An Investigation of the Evaporation of B$_2$O$_3$ and Na$_2$O in F-Free Mold Slags

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The present paper deals with the investigation of evaporation of B$_2$O$_3$ and Na$_2$O from F-free mold slags in the temperature range of 1573 to 1673 K by Thermogravimetric Analysis (TGA) method. The study was aimed at elucidating the evaporation mechanism during continuous casting and identifying the resulting effect on the flux composition. The basicity was found to slightly enhance the evaporation rate of mold slags, suggesting that the mass transport in the liquid phase plays a role in controlling the evaporation. TiO$_2$ addition resulted in an increasing evaporation rate due to the decrease of viscosity of the slag. The diffusional flux resulting from gas phase mass transfer from the gas/slag interface to the bulk gas was theoretically estimated and the results suggest that this process is not the controlling step. The evaporation rate was found to increase with increasing ZrO$_2$ addition possibly due to the fact that the solid particles existing in the slag act as nucleation sites of bubbles formation. The evaporation rate was also found to increase with increasing experimental temperatures.

KEY WORDS: F-free mold slag; evaporation; TiO$_2$; ZrO$_2$; thermogravimetric analysis.

1. Introduction

Commercial mold fluxes conventionally contain fluorides, which typically constitute around 5–7 wt% of the slag. Fluorine has two critical roles in controlling the continuous casting process, namely to reduce viscosity and break temperature to improve lubrication, and to control heat transfer through the precipitation of cuspidine (3CaO · 2SiO$_2$ · CaF$_2$).1–7) However, fluorine emission has attracted much attention in recent years due to the emission of fluorine containing gaseous species such as HF, SiF$_4$ or NaF. These gaseous species might contribute to acid rain, pollution of ground water from the wasted slags and they pose a potential health and safety hazard.8–10) Therefore, F-free mold slags have been developed during recent years11–14) with the objectives of tailoring the slag chemistries such that crystallization and viscosity which are controlled by constituents other than fluorine. Nakada11) investigated the crystalline behaviors of CaO–SiO$_2$–TiO$_2$ slag using differential thermal analysis (DTA) technique and suggested that the precipitated CaSiTiO$_5$ can substitute for cuspidine in commercial mold slags. Choi12) studied the glass system of CaO–SiO$_2$–Al$_2$O$_3$–Na$_2$O–B$_2$O$_3$ as a F-free mold flux and suggested that B$_2$O$_3$ and Na$_2$O are added to decrease the viscosity and to form the CaB$_2$SiO$_7$ and CaAl$_4$B$_2$[SiO$_4$]$_8$ as a substitution of cuspidine in a continuous casting of steel. Fox13) also reported that B$_2$O$_3$ and Na$_2$O can be used as alternative substitutes for CaF$_2$ and the plant trials results indicated that the new flux can be used in a continuous casting of steel. Wen14) investigated the F-free mold powders for peritectic steel slag casting, suggesting that the formation of perovskite (CaTiO$_3$) in F-free mold slag can substitute the cuspidine formed in commercial slags. These previous studies on F-free mold slag systems indicate that B$_2$O$_3$, Li$_2$O and Na$_2$O are added to decrease the viscosity and to control the heat transfer. TiO$_2$ addition is used to form perovskite as a substitutes for cuspidine to control the heat transfer. ZrO$_2$ can be added as nucleating agents to accelerate the formation of perovskite crystals. The melting points of the oxides B$_2$O$_3$ and Na$_2$O are 450°C and 1132°C, respectively, which may result in the escaping oxide gaseous species at high temperatures. This would change the chemical compositions of F-free mold slags, and the physicochemical properties such as viscosity, crystallization behaviors of slags are correspondingly changed. It is therefore necessary to understand the evaporation mechanism of these oxides in F-free mold slags. To the knowledge of present authors, no systematic studies have been carried out so far thus motivating the present study. The purpose in this work is to study the evaporation mechanism of B$_2$O$_3$ and Na$_2$O oxides in the F-free mold slags by thermogravimetric analysis (TGA) method. The effects of TiO$_2$ and ZrO$_2$ additions on the evaporation were also investigated.
2. Experimental

