Basicity of Alkaline Earth Silicate Melts Based on the $\text{Cr}^{6+}/\text{Cr}^{3+}$ Redox Equilibria[†]

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Differential pulse voltammetry of $\text{Cr}^{6+}/\text{Cr}^{3+}$ in alkali silicates, which has been worked in the previous study (Ref. (11)) was extended to silicate melts containing alkaline earth oxides. The basicity scale of new systems finds more relevant applications to practical slags. As compared at the disilicate composition, the basicity increase in the order of MgO, CaO and Li_2O , BaO, Na_2O , K_2O , Rb_2O , and Cs_2O .

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I. Introduction

Electrochemical techniques, such as the electromotive force method of concentration cells and voltammetry, provide useful information on thermodynamic activities, redox equilibria, and diffusion coefficients in oxide melts⁽¹⁾. Thus, numerous electrochemical studies have been carried out on the behavior of trace elements in the high temperature systems including silicate melts as a subject of great interest in the fields of metallurgy, window glass technology and geochemistry⁽²⁾⁻⁽⁸⁾. Recently, it was elucidated that the reduction potential of $\text{Cr}^{6+}/\text{Cr}^{3+}$ in melts varies widely as a linear function of basicity of the solvent melts and when sodium in the solvent was replaced by lithium to cesium at constant alkali content (disilicate composition)⁽⁹⁾⁻⁽¹¹⁾. The results made it possible to extend the basicity scale, which had been originally defined in terms of sodium oxide activity in the sodium silicates, to all alkali silicates.

In this paper, the experimental results of $\text{Cr}^{6+}/\text{Cr}^{3+}$ equilibrium measurements in the silicate melts including MgO, CaO and BaO, which are much more important components than alkali oxides in slags, are presented.

II. Experimental

Sample melts were prepared by heating mixtures of the guaranteed reagent grade Na_2CO_3 , CaCO_3 , BaCO_3 , MgO, SiO_2 and Cr_2O_3 . Since the liquidus' of alkaline earth oxide-silica binary systems are too high to be investigated, sodium oxide was added and the measurement was carried out as a function of its decreasing content. The

solvent composition ranged over $0 < x < 0.6$ of $(1-x)\text{Na}_2\text{O} \cdot x\text{RO} \cdot 2\text{SiO}_2$ ($\text{R} = \text{Mg}, \text{Ca}, \text{Ba}$) at the quasi-binary systems. The concentration of Cr_2O_3 was 0.5 mol%.

The details of the electrochemical experiment have been reported elsewhere⁽¹⁰⁾ but only briefly reported here. The electrochemical cell with three electrodes is schematically shown in Fig. 1. The reference and working electrodes were constructed from 0.5 mm diameter Pt-20% Rh wires. The reference electrode is a folded Pt-20%Rh wire in order to hold a large meniscus area and is located just on the melts surface. Its potential is given by eq. (1):

This reference electrode is not the standard but the real electrode. Thus, the potential changes with the basicity of each solvent.

On the other hand, the working electrode had a ring form whose immersed surface area was about 100 mm^2 . This electrode responds to the following reaction:

Therefore, the applied voltage between the two electrodes is concerned with the chemical reaction which is the sum of eqs. (1) and (2), that is,

Fig. 1 Schematic diagram of the electrochemical cell.

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when the reference states of compounds are used. The third counter electrode is provided by the crucible itself of Pt-20%Rh.

The voltammetric measurements using the differential pulse technique were performed using a potentiostat (Nichica NP-IR1000) and a personal computer to supply the potential and to record the current data, respectively. The pulse height ranged from 20 to 80 mV. The duration of the pulses and the interval of each pulse were 0.05 s, and 0.5 s, respectively. Measurements were undertaken at temperatures between 1500 and 1700 K at 50 K intervals in an atmosphere of 0.1 MPa oxygen flowing at the rate of 500 cm³/min.

III. Results

Figure 2 shows a typical observed voltammogram. A peak at about -100 mV is seen for the Cr⁶⁺ reduction and the reduction current for Si⁴⁺ in the solvent is also observed on the negative side beyond -500 mV. The relation between the observed peak potential, E_p , and the polarographic half-wave potential, $E_{1/2}$, is as follows (Bard and Faulkner 1980):

$$E_p = E_{1/2} - \frac{\Delta E}{2}, \quad (4)$$

where ΔE denotes the pulse height. Since $E_{1/2}$ is almost the same as the reduction potential except for the small correction term from the ratio of diffusion coefficients of the oxidized to reduced species, we treat $E_{1/2}$ as the reduction potential in this paper for the sake of convenience.

We investigated the redox potential of Cr ion in $(1-x)\text{Na}_2\text{O} \cdot x\text{RO} \cdot 2\text{SiO}_2$ (R=Mg, Ca, Ba) melts and the results are summarized in Fig. 3 at 1550 K. As shown in Fig. 3,

Fig. 2 Observed differential pulse voltammogram in $0.6\text{Na}_2\text{O} \cdot 0.4\text{BaO} \cdot 2\text{SiO}_2$ melt at 1500 K.

