In situ observation and numerical simulation of bubble behavior in CaO-SiO₂ based slag during isothermal and nonisothermal processes

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Abstract

The hot thermocouple technique was used to observe the variation of bubble size in CaO-SiO₂ based molten slag at above 1273 K. Considering that the physical properties of gases change with temperature, the effect of cooling rate on the single bubble behavior was studied according to the heat and mass transfer equations. In order to investigate the distribution of pore size in solidified layer, solidification of slag was conducted in laboratory by using a water-cooled detector, and the pore size in the solidified layer was counted under the scanning electron microscope. The heat flux measured by the water-cooled detector was used as boundary conditions to establish a mathematical model that is capable of describing the characteristics of bubble size distribution. Both the calculation and the observations indicate that the time-temperature history is an important factor that could affect the bubble behavior in molten slag. For slag with no Na₂SO₄, bubbles with large size concentrate on the detector side with high cooling rate, while bubbles with small size are likely to appear on the liquid side with low cooling rate. For slags containing Na₂SO₄, bubbles with large size mainly distribute on the medium layer of the solid slag film.

Keywords: bubble behavior; slag; hot thermocouple technique; nonisothermal process

1. Introduction

Molten slag plays an important role in metallurgical processes [1,2]. Generally, the additions of carbonates, sulphates, and fluorides could improve the fluidity of slags [3]. However, reactions among different components will generate gases with different compositions. The reaction between Na_2CO_3 and SiO_2 under 1000 K will generate CO_2 , as shown in **Eq. [1]** [4].

If the Na_2CO_3 is excess, the surplus Na_2CO_3 may decompose into Na, CO_2 and O_2 at higher temperature, as shown in **Eq. [2]** [4].

Besides carbonates, the decomposition of sodium sulfate occurs at above 1473 K, as shown in **Eq. [3]** [5].

In addition, the evaporation of fluoride at above 1673 K could also influence the composition and partial pressure of bubbles, as shown in **Eq. [4]** [6].

Due to the chemical reactions, bubbles could easily form in molten slag during melting process. On the one hand, the growth and coalescence of large bubbles during floating are beneficial for refining process of the molten slag. On the other hand, fine bubbles with low rising velocity are easily captured by the solidified layer during cooling process, leading to the formation of porous structure in the solid slag. For a nonisothermal process, the dynamics and movement of bubbles in the liquid phase could affect the distribution of pores and physical properties of the solid phase [7]. Therefore, fundamental research about bubble behavior in molten slag is important for understanding the processes related to

heat and mass transfer under high temperature.

Many experimental studies and numerical simulations were carried out to investigate the formation and dynamics of bubbles in various liquids. According to the Helmholtz free energy for the formation of critical nuclei, the nucleation rate at a given temperature for homogeneous bubble nucleation depends on the degree of supersaturation and the surface tension of bubble [8,9]. By using the thin-foil and fracture replication techniques, the mechanisms and kinetics of bubble formation could be observed under electron microscope [10]. In order to study the variation of bubble size in mass transfer process, the quasi-stationary approximation was used to predict the dissolution rates of O_2 and CO_2 bubbles in soda-lime glass melt [11]. Considering the interaction of gas mixtures containing SO_2 and O_2 with glass liquid, the mass transfer equations based on the diffusion mass flow on the boundary of a rising bubble were derived to calculate the bubble size as a function of time under different temperatures [12]. With the development of numerical techniques, numerous modeling studies have been conducted on the bubble behavior including bubble motion, bubble size distribution, bubble rise velocity and bubble coalescence under different ambient conditions. The Euler-Lagrange method and the Euler-Euler method are used for the phase-resolving simulation, and the motion of a single bubble can be obtained by solving its linear and angular momentum equation [13]. For the simulations of bubble diameter and velocity field, the computational fluid dynamic (CFD) technique is an effective method to study bubble behavior because this method could overcome the difficulties of determining the fluid field and concentration distribution around bubble [14]. Compared with two dimensional simulations, the volume of fluid model (VOF) has advantages in describing dynamics in bubble columns since the three dimensional VOF model show much realistic results for bubble rising [15]. Besides, the VOF model could be coupled with the level-set method to study the growth and merge of

bubbles in microchannel boiling flow [16]. In addition, the direct numerical simulation (DNS) method is employed to describe the behavior of deformable bubble in bubble columns [17].

These numerical methods play an important role in determination of movement and size of bubble in different system. In most of numerical simulations, the value of temperature remains a constant during mass transfer process. However, solidification of molten slag occurs at many industrial processes, such as production of glass, coal gasification and continuous casting [24]. Due to the high temperature gradient between the liquid and mold, the maximum cooling rate of molten slag may exceed 50 K/s [18]. Because the diffusion coefficient, gas solubility, and viscosity of liquid change with decreasing temperature [19], the rate of mass transfer between gas and liquid during cooling process may be different from the bubble behavior in isothermal process. As the solidified layer evolves, the cooling rate of the liquid near the interface between the solid phase and the liquid phase decreases with the increase of the thickness of the solidified layer. Meanwhile, the cooling rate of the solid phase near the mold wall decreases with time when the heat transfer process reaches the quasi-steady state. The transient heat transfer process and the moving interface lead to the formation of a solid slag film in which pores are unevenly distributed. Therefore, it is necessary to study the effect of temperature evolution on bubble behavior in molten slag by using the heat and mass transfer coupled equations with accurate boundary conditions and thermodynamic data of chemical reactions under high temperatures.

Besides the methods used in simulations, experimental apparatus and techniques related to gas-liquid reactor are also developed to obtain the key values of parameters in calculating mass transfer rate. The high speed camera and the microscopic visualization technique have been widely used to observe the formation mechanism and kinetics of bubbles in different liquids, such as ionic

liquid [20], molten slag [7], and boiling water [21]. However, it is difficult for the video techniques to record the behavior of bubble inside the vessel. In order to solve this problem, electrical resistance tomography (ERT) has been utilized to investigate the hydro-dynamics and flow patterns of bubble columns [22]. Another important reactor is gas-liquid-solid fluidized system [17]. For these three-phase processes, the direct visualization with image analysis has been developed to study dynamics of bubble in gas-liquid-solid fluidized system under high temperature and high pressure. [23]. Among these techniques, the temperature of system is kept a constant, which indicates that the bubble behavior in nonisothermal process may be difficult to be observed. However, if the visualization technique could be combined with a temperature controlling system, the in situ observations of bubble behavior during fast cooling process would be achieved. Recently, the hot thermocouple technique is used to study the crystallization behavior of molten slag [25]. As a temperature-measuring device, the thermocouple could also be used to heat slag sample, and the simultaneous measurement of temperature during heating or cooling process could be conducted [26].

