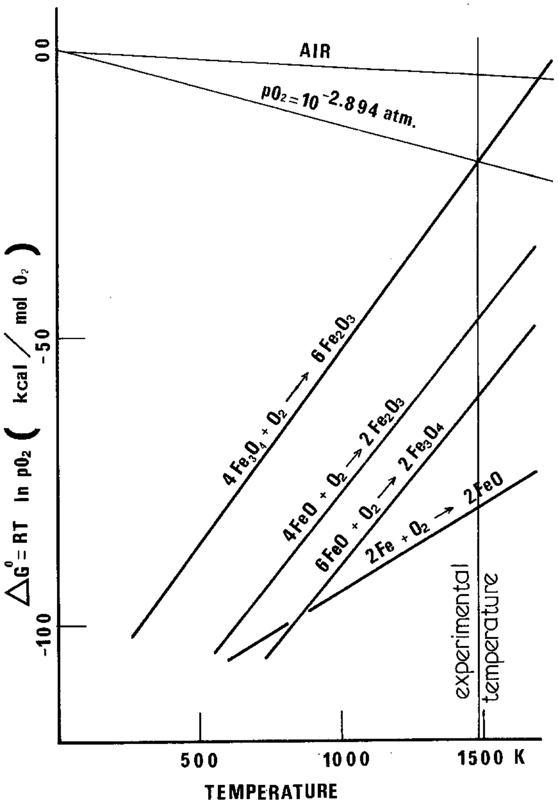

Figure 1 Standard free energies of the iron–oxygen system at different temperatures.

same equilibrium conditions in glass can be represented by any one of the following relations:

$$4FeO_{(glass)} + O_{2\,(glass)} \rightleftharpoons 2Fe_2O_{3(glass)} \quad (2)$$

$$\text{or}\quad 4Fe^{2+}_{(glass)} + O_{2(glass)} \rightleftharpoons 4Fe^{3+}_{(glass)} + 2O^{2-}_{(glass)}. \quad (3)$$

Choosing any one of equations 1, 2 and 3 is a matter of personal choice and convenience. From equation 1

$$K = \frac{[a_{Fe_2O_3}]^6_{glass}}{[a_{Fe_3O_4}]^4_{glass}} \cdot \frac{1}{p_{O_2\,(glass)}}. \quad (4)$$

In the present investigation, all the melts were unsaturated with respect to iron oxides. Thus $[a_{Fe_2O_3}]_{glass}$ and $[a_{Fe_3O_4}]_{glass}$ were both less than unity.

Under these conditions Equation 4 may be written as

$$K = \frac{[N_{Fe_2O_3}]^6_{glass}}{[N_{Fe_3O_4}]^4_{glass}} \cdot \frac{[\gamma_{Fe_2O_3}]^6_{glass}}{[\gamma_{Fe_3O_4}]^4_{glass}} \cdot \frac{1}{p_{O_2\,(glass)}} \quad (5)$$

$$= \frac{[N_{Fe_2O_3}]^6_{glass}}{[N_{Fe_3O_4}]^4_{glass}} \cdot \beta \cdot \frac{1}{p_{O_2}}, \quad (6)$$

where N_i and γ_i represent mol fraction and activity coefficient respectively of the component i, and β is the ratio of activity coefficients defined as:

$$\beta = \frac{[\gamma_{Fe_2O_3}]^6_{glass}}{[\gamma_{Fe_3O_4}]^4_{glass}}.$$

In Equation 6, K can be calculated from the standard free energy of reaction 1 at the appropriate temperature, p_{O_2} is known from experimental conditions (in this case 0.21 atm), $N_{Fe_2O_3}$ and $N_{Fe_3O_4}$ are known from chemical analysis (Table II), thus β can be calculated. β has been calculated for all the glasses in series B and are shown plotted as log β against wt% total iron (as Fe) in Fig. 2. It is clear that with small iron concentrations in the glass, β is very large; β decreases sharply with increasing total iron concentration up to about 3 wt%, and then decreases