Fig. 3 The composition dependences of the $\text{Cr}^{6+}/\text{Cr}^{3+}$ reduction potential in three melts. (A); $(1-x)\text{Na}_2\text{O} \cdot x\text{MgO} \cdot 2\text{SiO}_2$ (B); $(1-x)\text{Na}_2\text{O} \cdot x\text{CaO} \cdot 2\text{SiO}_2$ (C); $(1-x)\text{Na}_2\text{O} \cdot x\text{BaO} \cdot 2\text{SiO}_2$

the redox potential shifts toward the positive direction with increasing MgO, CaO, and BaO content in each melt. Whenever the cathodic wave caused by the reduction of Cr⁶⁺ is overlapped with the redox wave due to the O₂/O²⁻ pair, the determination of the potential was carried out with some difficulty, especially when the reduction potential is located on the positive side beyond 0 mV. The liquidus temperature increases with increasing alkaline earth content. Therefore, the present experiment covered only the range of $x < 0.6$.

IV. Discussion

1. Basicity of alkaline earth silicates

As previously described, the redox of chromium oxide depends so significantly on the basicity that it may become possible to tell the unknown basicity of a solvent from the redox potential. The reason for the dependence can be interpreted as follows; Cr⁶⁺ is a strong acid compared with Si⁴⁺ and always exists in the complex of CrO_4^{2-} , while the acidity of Cr³⁺ is located somewhere between Si⁴⁺ and the alkali or alkaline earth cation and it exists just octahedrally solvated by the non-bridging oxygen atoms of the silicate network. Therefore, the redox equilibrium of eq. (3) is better stated as,

which properly shows the basicity dependence.

In earlier days we started with the definition of the basicity⁽¹²⁾

$$pO = -\log a(\text{Na}_2\text{O}) \quad (6)$$

which was measured from the electromotive force of the concentration cells of sodium silicates. In the previous

report, the Cr⁶⁺/Cr³⁺ redox potential was measured as a function of the basicity in sodium silicates at 1373 K⁽¹¹⁾,

$$\begin{aligned} pO &= -\log a^*(\text{Na}_2\text{O}) \\ &= 6.17E_{1/2} + 9.69 \quad (\text{at } 1373 \text{ K}) \end{aligned} \quad (7)$$

In the second, it was confirmed that the potential changed linearly in $x\text{Na}_2\text{O}(1-x)\text{K}_2\text{O} \cdot 2\text{SiO}_2$, and the measurement was extended to $\text{R}_2\text{O} \cdot 2\text{SiO}_2$ systems where R denotes Li, Rb, and Cs. These measurements determined the basicities of these di-silicates other than sodium in the scale defined in terms of sodium oxide activity. It is to be noted that the underlining assumption of this procedure is that the redox depends not on the species but only on the basicity.

The next step is the evaluation of the basicities of the present alkaline earth di-silicates. The $E_{1/2}$ vs. pO relation at the temperature of the present experiments (1523 K) is as follows⁽¹¹⁾:

$$pO = 6.94E_{1/2} + 9.97 \quad (\text{at } 1523 \text{ K}) \quad (8)$$

It is somewhat uncertain to estimate the potentials at x being equal to 1, but linear relations may be assumed for the first approximation, since it was true in the sodium di-silicate-potassium di-silicate quasi-binary system⁽¹¹⁾. The estimated potentials are inserted into eq. (8) to evaluate the pO values of the alkaline earth di-silicates. Table 1 lists the results along with those of the alkali disilicates. It will be quite interesting to test the basicities in terms of Na_2O activity with the optical basicity⁽¹³⁾. The correlation shown in Fig. 4 was found to be satisfactory.

2. Basicity of Magmas

Instead of steelmaking slags, magmas provide better melts to which the present treatment can be applied. The representative compositions of typical magmas are quoted from Mysen's book⁽¹⁴⁾. Magmas are chemically classified by the silica content while the ferric-ferrous ratio will be the second factor to characterize the magmas. This is because FeO is a basic oxide that modifies the silica network, while Fe₂O₃ is an acidic oxide and takes part in the network formation. To be more accurate, Fe³⁺ forms both tetrahedral and octahedral complex ions, but only the former is the network former. At a given oxygen fugacity, the iron content and its physicochemical behavior depends on the basicity of the solvent. Thus, it is

Fig. 4 The basicity pO of various di-silicates vs. the optical basicities of the component oxide at their single oxide state.

quite important to see how high is the basicity level of the magma, which is governed not only by the ratio of the silica contents (and other acid oxides) to alkali and alkaline earth oxides but also by what is the species of the basic oxide. In the following, an attempt was made to evaluate the basicity of magmas with the aid of the basicity strengths of various basic oxides.