2.1. Preparation of Slags

Synthetic slags were prepared by mixing pure oxides (CaO, SiO2, Al2O3, B2O3, ZrO2, TiO2), and adding Na2CO3 as a source of Na2O. The chemical compositions of the slags studied are listed in Table 1 and these are based on the pre-mixed powder compositions prior to melting. As will be discussed in the results section, these compositions may differ from those of the fused samples due to evaporation losses. The powders were dried for 4 h at 200°C and then heated to 1 400°C at a rate of 5°C/min in order to obtain homogenous samples for the experiments. The liquid slag was subsequently poured into a steel mold which was cooled naturally. A slag sample of 50 g was used for the analysis of chemical composition by X-Ray fluoroscopy (XRF).

2.2. Experimental Procedures

The evaporation experiments were carried out in a SETARAM TGA 92 (France), which had a detection limit of 1 μg, as can be seen from Fig. 1. The system was controlled by an IBM PC* through a CS92 controller. The Pt crucible with weighed pre-melt slags was suspended in the even temperature zone of the furnace by Pt wire. During the evaporation experiments, the reaction tube was first evacuated for 5 min, and then filled with argon atmosphere at a fixed flow rate above the starvation rate. The furnace was then heated from room temperature to the preset temperatures at a fixed heating rate of 50 K/min. The furnace was heated up to the preset evaporation temperature in the range of 1 300–1 400°C in an argon atmosphere, and was held for 120 min. The furnace was subsequently shut down and the sample was cooled down to room temperature.

The collected powder deposits resulting from evaporation were analyzed by a Siemens XRF3000 spectrometer (Germany) which had a detection limit of 1 μg.

Table 1. Chemical compositions of the designed slag specimens (mass%).

| Brand | CS-1 | CS-2 | CS-3 | CS-4 | CS-5 |
|-------|------|------|------|------|------|
| CaO   | 39   | 44   | 47.8 | 44.6 | 41   |
| SiO2  | 47   | 42   | 38.2 | 35.4 | 39   |
| Al2O3 | 3    | 3    | 3    | 3    | 3    |
| Na2O  | 6    | 6    | 6    | 6    | 6    |
| B2O3  | 5    | 5    | 5    | 5    | 5    |
| TiO2  | 0    | 0    | 0    | 0    | 6    |

Table 2. Chemical compositions of post-measured slag (mass%).

| Brand | CS-1 | CS-2 | CS-3 | CS-4 | CS-5 |
|-------|------|------|------|------|------|
| CaO   | 39.62| 41.98| 46.20| 43.80| 38.29|
| SiO2  | 48.22| 42.90| 39.11| 36.91| 39.18|
| Al2O3 | 2.93 | 3.10 | 3.19 | 3.12 | 3.21 |
| Na2O  | 6.70 | 6.71 | 6.59 | 6.54 | 6.61 |
| B2O3  | 5.13 | 5.22 | 4.81 | 4.63 | 5.08 |
| TiO2  | 0.092| 0.081| 0.081| 0.081| 0.55 |

Fig. 1. A TG experimental set-up.

Fig. 2. (a) Isopleth phase diagrams computed by FactSage. (b) Crystallization temperature ranges versus basicity.
tion were analyzed by Scanning Electron Microscopy equipped with Energy Dispersive Spectrometer (SEM-EDS).

3. Results and Discussion

3.1. Pertinent Thermophysical and Thermodynamic Slag Properties

It is well known that a critical problem associated with Na₂O and B₂O₃ containing slags is the volatilization of Na or B, which may lead to the variation of chemical compositions during pre-melting slags and casting steels. In order to determine the variation of chemical composition during pre-melting of the slag, the chemical compositions of the pre-melted slags were analyzed through X-ray fluoroscopy (XRF), and the results are shown in Table 2. It can be seen that the contents of Na₂O and B₂O₃ are very close with that of the designed chemical compositions listed in Table 1, indicating that the evaporation of Na₂O and B₂O₃ during the pre-melting period are negligible under the present conditions.