From above analysis, experimental methods are conducive to in situ observation and determination of boundary conditions. Numerical simulations are important for quantification of bubble size and bubble movement. The aim of this study is to investigate the characteristics of single bubble in molten slag by numerical simulations and experimental methods, especially for the bubble behavior during nonisothermal process. In this work, the single hot thermocouple technique was used to study the effect of cooling rate and composition of slags on the behavior of single bubble during cooling process. Solidification for molten slag was conducted in laboratory by using a water-cooled detector, and the solid slag film obtained from the detector was used to analyze the bubble size distribution in the solidified layer. Meanwhile, the values of heat fluxes measured in experiments were used as the

boundary condition of heat transfer. Furthermore, based on the finite element analysis, the mathematical model coupled for both heat and mass transfer was proposed to describe the bubble size distribution in slag film, and the calculated results were compared with the statistical results observed under the scanning electron microscope (SEM).

2. Experimental

The target compositions of slags used in experiment are listed in **Table 1**. The mass fractions of raw materials in each slag are listed in **Table 2**. The five slags used in experiment were synthesized by CaO, SiO₂, Al₂O₃, Na₂SO₄, Na₂CO₃, Na₂SiO₃, CaF₂ and Li₂CO₃. Pure chemical reagent was used as raw material of each component. The purity of each reagent exceeds 99%. In order to study the effect of carbonate and sulphate on bubble behavior in molten slag, the contents of Na₂CO₃ and Na₂SO₄ in the five slags are different. Slag 1 contains no Na₂SO₄, and the Na₂O is prepared by adding Na₂CO₃ and Na₂SiO₃. For slag 2, slag 3, and slag 4, the content of Na₂CO₃ in the three slags is the same, but the contents of Na₂SO₄ are different. Slag 5 contains no Na₂CO₃, and the content of Na₂SO₄ is 4.5 %. The Heat Flux Simulator developed by Wen et al. was used to measure heat fluxes through the solidified layer [27], and the schematic of the apparatus is shown in **Fig. 1**. The appearance of the solid slag film attached on the water-cooled detector is shown in **Fig. 2**.

At the beginning of the experiment, an empty crucible was heated in the MoSi₂ furnace with a heating rate of 6 K per minute. After the temperature of the furnace reaches 1673 K, 350 gram of powder were added into the graphite crucible. Despite the low heating rate of the furnace, the melting process of the slag will take no more than 10 minutes due to the high electric powder and the high temperature of the furnace. When the temperature increases to about 1200 K, gases generated from the decomposition of Na₂CO₃ begins to dissolve due to the formation of liquid slag. In the initial stage of

melting, due to the high viscosity of liquid slag, the floating speed of bubble is very slow, which indicates that bubbles with small size could remain in the molten slag. The temperature of molten slag will be maintained at 1673 K for 10 minutes so that a homogeneous pool could form. Before the beginning of the solidification test, a locating rod will move downward automatically until the fluid level of the molten slag is detected. When the position of fluid level was determined, a water-cooled detector was immersed into the molten slag. The initial temperature of cooling water is kept at 308 K $\pm$ 0.5 K. The flow of cooling water is maintained at 0.056 kg $\cdot$ s⁻¹. When the top surface of detector and the fluid level of molten slag are on the same plane, the temperatures of cooling water at inlet and outlet are recorded by the computer. As the solidification process evolves, the heat of molten slag is taken away by flowing cooling water, meanwhile, the thickness of the solid slag film increases with time. After 45 s, the water-cooled detector moves upward automatically, and the solid slag film around the detector could be obtained. The longitudinal section of solid slag film is observed under scanning electron microscope, as shown in **Fig. 3**. In addition, for the solid slag films prepared in experiment, the X-ray diffraction (XRD) was used for the phase identification. The XRD patterns of the five slag films are shown in **Fig. 4**. From **Fig. 4**, no obvious diffraction peak is observed, which indicates that the five solid slag films are glassy. According to the temperature difference of cooling water, the total heat flux through the solid slag film during solidification could be calculated by **Eq. (5)**.

$$q = \frac{W \cdot C \cdot \Delta T}{F} \quad (5)$$

In **Eq. (5)**, q is the total heat flux that is equal to the sum of conductive heat flux and radiative heat flux, W $\cdot$ m⁻². W is flow of cooling water, kg $\cdot$ s⁻¹; C is the heat capacity of cooling water, J $\cdot$ (kg $\cdot$ K)⁻¹; ΔT is temperature difference of cooling water, K. F is the effective heat transfer area on the detector, m².

The hot thermocouple technique was applied to study the bubble behavior in molten slag during

cooling process. There are two modes in operation of the hot thermocouple technique. The first is single hot thermocouple technique (SHTT), and the second is double hot thermocouple technique (DHTT). For the single hot thermocouple, the temperature of molten slag is controlled by a single thermocouple. For the double thermocouple technique, the temperatures of the two thermocouples are always set to different values so that a desired temperature gradient could form in the molten slag. In this work, the single hot thermocouple technique was applied for the in situ observations of bubbles under high temperature. The schematic of experimental apparatus used in SHTT tests is shown in **Fig. 5**. After setting the temperature profile, slag sample mixed with raw materials is heated on the tip of the thermocouple. Meanwhile, the temperature measured by thermocouple is shown on the screen of computer. The bubble behavior in molten slag is recorded by a CCD microscope, as shown in **Fig. 5**. The errors of temperature control can be corrected by measuring the melting point of CaF_2 .

3. Mathematical models

A mathematical model based on one dimensional transient heat transfer coupled of conduction and radiation is established to describe the variation of temperature during solidification of molten slag.

The energy equation can be written as

$$\frac{\partial(\rho \cdot Cp \cdot T)}{\partial t} = -\frac{\partial}{\partial x} \left(-l \frac{\partial T}{\partial x} \right) - \nabla q_{rad} \quad (6)$$

where ρ is the density of molten slag, $\text{kg} \cdot \text{m}^{-3}$; Cp is the heat capacity, $\text{J} \cdot (\text{kg} \cdot \text{K})^{-1}$; T is temperature, K; t is time, s; x is the distance from the detector, m; l is the thermal conductivity, $\text{W} \cdot (\text{m} \cdot \text{K})^{-1}$; q_{rad} is the radiative heat flux, $\text{W} \cdot \text{m}^{-2}$. The molten slag in the crucible can be divided into many control volumes. For the v th control volume, the energy equation can be expressed by explicit difference scheme, as shown in **Eq. (7)**.