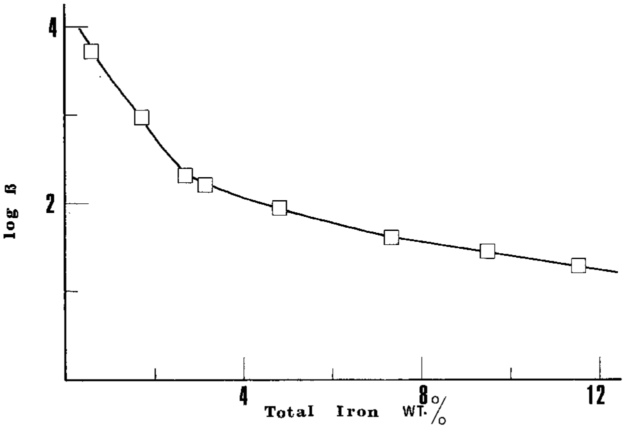

Figure 2 Variation of activity coefficient ratio with total iron content in 30 BaO, 70 B_2O_3 glass.

TABLE II Iron content (by chemical analysis) and calculated log β

Glass no.	Total iron (as Fe, wt%)	$N_{Fe_3O_4}$	$N_{Fe_2O_3}$	Log β
B_1	0.618	0.000638	0.004298	3.7387
B_2	1.735	0.001927	0.011955	2.9932
B_3	2.694	0.002704	0.019115	2.3588
B_4	3.148	0.003206	0.022339	2.2485
B_5	4.811	0.005131	0.034153	1.9592
B_6	7.337	0.007463	0.049784	1.6281
B_7	9.532	0.011096	0.068390	1.4897
B_8	11.544	0.013540	0.083808	1.3058

smoothly and at a much slower rate with further increase of total iron content in the melt. These changes in β may be either due to changes in $[\gamma_{Fe_2O_3}]_{glass}$ or/and $[\gamma_{Fe_3O_4}]_{glass}$.

3.1. Effect of BaO/B_2O_3 ratio on the ferrous–ferric equilibrium in the melt

In a binary barium borate system, a melt containing less than 17 mol% BaO separates into two liquid phases at $T = 1200°$ C; on the other hand melts containing more than 40 mol% BaO crystallize on cooling [9]. Five barium borate compositions were melted during this investigation (series A) containing 10, 20, 30, 40 and 50 mol% BaO. To each melt was added about 2 wt% iron oxide (as Fe) and equilibrated at 1200° C with air as the furnace atmosphere. The results of ferrous–ferric equilibrium are plotted as log (ferric/ferrous) against mol% BaO in the melt in Fig. 3. The usual [10] linear relationship has been observed, and this can be interpreted as due to increasing basicity with larger amounts of BaO in the melt [11]. As expected, melt A_1 separated into two glassy phases; most of the added iron oxide was enriched into the BaO-rich phase containing about 18 mol% BaO, and the ferric/ferrous ratio in this sample seems to represent that composition satisfactorily. Melt A_5 containing 50 mol% BaO crystallized on cooling and could not be dissolved in 6 N HCl for chemical analysis. However, a rough guide about the ferric/ferrous ratio in this melt at 1200° C can be obtained by linear extrapolation of the line in Fig. 3, and this corresponds to about ferric/ferrous ~ 28.

3.2. Effect of temperature on the ferrous–ferric equilibrium in glass

The oxidation–reduction equilibrium in glass is known to move towards the reduced side with increasing temperature [11]. This is expected from the standard free energy diagram (Fig. 1) where all the free energy lines have positive slopes. To study the effect of temperature on the Fe_3O_4–Fe_2O_3 equilibrium in glass, glasses containing 30 mol% BaO, 70 mol% B_2O_3 and a constant amount of iron oxide (2 wt% total iron as Fe) were equilibrated at four different temperatures (1100, 1200, 1300 and 1400° C), and the ferrous–ferric distributions in these glasses, after chemical analysis, are shown in Table I. From Table I it is clear that the equilibrium ferrous content of the melt increases with increasing temperature; and a plot of log [ferric/ferrous] versus $1/T$(K) produces a satisfactory straight line (Fig. 4) as has been found in many other redox systems in glass [12, 13]. On the other hand, a plot of log