In order to understand the phase stability in F-free mold slag, isopleth phase diagrams were computed by using the FactSage software, and the results are shown in Fig. 2(a). The arrows labeled in the figures are indicative of the evaporative temperature ranges explored under the present experiment. It can be seen that the precipitates are observed at the low experimental temperature ranges. Figure 2(b) gives the crystallization temperatures versus basicity of mold slags. The crystallization temperatures were determined using Confocal Scanning Laser Microscopy (CSLM) method. It can be seen that no crystals were formed at the evaporation temperature ranges. The discrepancy between the predicted crystals by FactSage and the experimental values is probably due to that the nucleation may act as the controlling step in these regions.

3.2. TG Results

The measured TG curves for mold slags containing B₂O₃ and Na₂O have the general appearance of those shown in Figs. 3 and 4, where the weight loss is associated with the evaporative loss at high temperatures. The numbers labeled in the figures correspond to the compositions in Table 1. In order to establish the reproducibility of the experimental results, selected experiments were repeated, which is shown in Fig. 4. As can be seen, the experimental results for slag CS-3 carried out under the same conditions in terms of temperature and flow rate have good repeatability. Figure 3 shows the weight losses of F-free mold slags with varying chemical compositions as a function of time, indicating that temperature and chemical compositions have significant effect on the weight loss of F-free mold slags. The degree of weight loss increases with increasing temperature. Figures 5, 6 and 7 show the effects of basicity, TiO₂ and ZrO₂ additions on the weight loss of F-free mold slags, respectively. It can be seen that TiO₂ and ZrO₂ additions obviously increase the evaporation while an increasing basicity slightly enhances the degree of weight loss of mold slags. Considering the fact that the slag chemical compositions may change at longer evaporation times, the present paper takes the initial 15 min to calculate the evaporation rates. It can be seen from Fig. 8, that the curves for weight loss versus time shows the linear relationship for all slags during the initial 15 min, and the evaporation rates and activation ener-
gies were estimated. The logarithmic evaporation rate versus reciprocal temperature along with the activation energies are plotted in Fig. 9. It can be seen that the calculated apparent activation energy for the mechanism(s) responsible for evaporation of slag CS-3 is larger than those of slag CS-3 containing ZrO₂ and slag CS-4 containing TiO₂.

3.3. Kinetics of Evaporation

3.3.1. Evaporated Gaseous Species

In order to analyze the weight loss behaviors based on the theoretical models, it is essential to know the evaporated gaseous species from the investigated slags. In the present study, the reactions that may cause the weight losses are:

\[
\begin{align*}
\text{Na}_2\text{O}_{(l)} + \text{B}_2\text{O}_3_{(l)} & = 2\text{NaBO}_2_{(g)} & \text{(1)} \\
\text{Na}_2\text{O}_{(l)} + \text{B}_2\text{O}_3_{(l)} & = (\text{NaBO}_2)_{2(g)} & \text{(2)} \\
\text{B}_2\text{O}_3_{(l)} & = \text{B}_2\text{O}_3_{(g)} & \text{(3)}
\end{align*}
\]

Fig. 4. The repeatability of CS-3 tested under the same temperature and flow rate.

Fig. 5. The effect of basicity on the evaporation rate.

Fig. 6. The effect of TiO₂ addition on the weight loss of F-free mold slags.

Fig. 7. The effect of ZrO₂ addition on the evaporation rate of F-free mold slags.