$$\rho C_p \frac{T_p^{m+1} - T_p^m}{\Delta t} = l \cdot \frac{T_{p+1}^m - 2T_p^m + T_{p-1}^m}{\Delta u^2} + \Phi_{rad,v}^m \quad (7)$$

In **Eq. (7)**, T_p^m is the temperature of p th surface when time is m , K; Δt is time step, s; Δu is the thickness of a control volume; $\Phi_{rad,v}^m$ is the radiative source term of v th control volume when time is m , $J \cdot (m^3 \cdot s)^{-1}$. The value of the radiative source term can be calculated according to the ray tracing method [28]. For the one dimensional transient heat conduction model, the stability condition is that the value of the Fourier number is no more than 0.5, as shown in **Eq. [8]**.

$$\frac{k_{eff} \cdot \Delta t}{\rho \cdot C_p \cdot \Delta x^2} \leq 0.5 \quad (8)$$

In **Eq. [8]**, ρ is $2500 \text{ kg} \cdot \text{m}^{-3}$, and the value of C_p is higher than $1000 \text{ J} \cdot (\text{kg} \cdot \text{K})^{-1}$. According to the stability condition shown in **Eq. [8]**, the value of Δt is chosen as 0.02 s, and the value of Δx is chosen as 0.2 mm. It is noted that the position of the interface between liquid and solid phase changes with the increase of the slag film thickness. The thickness of solidified layer is determined by

$$d = k' t^m \quad (9)$$

where d is thickness of solid slag film, m; k' and m are constants [29]. The thickness of the solid slag film at 45 s can be measured by the vernier caliper. Therefore, **Eq. (9)** is written as

$$d^m = d_f \left(\frac{t}{45} \right)^{k'} \quad (10)$$

where d^m is the thickness of the solid slag film when t is m , m; d_f is the thickness of solid slag film at 45 s. The enumeration method is used to determine the value of k' by using **Eq. (10)**.

$$T_{in}^{45} = T_f \quad (11)$$

where T_{in}^{45} is the temperature of interface at 45 s, K; T_f is the fluid temperature of molten slag that can be measured by a high temperature microscope, K. During computation, the value of k' will not be determined until the **Eq. (11)** is satisfied. The initial condition of the calculation is that the temperature

of molten slag is 1673 K. Two boundary conditions are necessary for the calculation. Firstly, the thickness of the air gap between the solidified layer and the detector is very small (lower than 50 μm). In addition, the heat capacity of the detector is much lower than that of water. Therefore, it is assumed that the energy through the solid slag film could be taken away by the cooling water, and the total heat flux through the solid slag film can be written as:

$$q = l \frac{T_1^m - T_0^m}{\Delta u} + \varepsilon_{cu} q_{rad,0}^m \quad (12)$$

where ε_{cu} is emissivity of the water-cooled detector; $q_{rad,0}^m$ represents the radiative heat flux through the solid slag film. Secondly, the bulk temperature of the liquid is considered as the initial temperature of the molten slag, as shown in **Eq. (13)**.

$$T_{x=0.01}^m = 1673 \quad (13)$$

The distribution of temperature in molten slag can be obtained by using **Eqs. (5)-(13)**, and the calculated results can be used to study the bubble behavior in molten slag during solidification. According to the mass transfer equation proposed by Nmec and Klouek [12], the diffusion mass transfer of i th gas through the bubble surface is given by

$$J_i = \frac{1}{A} \frac{dn_{b,i}}{dt} = \frac{0.381(C_{g,i} - C_{f,i})D_i^{\frac{2}{3}}g^{\frac{1}{3}}\rho^{\frac{1}{3}}}{\eta^{\frac{1}{3}}} \quad (14)$$

where J_i is the mass flow of the i th gas through the bubble surface, $\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$; A is the surface area of the bubble, m^2 ; $n_{b,i}$ is the amount of the i th gas in the bubble, mol ; D_i is the diffusion coefficient of the i th gas, $\text{m}^2 \cdot \text{s}^{-1}$; g is the gravity, $\text{m} \cdot \text{s}^{-2}$; η is the viscosity of molten slag, $\text{Pa} \cdot \text{s}$; $C_{g,i}$ is the concentration of the i th gas in molten slag, $\text{mol} \cdot \text{m}^{-3}$; $C_{f,i}$ is the concentration of i th gas on the bubble surface, and the value of $C_{f,i}$ can be obtained according to the Henry's law, as shown in **Eq. (15)**.

$$C_{f,i} = L_i \cdot p_i \quad (15)$$

where L_i is the physical solubility of the i th gas in molten slag, $\text{mol} \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}$; p_i is the partial pressure of the i th gas in the bubble, Pa; Considering the decomposition of sulphate under high temperature, the equilibrium constant of **Eq. (3)** is written as:

$$K_{\text{SO}_4^{2-}} = \frac{C_{\text{SO}_2,s} C_{\text{O}_2,s}^{\frac{1}{2}}}{C_{\text{SO}_4^{2-},s}} \quad (16)$$

where $K_{\text{SO}_4^{2-}}$ is the equilibrium constant of **Eq. (3)**, $\text{mol}^{1/2} \cdot \text{m}^{-3/2}$; $C_{\text{SO}_2,s}$ and $C_{\text{O}_2,s}$ are the concentrations of SO_2 and O_2 when the reaction is in equilibrium, $\text{mol} \cdot \text{m}^{-3}$; $C_{\text{SO}_4^{2-},s}$ is the concentration of sulphate in molten slag, $\text{mol} \cdot \text{m}^{-3}$. The mass flow of SO_2 or O_2 through the bubble surface can be written as:

$$J_i = \frac{1}{A} \frac{dn_{b,i}}{dt} = \frac{0.381(C_{g,i} - C_{f,i}) D_i^{\frac{2}{3}} g^{\frac{1}{3}} \rho^{\frac{1}{3}}}{\eta^{\frac{1}{3}}} - \frac{k_r}{M_i} \left(p_{\text{SO}_2} p_{\text{O}_2}^{\frac{1}{2}} - p_{\text{SO}_2,s} p_{\text{O}_2,s}^{\frac{1}{2}} \right) \quad (17)$$

where k_r is the rate constant of reaction, $\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-3/2}$; p_{SO_2} and p_{O_2} are partial pressures of SO_2 and O_2 in bubble, Pa; $p_{\text{SO}_2,s}$ and $p_{\text{O}_2,s}$ are partial pressures of SO_2 and O_2 when reaction is in equilibrium, Pa;