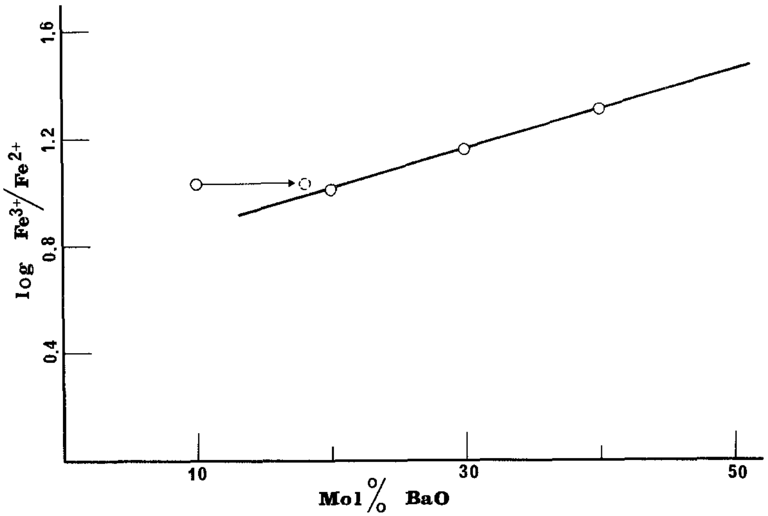

Figure 3 Variation of ferrous–ferric equilibrium with BaO content in BaO–B_2O_3 glasses.

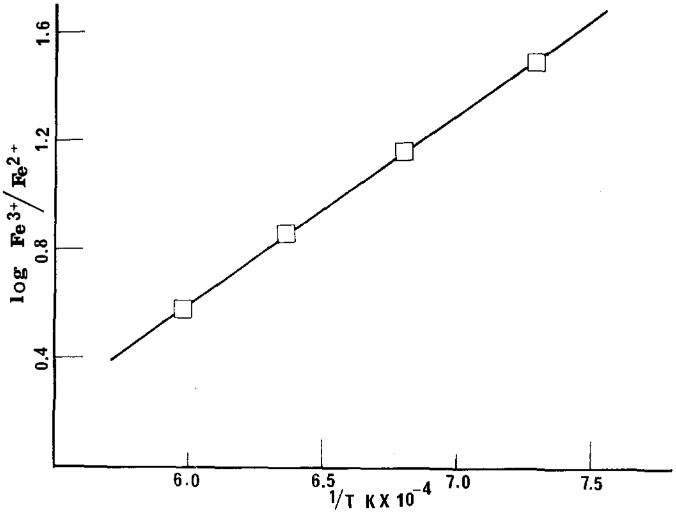

Figure 4 Variation of ferrous–ferric equilibrium in 30 BaO, 70 B_2O_3 glass with temperature.

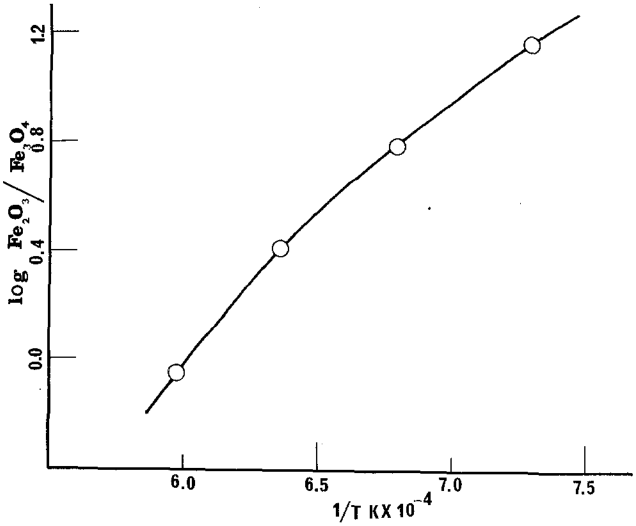

Figure 5 Variation of ferrous–ferric equilibrium in 30 BaO, 70 B_2O_3 glass with temperature.

[Fe_2O_3/Fe_3O_4] versus $1/T$(K) as shown in Fig. 5 does not produce a linear relationship, and a plot as shown in Fig. 4 seems to represent the system in a more convenient and simpler way than plots in Fig. 5.

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