Fig. 8. The weight loss plotted as function of time during the initial 15 min.
Detailed measurements on the Na$_2$O–B$_2$O$_3$–SiO$_2$ ternary systems using high temperature mass spectrometer techniques have shown that the equilibrium gaseous species predominantly contain sodium metaborate (NaBO$_2$) and a small portion of (NaBO$_2$)$_2$, and B$_2$O$_3$ was also observed at the temperatures above 1 300 K, and it is expected that the vapor pressure of B$_2$O$_3$ increased with rising temperature, and it would therefore be expected that reactions (1) and (3) will play significant roles in the volatilization process, i.e., NaBO$_2$ and B$_2$O$_3$ are the main volatilized gas species in the Na$_2$O–B$_2$O$_3$–SiO$_2$ ternary systems. Due to their stability, CaO and Al$_2$O$_3$ would not be expected to volatilize significantly. It is therefore reasonable to assume the present slag system has the same volatile gas species.

$$\text{Na}_2\text{O}(l) = \text{Na}_2\text{O}(g)$$

was the main component, while B was not detected by the EDS due to its low atomic weight, i.e., Na and B may exist as NaBO$_2$, NaBO$_2$ and/or B$_2$O$_3$. The gaseous species could potentially form as gas bubbles inside the melt or at the slag surface.

### 3.3.2. Rate-controlling Process

The possible rate-controlling processes, schematically shown in Fig. 11, are as follows:

(a) Transport of the anions and cations involved in Eqs. (1)–(4) to the active site for gas bubble formation.

(b) Chemical reactions according to Eqs. (1)–(4).

(c) Nucleation of NaBO$_2$, (NaBO$_2$)$_2$, B$_2$O$_3$ and Na$_2$O molecules to form bubbles in the slag melt.

(d) Transport of bubbles from bulk liquid slag to the slag/gas interface through liquid boundary layer.

(e) Transport of gas from the slag/gas interface to the bulk gas flow through the stagnant gas film.

(f) Flow of bulk gas stream from the nozzle of crucible.

Among the rate-controlling steps, the last step (f) may not be the rate-controlling step, because the rate of bulk gas flow used under the present experiment is five times larger than what is expected for it to be rate controlling according to a study in literature where conditions were similar. This consequently leads to the conclusion that the bulk flow-rates can be excluded from the consideration. According to Fig. 5, a comparison of weight changes between CS-1 and CS-3 as well as CS-4 and CS-5 at different temperatures, an increasing basicity slightly enhances the evaporation rate. In the silicate slag, it is well known that the siliccon ion forms the tetrahedral unit with four oxygen ions which would link together to form a three dimensional networks. CaO oxide however would break the network as a network breaker. Figure 12 shows the viscosity estimated by NPL model as a function of basicity. It can be seen that an increase of basicity slightly decreases the viscosity. This would result in an increase of the transport of bubbles and the mobility of ions in the liquid slag that are transported to the bubble/slag interface. This suggests that the growth of bubbles and the transport of gaseous species from the melt to the interface would be expected to increase with increasing basicity. This is in agreement with the present experimental observation (Fig. 5) that the steps (a) and (d), transport of cations and anions to the reaction sites or the transport of bubbles to the slag/gas interface play a significant role in controlling the evaporation under the present experiment. TiO$_2$ addition plays the similar role on the
evaporation rate. It is generally accepted that the addition of TiO₂ reduces the viscosity. It should be pointed out however, that the results are not consistent with each other. Wen et al.\textsuperscript{14)} reported that 6 wt% TiO₂ addition decreases the viscosity from 2.46 to 2.24 Pa s at 1300°C, however, the results from Mukongo et al.\textsuperscript{24)} indicated that the viscosity decreased from 0.4 to 0.3 Pa s with 6 wt% TiO₂ addition at 1300°C. Shankar et al.\textsuperscript{25)} studied the influence of TiO₂ addition on the viscosity in the slag melt for both low and high basicity and reported that the slag viscosity decreases with addition of even 2 wt% TiO₂ in the slag. These results indicated that Ti⁴⁺ act as the network breaker when the TiO₂ addition is low. It was noted from Fig. 2(b) that there is no observable crystallization at the experimental temperature ranges (1300–1400°C) indicating that there are at least no large solid crystals present which could influence nucleation or viscosity. While the quantitative effect of TiO₂ on the viscosity can not be established it might however have a role in lowering the viscosity and thereby enhance evaporation. This is in agreement with a previous study, which investigated the evaporation mechanism in a ternary CaF₂–SiO₂–CaO slag system, and the results indicated that the liquid phase mass transport of SiO₄²⁻ controlled the evaporation rate in part.\textsuperscript{10)}