The value of M_i is determined by

$$M_i = \begin{cases} M_{\text{SO}_3} & i = \text{Na}_2\text{SO}_4 \\ M_{\text{SO}_3} & i = \text{SO}_2 \\ 2M_{\text{SO}_3} & i = \text{O}_2 \end{cases} \quad (18)$$

where M_{SO_3} is the molar mass of SO_3 , $\text{kg} \cdot \text{mol}^{-1}$; According to **Eqs. (15)-(17)**, the mass flow of SO_2 or O_2 through the bubble surface can be written as:

$$J_i = \frac{1}{A} \frac{dn_{b,i}}{dt} = \frac{0.381(C_{g,i} - C_{f,i}) D_i^{\frac{2}{3}} g^{\frac{1}{3}} \rho^{\frac{1}{3}}}{\eta^{\frac{1}{3}}} - \frac{k_r}{M_i} \left(p_{\text{SO}_2} p_{\text{O}_2}^{\frac{1}{2}} - \frac{K_{\text{SO}_4^{2-}} C_{\text{SO}_4^{2-},s}}{L_{\text{SO}_2} L_{\text{O}_2}^{\frac{1}{2}}} \right) \quad (19)$$

The conservation of mass during mass transfer is described as:

$$-N \frac{dn_{b,i}}{dt} = V_g \frac{dC_{g,i}}{dt} \quad (20)$$

where N is the number of bubbles in molten slag; V_g is the volume of molten slag, m^3 ; The state equation of idea gas is used to describe the relationship between the partial pressure and the temperature in bubble:

$$p_i V_b = n_{b,i} R T_b \quad (21)$$

where V_b is the volume of the bubble, m^3 ; R is the idea gas constant, $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$; T_b is the temperature of the bubble, K; The total pressure inside of the bubble is written as:

$$p = \sum p_i = p_0 + \rho g H + \frac{2\sigma}{r} \quad (22)$$

where p_0 is atmospheric pressure, Pa; H is the height between bubble and fluid level, m; σ is the surface tension of the bubble, $\text{N} \cdot \text{m}^{-1}$; r is the radius of the bubble, m; The bubble rising velocity is determined by Stokes' equation:

$$-\frac{dH}{dt} = \frac{2g\rho r^2}{9\eta} \quad (23)$$

The size of the water-cooled detector and the meshes used for calculation are shown in **Fig. 6**.

As shown in **Fig. 6**, the molten slag in crucible can be divided into 5131 elements, and the dense mesh around the detector is designed to match the high temperature gradient during solidification. In order to describe the state of bubble in molten slag, the value of St is defined as:

$$St = \begin{cases} 0 & H \leq 0 \\ 1 & r \leq 0.1 \mu\text{m} \\ 2 & H > 0, r > 0.1 \mu\text{m}, d_p < d^m \end{cases} \quad (24)$$

The value of St is determined according to the size and position of bubbles. Different values of St represent different state of bubble during solidification. The value of 0 represents that the bubble moves to environment. The value of 1 represents that the bubble is absorbed by the molten slag. The value of 2 represents that the bubble is captured by the solidified layer. In **Eq. (24)**, d_p represents distance between the bubble and outside surfaces of copper detector, and the value of d_p is obtained

from Eqs. (25)-(26).

$$a = \begin{cases} j \% 50 & 1 \leq j \leq 1000 \\ (j - 1001) \% 51 & 1000 < j \leq 5131 \end{cases} \quad (25)$$

$$d_p = \begin{cases} ((j - 1001) / 51 + 1) \times 0.0002 & a = 0 \\ a \times 0.0002 & 0 < a < 20 \end{cases} \quad (26)$$

In Eq. (25), j represents the number of mesh; The symbol “%” is to obtain the remainder, and the symbol “/” is to obtain the quotient. The distribution of bubble size in solid slag film could be analyzed according to the state of bubbles in each mesh, as shown in Eqs. (27)-(29).

$$p_i = \begin{cases} 1 & St = 2, r = rd \\ 0 & St = 2, r \neq rd \end{cases} \quad (27)$$

$$q_j = \begin{cases} 1 & St = 2 \\ 0 & St \neq 2 \end{cases} \quad (28)$$

$$\Theta(r = rd) = \frac{\sum_{i=1}^{5131} p_i}{\sum_{j=1}^{5131} q_j} \quad (29)$$

where Θ is the proportion of bubbles with different sizes.

There are five basic assumptions in the numerical simulations:

- 1) The shape of bubble is spherical, and the temperature inside of the bubble is equal to the temperature of the molten slag;
- 2) The gases in the bubble can be considered as idea gas;
- 3) The density and surface tension of the bubble are regarded as temperature-independent physical properties;
- 4) Bubbles distribute evenly in molten slag at the initial moment;
- 5) Due to the high viscosity of molten slag during cooling process, bubbles can only move upward, and the merge of bubble is not taken into consideration.

The flow chart of calculations is shown in **Fig. 7**, and the data used in calculations are listed in **Table 3** and **Table 4** [19,30,31]. The initial concentrations of SO₂, CO₂, O₂ and N₂ in molten slag are 0.60 mol·m⁻³, 0.68 mol·m⁻³, 0.05 mol·m⁻³, 0.16 mol·m⁻³ respectively.

4. Results

4.1. Results of temperature distribution in molten slag

The heat fluxes measured during solidification are shown in **Fig. 8**. It can be found from **Fig. 8** that the heat flux first increases, and then decreases with time. The value of the heat flux reaches the maximum at about 6 s. After 30 s, the heat flux changes slightly with time, which indicates that the heat transfer process comes into the steady state. In the initial stage of solidification, the radiative energy emitted from the inner surface of crucible is absorbed by the water-cooled detector, which may lead to a temperature drop in molten slag. The formation of the temperature gradient results in the conductive heat transfer from molten slag to the water-cooled detector. Due to the couple effect of conduction and radiation, it is observed that the total heat flux increases sharply with time before 6 s. When the temperature decreases below the solidification temperature of molten slag, the solid slag film begins to form, and part of radiative energy is reflected by the solidified layer. Meanwhile, the heat resistance of conductive heat transfer increases with time due to the growth of air gap between the solidified layer and the detector, leading to the decrease of total heat flux after 6 s. In the later stage of solidification, the interface between the two phases moves slowly with time, and the heat transfer process enters the quasi-steady state. For the five slags with similar compositions, the differences in the total heat fluxes could be analyzed from the radiative heat transfer. On the one hand, the addition of sulphate has an effect on the optical properties of the solid slag film, which indicates that the radiative heat flux through solid slag films containing sulphate may be different from that through slag

films containing no sulphate. On the other hand, the distribution of pores in the solid slag film could also influence the reflectivity and the transmissivity of slag film. The results of the reflectivity and the transmissivity measured under room temperature are shown in **Fig. 9**.