The contents of the components are shown in Table 2 on a mole fraction scale. The evaluation needs the following assumptions;

(1) $\log a(\text{Na}_2\text{O})$ vs $x(\text{Na}_2\text{O})$ is approximately linear when the Na_2O content is not more than 0.667. Further, $\log a^*(\text{Na}_2\text{O})$ vs $x(\text{MO})$ in the other silicates show nearly the same slope while the intercept on the $\log a^*(\text{Na}_2\text{O})$ axis is different⁽¹²⁾⁽¹⁵⁾. Here, $\log a^*(\text{Na}_2\text{O})$ is the basicity of non-sodium silicate in the Na_2O activity scale.

(2) The basicity of a silicate mixture is assumed to be given by their weighted mean of the component silicates with the same MO to silica ratio,

$$pO = \frac{\sum_i x_i(\text{M}_i\text{O}) \cdot pO_i}{\sum_i x_i(\text{M}_i\text{O})} \quad (9)$$

Table 1 Redox potential of Cr⁶⁺/Cr³⁺ in various di-silicate (1523 K) and evaluated basicity values.

Material	$E_{1/2}$ (mV)	pO
$\text{Li}_2\text{O} \cdot 2\text{SiO}_2$	66	10.3
$\text{Na}_2\text{O} \cdot 2\text{SiO}_2$	-101.2	9.1
$\text{K}_2\text{O} \cdot 2\text{SiO}_2$	-341.6	7.4
$\text{Rb}_2\text{O} \cdot 2\text{SiO}_2$	-451.8	7.1
$\text{Cs}_2\text{O} \cdot 2\text{SiO}_2$	-546.8	6.2
$\text{MgO} \cdot 2\text{SiO}_2$	201	11.4
$\text{CaO} \cdot 2\text{SiO}_2$	138	10.9
$\text{BaO} \cdot 2\text{SiO}_2$	-4	9.9

Table 2 Composition and basicity values of representative magmas.

	Phyolite	Dacite	Andesite	Tholeiite	Alkali Basalt	Basanite
SiO_2	0.794	0.720	0.639	0.527	0.506	0.483
Al_2O_3	0.089	0.103	0.112	0.096	0.096	0.092
Fe_2O_3	0.008	0.010	0.013	0.014	0.019	0.018
FeO	0.009	0.023	0.041	0.070	0.065	0.067
MgO	0.007	0.027	0.057	0.120	0.132	0.142
CaO	0.016	0.054	0.084	0.118	0.116	0.124
Na_2O	0.043	0.039	0.036	0.029	0.034	0.038
K_2O	0.031	0.015	0.011	0.006	0.009	0.014
pO	11.8	12.1	11.8	10.6	10.5	10.2

where x_i and pO_i are the mole fractions of the i th basic oxide and the basicity of the i th-silicate.

(3) For the time being, Al_2O_3 and Fe_2O_3 are the same as SiO_2 in acidity strength, the capacity being 3/2 times as great as the SiO_2 per mole.

(4) The basicity of FeO is assumed to have the same value as that of MgO .

(5) P_2O_5 and TiO_2 are not weak acids but are neglected in this evaluation since their contents are small.

Equation (9) can be derived as follows. After the content of SiO_2 is corrected by the amount of Fe_2O_3 and Al_2O_3 , the magma is seen as a mixture of alkali and alkaline earth silicates with a common basic oxide to SiO_2 ratio. In other words,

$$\begin{aligned} & \text{one mole melt of } M_1O, M_2O, \dots M_nO, \text{ and } SiO_2 \\ &= x_1M_1O + x_2M_2O + x_nM_nO + (1-X)SiO_2 \\ &= \sum_i x_iM_iO + (1-X)SiO_2 \end{aligned} \quad (10)$$

where $\sum x_i = X = \text{total mole fraction of the basic oxides}$. The basicity is determined by taking the mean of the basicities of the di-silicates of the component basic oxide and shifting the corresponding value of the basic oxide to SiO_2 ratio from the di-silicate of Na_2O as follows:

Fig. 5 The composition and the estimated basicities of six representative magmas.

$$\begin{aligned} pO &= \frac{\sum_i x_i pO_i}{\sum_i x_i} = \frac{\sum_i x_i \{ pO_i(0.333) + b(x_i - 0.333) \}}{X} \\ &= \sum_i x_i pO_i(0.333) / X + b(X - 0.333) \end{aligned} \quad (11)$$

where b is the common slope of pO vs. the mole fraction of the basic oxide.

The results are shown in Table 2 and Fig. 5. Direct experimental confirmation of the Fe^{3+}/Fe^{2+} redox potential failed probably because the current-potential curve overlapped with the electronic conduction. We hope that magma should be discussed not by the concentration alone but by the activity of the components which are governed by the basicity. In the same way, the basicity of slags will be better evaluated not by the CaO/SiO_2 ratio but by the weighted mean of various basic oxide and the ratio of total basic oxides to acid oxides.

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