Figure 7 shows that the addition of ZrO₂ into slag CS-3 accelerated the evaporation rate, and this may arise from the fact that ZrO₂ particles have the limited solubility in molten slags. The solubility of ZrO₂ particle in the slag CS-3 with 2 wt% addition was also examined using Confocal Scanning Laser Microscope (CSLM) technique equipped with a golden image furnace. The solubility of ZrO₂ particle in the slag CS-3 with 2 wt% addition was also examined using Confocal Scanning Laser Microscope (CSLM) technique equipped with a golden image furnace. The solubility experiment was conducted under Ar atmosphere, and one large piece of ZrO₂ particle with the size around 1 mm that is 2 wt% in the slag mixture was applied in the present experiment. The reason we selected this large but rare particle is due to ease of following it. The slag mixture was then heated to 1500°C and held for 60 s, followed by a rapid cooling to 1350°C at a cooling rate of 50 K/s and was held for 30 min. In order to verify the existence or the role of ZrO₂ particle in the slag melt, the ZrO₂ particle was focused during the whole experimental processes. Figure 13 shows the CSLM images of slag CS-3 with and without ZrO₂ addition. It was found that the ZrO₂ particle existed in the whole experimental processes even when the flux was being held at 1500°C for 60 s, while no solid particle was found in the slag melt CS-3 without ZrO₂ addition when the isothermal temperature is at 1350°C. X-Ray Diffraction (XRD) analysis (Fig. 14) also confirms the existence of ZrO₂ particle in the slag CS-3 with 2 wt% addition which was heat-treated at 1500°C for 60 s, then at 1350°C for 30 min. This may suggest that the solubility of ZrO₂ in the present slag melt is under 2 wt%. This is consistent with the previous work that reported that ZrO₂ particles have the limited solubility in molten slags.\textsuperscript{26)} It is also noted that the crystals are formed along ZrO₂ particles as shown in Fig. 13(d). The existing ZrO₂ particles as well as the formed crystals might act as the heterogeneous nucleation sites. The concentrations of gaseous species are therefore increased, resulting in the increase of the bubble transport through liquid slag. It should be pointed out that the existing solid particles would increase the apparent viscosity of slag melt. This may cause an increase of resistance to transport of species in the slag melt. However, it is reasonable to assume that the melt phase viscosity of the slag melt keeps.
constant due to its limited solubility and relatively low crystalline fraction under the evaporation temperature ranges. These may indicate that the nucleation of NaBO$_2$ and B$_2$O$_3$ gases in the melt and formation of bubbles may act as a controlling step, at least under the present experimental conditions.

The transport of gaseous vapor from the surface of the slag melt to the bulk gas through gaseous boundary layer needs to be considered. The Pt crucible used under the present experiment is schematically shown in Figs. 1 and 11, which is similar as the diffusion cell setup.\(^{27}\) Once the evaporation starts, gaseous species will evaporate from the interface and leaves by way of the carrier argon gas. Moreover, the argon gas will diffuse down the crucible. After a certain time, a steady-state will be established in which the concentrations of gaseous species and argon gas become constant.\(^{28}\) Under this condition, there is a net flow gas upward from the gas/slag interface, and that the gas velocity at the cylinder wall will be smaller than that in the center of the crucible. In order to simplify the problem, we neglect this effect and assume that there is no convection occurring inside the crucible, only diffusion of gaseous species takes place. Hence, the flux of NaBO$_2$ and B$_2$O$_3$ gases evaporating from the gas/slag interface are given\(^{27,29}\), respectively,

$$J_{\text{NaBO}_2} = \frac{D_{\text{NaBO}_2}}{L \cdot RT} (P^i_{\text{NaBO}_2} - P^b_{\text{NaBO}_2}) \quad \text{(5)}$$