It can be seen from **Fig. 9** that for slags with carbonate and sulphate, the apparent reflectivity increases with increasing wavelength. For slag 1 with no sulphate, the apparent reflectivity changes slightly with wavelength, and the values are between 0.2 and 0.4. For slag 5 with 4.5 % Na_2SO_4 , the apparent transmissivity is close to 0, which indicates that the radiative heat flux through the solid slag film is very small. The temperature distributions at different moments for the five slags are shown in **Fig. 10**.

Obvious difference in temperature distribution is not observed for the five slags, as shown in **Fig. 10**. The temperature of molten slag increases with the increase of distance from the detector. When the distance is higher than 4 mm, the temperature of the molten slag is around 1673 K. It is found from **Fig. 10** that the maximum of cooling rate exceeds 50 K/s before 10 s. With the evolution of the solid slag film and the air gap, the cooling rate of solid slag film on the detector side decreases due to the increase of thermal resistance. Meanwhile, the cooling rate of the slag film on the detector side is higher than that on the interface between the solid phase and the liquid phase. The changes of temperature during solidification may influence the bubble behavior in molten slag, which may lead to an uneven distribution of pores in the solid slag film.

Both the conduction and the radiation could influence the temperature distribution of mold slag during solidification. The radiative energy emitted from the inner surface of crucible could be absorbed by the liquid, which indicates that the value of Φ_{rad} is positive. Because the source term of radiation is positive, the input energy due to conduction is lower than the output energy so that a

continuous cooling process in molten slag could be realized. This suggests that the temperature gradient near copper detector is higher than the temperature gradient on the interface, as shown in **Fig. 10(a)-(d)**.

4.2. Single bubble behavior

4.2.1. Single bubble behavior in isothermal process

Case 1: Bubble contains only CO₂

When bubble contains only CO₂, the concentrations of CO₂ in the liquid and on the bubble surface are shown in **Fig. 11**. The variation of bubble size during isothermal process is shown in **Fig. 12**. Initially, due to the high solubility of CO₂ in molten slag, the concentration of CO₂ on the bubble surface is higher than that in liquid, which indicates that the mass flow is from bubble to liquid. The shrinkage of bubble leads to the increase of the additional pressure on the bubble surface. According to the Henry's law, the concentration of gas on the bubble surface increases with the increase of the partial pressure for a given temperature. Therefore, when the temperature remains constant, it is observed that the concentration of CO₂ on the bubble surface increases with time, as shown in **Fig. 11**. In the whole process, the concentration of CO₂ in the liquid is lower than that on the bubble surface, which suggests that the bubble could be absorbed by molten slag.

Case 2: Bubble contains CO₂ and N₂

When bubble contains both CO₂ and N₂, the variation of concentration for the two gases during isothermal process is shown in **Fig. 13**.

From **Fig. 13**, the concentration of N₂ in liquid remains almost constant in mass transfer process. This is because the solubility and diffusion coefficient of N₂ are much lower than that of other gases.

However, the N_2 in the bubble could influence the partial pressure of CO_2 despite its low mass transfer rate on bubble surface. The calculated results show that the concentration of CO_2 on the bubble surface decreases with time, which indicates that the direction of mass transfer is from the bubble to the liquid. After 70 s, the concentration of CO_2 on the bubble surface is lower than the concentration of CO_2 in liquid, which leads to the growth of bubble after 70 s, as shown in **Fig. 12**. Compared with case 1, it is found that the retention time of bubble in liquid is much longer, which may be caused by the different dissolution rates between the two kinds of gases.

Case 3: Bubble contains SO_2 , O_2 and N_2

When bubble contains SO_2 , O_2 , and N_2 , the variation of the concentrations of SO_2 on the bubble surface and in the liquid are shown in **Fig. 14(a)**. The variation of partial pressures for the three gases is shown in **Fig. 14(b)**. For molten slag with sulphate, the direction of mass flow could not be determined according to the difference of C_g and C_f because the SO_2 and O_2 generated from the decomposition of sulphate could also transfer into the bubble. Therefore, the direction of mass transfer depends on the concentration of SO_2 in liquid (C_g), the concentration of SO_2 on the bubble surface (C_f) and the decomposition of sulphate. From **Fig. 14(a)**, the concentration of SO_2 on the bubble surface increases due to the increase of the partial pressure. Although the concentration of SO_2 in liquid is lower than that on the bubble surface, the decomposition of sulphate could enhance the driving force of mass transfer from liquid to bubble. Due to the amount of SO_2 generated from the chemical reaction ($n_{r,SO_2}/k_{SO_2}$), the concentration of SO_2 in the boundary layer is much higher than that on the bubble surface, which leads to the growth of the bubble after 10 s, as shown in **Fig 12**.

Case 4: Bubble contains SO_2 , O_2 , CO_2 and N_2 .

When bubble contains SO_2 , O_2 , CO_2 and N_2 , the concentration of SO_2 on the bubble surface and in

liquid as a function of time is shown in **Fig. 15(a)**. The partial pressures of the four gases are shown in **Fig. 15(b)**. From **Fig. 15(a)**, the variations of C_g , C_f and $n_{r,SO_2}/k_{SO_2}$ are similar to the changes described in case 3. However, it is seen from **Fig. 15(b)** that the CO_2 in bubble decreases the partial pressure of SO_2 , which results in the lower concentration of SO_2 on the bubble surface. Therefore, compared with the bubble containing no CO_2 (case 3), the concentration gradient of SO_2 in the boundary layer is much higher, which may be the reason why the growth rate of the bubble containing CO_2 is higher than that of the bubble containing no CO_2 , as shown in **Fig. 12**.

4.2.2. Single bubble behavior during nonisothermal process

During nonisothermal process, the cooling rate may influence the bubble behavior since the solubilities of gases are different under different temperatures. For different gas compositions, the variations of bubble size under different cooling rates are shown in **Fig. 16**.

It is seen from **Fig. 16** that the radius of bubble decreases with time during cooling process. Compared with SO_2 and N_2 , the influence of temperature on the solubility of CO_2 is more obvious. Therefore, when the major composition of bubble is CO_2 , the cooling rate has apparent effect on the bubble size. The calculated results show that the radius of bubble under a given temperature increases with the increase of cooling rate, which indicates that high cooling rate may result in a low rate of shrinkage. In addition, when cooling rate is higher than 5 K/s, the rate of shrinkage for bubble with high concentration of SO_2 is lower than that for bubble with high concentration of CO_2 .

4.2.3. Results of SHTT tests

In order to verify the calculated results, the hot thermocouple technique was used to observe the bubble behavior under different temperature regimes. For slag 1 containing no Na_2SO_4 , the bubble

behavior during isothermal process is shown in **Fig. 17**.

From **Fig. 17**, initially, a small amount of powder is not melted completely, and bubbles are observed around the single thermocouple. It is observed that the bubble size decreases continuously until the bubble is absorbed by the molten slag at 25 s. This process is similar to the calculated results described in case 1. For slag 1 with no sulphate, the source of bubble may come from the chemical reaction between Na_2CO_3 and SiO_2 . Because the reaction occurs below 1000 K, the bubble containing CO_2 could exist before the slag is melted completely. Both the results of calculation and in situ observation indicate that this kind of bubble is likely to shrink during isothermal process due to the high solubility of CO_2 in molten slag. For slag 5 containing 4.5 % Na_2SO_4 , the bubble behavior during isothermal process is shown in **Fig. 18**.

It can be seen from **Fig. 18** that fine bubbles distributed in mushy slag are merged into large bubbles before 10 s. During isothermal process, the size of bubble increases gradually after coalescence, which is consistent with the calculated results in case 3. After 30 s, the bubble with large size is likely to move towards the edge of the liquid phase, as shown in **Fig. 18(i)**. This phenomenon suggests that the dissolution of gases in molten slag with Na_2SO_4 is more difficult than that in slag with no Na_2SO_4 . Therefore, the gas compositions in the bubble have an effect on bubble behavior. The decomposition of a sulphate layer under high temperature could improve the growth of bubble, which may also increase the floating speed during mass transfer process.

For slag 1, the SHTT tests were conducted to observe the bubble behavior in molten slag during cooling process. During tests, the temperature was decreased from 1523 K to 1373 K. The bubble behavior during nonisothermal process when cooling rate is 5 K/s is shown in **Fig. 19**. **Fig. 20** shows the bubble behavior when cooling rate is 10 K/s.

When cooling rate is 5 K/s, bubbles with different size are observed around the thermocouple at the beginning of cooling process. With the decrease of temperature, the size of bubble decreases gradually, and the bubble with large size contracts rapidly during cooling process. When the temperature decreases below 1473 K, the bubble size decreases slowly with time, as shown in **Fig. 19**. The shrinkage of bubble is also observed when cooling rate is 10 K/s. However, the shrinkage rate is much lower than that in the cooling process with a rate of 5 K/s, especially when temperature is lower than 1473 K. From the results of in situ observations, it is obtained that the bubble behavior in cooling process is different from the behavior in isothermal process, and the main difference is attributed by the effect of the cooling rate on the bubble size under different thermal history.

From the results of SHTT tests, both the compositions of slag and the cooling rate could affect bubble behavior in molten slag. When slag contains no Na_2SO_4 , bubble in molten slag is likely to shrink in molten slag, whether for the isothermal process or for the nonisothermal process. It is observed that the rate of shrinkage decreases with the increase of cooling rate, which is consistent with the calculated results for bubbles with high concentration of CO_2 . When slag contains Na_2SO_4 , the decomposition of sulphate layer under high temperature could enhance the driving force of mass flow from liquid to bubble, which may lead to the growth of bubble during isothermal process. Compared with slags with no Na_2SO_4 , the addition of sulphate is beneficial for the refining process because bubbles with high concentration of SO_2 have more opportunity to grow up in molten slag.

5. Discussion

5.1. Distribution of pore size in solid slag film

From above analysis, when the initial composition of bubble is given, the behavior of single bubble is mainly influenced by the partial pressure of gases and the cooling rate. During solidification of molten slag, the cooling rate of liquid changes with time and position, which may lead to an uneven distribution of pore size in the solid slag film. Furthermore, due to the difference of solubility among gases, the addition of sulphate or carbonate could also influence the distribution of pores in the solid slag film. Combined with heat and mass transfer equations, the distribution of pore size in solid slag film can be calculated according to the finite elements analysis. For different initial bubble compositions, the distributions of pore size on x-z direction and x-y direction are shown in **Figs. 21-23**. The initial compositions of bubbles are the same as the four cases described in 4.1.

When the main composition in bubble is SO_2 , calculated results indicate that the average radius of pores is larger than that of pores with high concentration of CO_2 . For bubbles containing 80% SO_2 , 10% O_2 and 10% N_2 , the distribution of bubble size is uniform on the liquid side, which is similar to the distribution of bubbles with high content of CO_2 . However, an uneven distribution of pore size on the detector side is observed. With the increase of distance from detector, the radius of pore first increases, and then decreases. Pores with large size concentrate on the medium layer of the solid slag film, as shown in **Fig. 22**. This kind of uneven distribution could be analyzed from the cooling rate and the temperature-time history of single bubble during floating. According to the Stokes formula, the rising velocity depends on the viscosity of liquid when the size and gas composition are given. During solidification, the rising velocity will decrease until the bubble is captured by the solid slag film. Because the cooling rate of liquid on the detector side is higher than that on the liquid side, the

isothermal process for a bubble on the liquid side is longer than that for a bubble on the detector side. It could be concluded from the results of the single bubble behavior that the bubble with high concentration of SO_2 is more likely to grow up during isothermal process. As a result, although the bubble may shrink rapidly during the next cooling process, the bubble on the liquid side may have a large size after growth. Therefore, the sizes of pores on the detector side are dominated by the cooling rate of liquid phase during floating process. However, for bubbles on the middle layer, the long isothermal process may lead to the appearance of large pores in the solid slag film.

When bubbles contain SO_2 , CO_2 , O_2 and N_2 , the distributions of pore size on x-y surface and x-z surface are similar to the distribution of pores containing SO_2 , O_2 and N_2 . However, it is found from **Fig. 23** that the pore size for slag containing Na_2CO_3 is higher than that of bubble containing no Na_2CO_3 . This is because the formation of CO_2 may increase the growth rate of bubble during isothermal process, according to the calculated results of the single bubble behavior.

In order to verify the calculated results of the pore size distribution, the longitudinal section of the solid slag film is observed under the SEM, and the images of the five slags are shown in **Fig. 24**. The statistical results of the pore size distribution are listed in **Table 5**.