and

$$J_{\text{B}_2\text{O}_3} = \frac{D_{\text{B}_2\text{O}_3}}{L \cdot RT} (P^i_{\text{B}_2\text{O}_3} - P^b_{\text{B}_2\text{O}_3}) \quad \text{(6)}$$

where $i$ and $b$ are the interface and bulk, respectively. $R$ and $T$ are gas constant and experimental temperature ($K$), respectively. $L$ is the distance between the surface of liquid slag and the end of crucible. $P^i$ and $P^b$ are the pressures at the interface and bulk gas, respectively, and $P^b$ is assumed to be zero since the gas flow rate is not starved under the present experiment. $D_{\text{NaBO}_2}$ and $D_{\text{B}_2\text{O}_3}$ are the diffusion coefficients of NaBO$_2$ and B$_2$O$_3$ gaseous species through Ar gas, which can be calculated by Chapman–Enskog equation.\(^{27}\)

$$D_{\text{AB}} = 1.858 \times 10^{-3} \times \frac{1}{P \cdot \sigma_{\text{AB}}^2 \cdot \Omega_{\text{AB}}} \sqrt{T^{-1} \left( \frac{1}{M_A} + \frac{1}{M_B} \right)} \quad \text{(7)}$$

Here, $D_{\text{AB}}$ is the mass diffusivity of A through B in cm$^2$/s; $T$ is the absolute temperature ($K$); $P$ is the absolute pressure (atm); $M_A$, $M_B$ are molecule weight of NaBO$_2$(g) or B$_2$O$_3$(g) and argon gas, respectively; $\Omega_{\text{AB}}$, $\sigma_{\text{AB}}$ are the Lennard–Jones parameters, and $\Omega_{\text{AB}}$ is the collision integral, which is functional of $T(\kappa \epsilon)$.\(^{27}\) The parameters for Ar gas is available from the experimentally evaluated values, for NaBO$_2$(g) and B$_2$O$_3$(g), however, are not available from the literatures. In the present study, the values were estimated by the following empirical relations,\(^{30}\)

$$\epsilon/\kappa = 1.92T_m^{-1} (K) \quad \text{(8)}$$

$$\sigma = 1.22V_m^{1/3} (\text{Å}) \quad \text{(9)}$$

where $T_m$ is the melting temperature ($K$); $V_m$ are the molecular volume (cm$^3$/mol); The estimated values along with the experimental values were listed in Table 3. $\sigma_{\text{AB}}$ and $\epsilon_{\text{AB}}$ can be calculated by the following empirical expressions,\(^{30}\)

$$\sigma_{\text{AB}} = \frac{1}{2} (\sigma_A + \sigma_B) \quad \text{(10)}$$

$$\epsilon_{\text{AB}} = \sqrt{\epsilon_A \epsilon_B} \quad \text{(11)}$$

The diffusivities of NaBO$_2$(g) or B$_2$O$_3$(g) are therefore calculated by Eq. (7), and are listed in Table 4 with the data from references. As can be seen, the diffusivities of NaBO$_2$ and B$_2$O$_3$ are much higher than those of CaF$_2$, NaF and SiF$_4$ at the present experimental temperature ranges,\(^{10}\) resulting in higher evaporation rate correspondingly. This is consistent with the previous paper that showed the evaporation rate of F-containing mold slags is very slow when the experimental temperature is lower than $1400^\circ C$.\(^{29}\) This may change the physicochemical properties of F-free mold slag containing Na$_2$O and B$_2$O$_3$ during the casting.