For slag 1 with 10.9 % Na_2CO_3 , it is observed from **Fig. 24(a)** that dense pores are distributed on the longitudinal section of the solid slag film, and the number of pores per unit area reaches 14.45. With the increase of Na_2SO_4 , the number of pores observed under SEM decreases. When the content of Na_2SO_4 is increased to 4.5 %, the number of pores per unit area is only 0.38. Besides the number density of pores, the distribution of pores in the solid slag film is also different among slags with different compositions. It is found from **Fig. 24(a)** that pores with small size concentrate on the liquid side, while dispersed pores with large size are distributed on the detector side. This kind of distribution

is not observed in the four slags with a certain amount of Na_2SO_4 . For slag with 0.5 % Na_2SO_4 , it is observed that pores with small size are likely to distribute on the detector side with high cooling rate, and pores with larger size appear in the middle layer of solid slag film, as shown in **Fig. 24(b)**. With the increase of Na_2SO_4 , the number of pores on the liquid side decreases. When the content of Na_2SO_4 reaches 4.5 %, the percentage of pores with diameter higher than 150 μm reaches 85%. However, the Sauter diameter of pores in solid slag film with no Na_2CO_3 is obviously lower than that of the three slags with 10.9% Na_2CO_3 . From the observed results, it could be summarized that the effect of Na_2SO_4 or Na_2CO_3 on the bubble behavior in molten slag is mainly reflected on the positions where large pores appear. The distribution of pores observed under SEM is in agreement with the calculated results shown in **Figs. 21-23**, which suggests that the mathematical model in this work could describe the feature of pore size distribution on different positions. However, the estimation of pore size by this model is not very precise, and the calculated pore size is larger than the result observed under SEM. This may be caused by the inaccurate initial gas concentrations used in calculation. Therefore, it is necessary to investigate the effect of initial gas concentration on bubble size distribution in the solidified layer.

5.2. Effect of gas concentration on pore size

The calculated results of pore size distribution under different concentrations of CO_2 (C_{g,CO_2}) and SO_2 (C_{g,SO_2}) are shown in **Fig. 25(a)** and **Fig. 25(b)** respectively. According to the statistical results, the effect of Na_2SO_4 on the proportion of pores with different sizes is shown in **Fig. 26**.

When the concentration of SO_2 in the liquid is given, it could be obtained from **Fig. 25(a)** that the proportion of pores with large size increases with the increase of C_{g,CO_2} . When the value of C_{g,CO_2} is

0.25 mol·m⁻³, the percentage of pores with radius less than 60 μm reaches 44 %, and pores with radius higher than 80 μm are not observed. When the value of C_{g,CO_2} reaches 1.00 mol·m⁻³, there are 10 percentage of pores with radius higher than 100 μm, and this kind of pores with large size is not observed in the three cases with lower initial gas concentration. The effect of C_{g,SO_2} on pore size distribution is similar to that of C_{g,CO_2} . It is found from **Fig. 25(b)** that the percentage of pores whose radius is between 70 μm and 100 μm increases with the increase of C_{g,SO_2} .

According to the statistical results shown in **Fig. 26**, when the content of Na₂SO₄ is higher than 0.5 %, the proportion of pores with radius higher than 75 μm increases with the increase of Na₂SO₄, while the proportion of pores with radius lower than 50 μm decreases with increase of Na₂SO₄. These results are in agreement with the effect of C_{g,SO_2} on pore size distribution shown in **Fig. 25(b)**. In addition, from the SEM images of slag 4 and slag 5, obvious differences in distribution of pore size could be found despite the same content of Na₂SO₄. For slag 5 with no Na₂CO₃, the percentage of pores with radius less than 100 μm reaches 63 %. However, pores with the same size are not observed in the slag 4 containing Na₂CO₃, which indicates that low concentration of CO₂ and high content of Na₂SO₄ may improve the formation of bubbles with small size.

Combined with the results of observations, it could be concluded that accurate initial gas concentrations in liquid is necessary for the mathematical model to describe the characteristics of bubble size distributions on different positions. On the one hand, the bubble behavior influenced by the temperature-time history dominates the variation of bubble size during mass transfer process. On the other hand, the porous structure of the solid slag film also depends on the compositions of slag since the gas concentration of CO₂ or SO₂ has an obvious effect on the proportion of pores with different sizes in the solidified layer.

6. Conclusions

In this work, in situ observations, statistical analysis and numerical simulations are carried out to investigate the bubble behavior in molten slag based CaO-SiO_2 during isothermal and nonisothermal processes. Also, the characteristics of bubble size distributions on different positions are analyzed based on studies of single bubble behavior. From the calculated results and experimental results, there are three main factors that could affect the bubble behavior in molten slag, including gas composition in bubble, initial concentration of gases in liquid and the time-temperature history of the liquid phase. Due to the variation of partial pressure and the difference of solubility among gases during solidification, an uneven distribution of pore size is observed in the the solidified layer, and this kind of porous structure may influence the conductivity and optical properties of slag after solidification. The conclusions obtained from this work are summarized as follows:

- 1) Combined with the transient heat transfer equation, the mass transfer model based on the infinite element analysis could describe the effect of temperature variation on the bubble size distribution and the porous structure in the solidified layer. However, the accurate values of gas concentrations in the liquid are also very important for estimation of the proportion of bubbles with different sizes.
- 2) The single bubble behavior during isothermal process mainly depends on the bubble compositions, while the single bubble behavior during cooling process is influenced by the cooling rate. When the main composition of bubble is SO_2 , the decomposition of sulphate under high temperature will improve the growth of bubble in isothermal process. When the main composition is CO_2 , the shrinkage of bubble is observed during isothermal process due to the high solubility of CO_2 in molten slag. During cooling process, bubbles with high content of CO_2 are more likely to contract, and the shrinkage velocity increases with the decrease of cooling rate.

3) The variation of cooling rate during solidification may lead to the uneven distribution of pore size in molten slag. For slag with no Na_2SO_4 , pores with large size concentrate on the detector side with high cooling rate, while pores with small size are likely to appear on the liquid side with low cooling rate. For slags with an amount of Na_2SO_4 , pores with large size mainly distribute on the medium layer of the solid slag film, and the number of pores per unit area decreases with the increase of Na_2SO_4 .

4) According to the statistical results, the distribution of pore size in the solidified layer changes with the content of Na_2SO_4 or Na_2CO_3 . This phenomenon may be caused by the differences of initial gas concentrations among slags, which could be verified by the results of numerical simulations. From the calculated results, with the increase of the initial concentration of CO_2 in liquid, the percentage of pores with radius less than $60\text{ }\mu\text{m}$ decreases, and the proportion of pores with radius higher than $80\text{ }\mu\text{m}$ increases. In addition, when molten slag contains Na_2CO_3 , the addition of Na_2SO_4 could improve the formation of bubbles with radius higher than $100\text{ }\mu\text{m}$, which leads to the increase of the rising velocity of bubbles during floating.

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Figure Captions

Fig. 1. Schematic of the Heat Flux Simulator.

Fig. 2. Appearance of the solid slag film.

Fig. 3. The longitudinal section of the solid slag film.

Fig. 4. The XRD patterns of the five solid slag films.

Fig. 5. The schematic of experimental apparatus used in SHTT tests.

Fig. 6. Meshes used for calculation.

Fig. 7. Flow chart of calculation for size distribution of pores in the solid slag film.