The vapor pressures of NaBO$_2$ and B$_2$O$_3$ were estimated from ternary slag systems Na$_2$O–B$_2$O$_3$–SiO$_2$ which are used in the present calculation. In view of the fact that the Na$_2$O and B$_2$O$_3$ contents are same in the slag systems, it is reasonable to assume that the vapor pressures are the similar for all slags at the same isothermal temperature. The estimated vapor pressures are listed in Table 5. It can be seen that the partial pressure of NaBO$_2$ is much larger than that of B$_2$O$_3$, i.e., NaBO$_2$ is the dominant volatile phase. The rate of total weight loss of the molten slag can therefore be calculated by following equation,

$$\frac{dw}{dt} = M_{B_2O_3} \cdot J_{B_2O_3} + M_{NaBO_2} \cdot J_{NaBO_2} \quad \text{(12)}$$

| Table 3. Summary of values of $\epsilon/\kappa$ and $\sigma$ for different gaseous species. |
|------------------------------------------|
| Gaseous Species | $\epsilon/\kappa$ (K) | $\sigma$ (Å) | Molecular Weight (g/mol) | Molecular Volume (cm$^3$/mol) |
|-----------------|----------------------|------------|------------------------|-----------------------------|
| NaBO$_2$(g)    | 122.4                | 3.432      | 39.948                 | 75.2                        |
| B$_2$O$_3$(g)  | 2378.88              | 3.65       | 65.8                   | 26.7                        |
| NaBO$_2$(g)    | 1388.16              | 4.23       | 69.62                  | 41.69                       |

| Table 4. Estimated diffusion coefficient of gaseous species in Ar gas (10$^{-7}$ m$^2$/s). |
|------------------------------------------|
| Item                                      | 1300 °C | 1350 °C | 1400 °C |
| D(NaBO$_2$–Ar)                           | 1.93    | 2.05    | 2.16    |
| D(B$_2$O$_3$–Ar)                          | 1.75    | 1.85    | 1.94    |

| Table 5. Calculated vapor pressure of NaBO$_2$ and B$_2$O$_3$ (Pa). |
|------------------------------------------|
| Vapor pressure (Pa)                      | 1300 °C | 1350 °C | 1400 °C |
| P$_{NaBO_2}$                             | 2298    | 4417    | 8164    |
| P$_{B_2O_3}$                             | 1.46    | 4.69    | 14.06   |

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Temperature, and the evaporation rate increases with increasing temperature range of 1573 to 1673 K through thermogravimetric analysis. It was found that:

The evaporation of volatiles in F-free mold slags containing B2O3 and NaBO2 have been investigated in the temperature range of 1573 to 1673 K through thermogravimetric analysis. Table 6 shows a comparison of the measured evaporation rate constant and calculated ones using Eq. (12). As can be seen, the flux resulting from gas phase mass transfer from the slag/gas interface to the bulk gas flow may thus not be the controlling step under the present experimental conditions. This is not consistent with the previous results suggested that the evaporation rate was controlled, at least partly, by the gas phase mass transfer.21) The major reason is considered to be the different volatile species, which results in the different diffusion coefficient in carrier gases (Table 4).

Based upon the aforementioned discussions, it appears that both the liquid phase transfer and the nucleation could be pertinent factors for the vaporization of Oxide Systems, Chichester, Wiley and Sons, (1994).

4. Conclusions

The evaporation of volatiles in F-free mold slags containing B2O3 and Na2O have been investigated in the temperature range of 1573 to 1673 K through thermogravimetric analysis. It was found that:

1. The evaporation is strongly dependent on the temperature, and the evaporation rate increases with increasing temperature.

2. The addition of ZrO2 accelerates the evaporation rate which could be due to the provision of nucleation sites for gas bubbles inside the slag melt.

3. An increasing basicity and TiO2 addition into the mold slag increase the evaporation rate, suggesting that the liquid phase transfer also play a key role to control the evaporation.

4. Both the liquid phase transfer and the nucleation act as controlling steps of evaporation loss of NaBO2 and B2O3 gases under the present experimental conditions.

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| Table 6. A comparison of estimated and measured evaporation rates. |
|------------------|------------------|------------------|------------------|
| Temp (°C) 1300 1350 1400 | CS-3 5.46 14.5 20.4 | CS-3+ZrO2 9.64 20.1 28.1 | CS-4 8.78 15.3 24.4 | Estimated (x10^5 mg/cm²/s) 1.12 2.21 4.18 |