Fig. 8. Heat fluxes through the solid slag film during solidification.

Fig. 9. Optical properties of the five slags. (a) reflectivity, (b) transmissivity.

Fig. 10. Variation of temperature with distance during solidification of slag.

(a) $t = 10$ s, (b) $t = 20$ s, (c) $t = 30$ s, (d) $t = 45$ s.

Fig. 11. Concentrations of CO_2 on the bubble surface and in the bulk.

Fig. 12. Variation of bubble size for different gas compositions during isothermal process.

Fig. 13. Concentrations of CO_2 and N_2 on the bubble surface and in the bulk. (a) CO_2 , (b) N_2 .

Fig. 14. Concentration of SO_2 and partial pressures of gases when bubble contains no CO_2 .

(a) concentration of SO_2 , (b) partial pressure of gases.

Fig. 15. Concentration of SO_2 and partial pressures of gases when bubble contains CO_2 .

(a) concentration of SO_2 , (b) partial pressure of gases.

Fig. 16. Effect of cooling rate on bubble size during cooling process. (a) 100% CO_2 , (b) 90% CO_2 +

10% N_2 , (c) 80% SO_2 + 10% O_2 + 10% N_2 , (d) 50% SO_2 + 30% O_2 + 10% CO_2 + 10% N_2 .

Fig. 17. SHTT images of slag 1 at 1573 K.

Fig. 18. SHTT images of slag 5 at 1573 K.

Fig. 19. Bubble behavior in molten slag when cooling rate is 5 K/s.

Fig. 20. Bubble behavior in molten slag when cooling rate is 10 K/s.

Fig. 21. Bubble size distribution in the solidified layer when initial gas composition is 90% CO₂ and 10% N₂. (a) x-z direction, (b) x-y direction.

Fig. 22. Pore size distribution in the solidified layer when initial gas composition is 80% CO₂, 10% O₂ and 10% N₂. (a) x-z direction, (b) x-y direction.

Fig. 23. Pore size distribution in the solidified layer when initial gas composition is 50% SO₂ and 30% O₂, 10% CO₂ and 10% N₂. (a) x-z direction, (b) x-y direction.

Fig. 24. SEM images of the longitudinal section of the solidified layer.

(a) slag 1, (b) slag 2, (c) slag 3, (d) slag 4, (e) slag 5.

Fig. 25. Effect of initial gas concentration on the distribution of pore size in the solidified layer.

(a) CO₂, (b) SO₂.

Fig. 26. Effect of Na₂SO₄ on the distribution of pore size on the longitudinal section of the solid slag film.

Table Captions

Table 1 The target compositions of five slags used in experiment.

Table 2 The mass fractions of raw materials in each slag (%).

Table 3 Data used in calculations for mass transfer.

Table 4 Data used in calculations for heat transfer.

Table 5 Statistical results of pore size distribution.

Figures

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(a) $t = 10$ s

(b) $t = 20$ s

(c) $t = 30$ s

(d) $t = 45$ s

Fig. 10. Variation of temperature during solidification of slag.

(a) $t = 10$ s; (b) $t = 20$ s; (c) $t = 30$ s; (d) $t = 45$ s.

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(a) concentration of SO_2

(b) partial pressure of gases

Fig. 15. Concentration of SO_2 and partial pressures of gases when bubble contains CO_2 .

(a) concentration of SO_2 , (b) partial pressure of gases.

(a) 100% CO_2

(b) 90% CO_2 + 10% N_2

(c) 80%SO₂ + 10%O₂ + 10%N₂

(d) 50%SO₂ + 30%O₂ + 10%CO₂ + 10%N₂

Fig. 16. Effect of cooling rate on bubble size during cooling process. (a) 100% CO₂, (b) 90% CO₂ + 10% N₂, (c) 80% SO₂ + 10% O₂ + 10% N₂, (d) 50%SO₂ + 30%O₂ + 10%CO₂ + 10%N₂.

Fig. 17. SHTT images of slag 1 at 1573 K.

(g) 30 s

(h) 35 s

(i) 40 s

Fig. 18. SHTT images of slag 5 at 1573 K.

(a) 0 s

(b) 5 s

(c) 10 s

(d) 15 s

(e) 20 s

(f) 25 s

Fig. 19. Bubble behavior in molten slag when cooling rate is 5 K/s.

(a) 0 s

(b) 3 s

(c) 6 s

(d) 9 s

(e) 12 s

(f) 15 s

Fig. 20. Bubble behavior in molten slag when cooling rate is 10 K/s.

Fig. 21. Pore size distribution in the solidified layer when initial gas composition is 90% CO₂ and 10% N₂. (a) x-z direction, (b) x-y direction.

Fig. 22. Pore size distribution in the solidified layer when initial gas composition is 80% CO₂, 10% O₂ and 10% N₂. (a) x-z direction, (b) x-y direction.

(a) x-z direction

(b) x-y direction

Fig. 23. Pore size distribution in the solidified layer when initial gas composition is 50% SO₂ and 30% O₂, 10% CO₂ and 10% N₂. (a) x-z direction, (b) x-y direction.

(a) slag 1

(b) slag 2

(c) slag 3

(d) slag 4

(e) slag 5

Fig. 24. SEM images of the longitudinal section of the solidified layer.
(a) slag 1, (b) slag 2, (c) slag 3, (d) slag 4, (e) slag 5.

Fig. 25. Effect of initial gas concentration on the distribution of pore size in the solidified layer. (a) CO₂, (b) SO₂.

Fig. 26. Effect of Na_2SO_4 on the distribution of pore size on the longitudinal section of the solid slag film.

Tables

Table 1 The target compositions of slags used in experiment.

CaO	SiO ₂	Al ₂ O ₃	Na ₂ O	F	Li ₂ O	Total
40.0	35.6	6.7	9.0	7.8	1.0	100.0

Table 2 The mass fractions of raw materials in each slag (%).

NO.	CaO	SiO ₂	Al ₂ O ₃	Na ₂ SO ₄	Na ₂ CO ₃	Na ₂ SiO ₃	CaF ₂	Li ₂ CO ₃
1	27.7	32.3	6.5	0.0	10.9	4.4	15.5	2.7
2	27.6	32.5	6.5	0.5	10.9	4.0	15.5	2.7
3	27.4	32.8	6.4	2.0	10.8	2.6	15.3	2.6
4	27.0	33.4	6.3	4.5	10.6	0.4	15.1	2.6
5	29.1	29.4	6.8	4.5	0.0	14.0	16.3	0.0

Table 3 Data used in calculations for mass transfer.

	Diffusion coefficient D_i (m ² ·s ⁻¹)	Solubility of gas S_i (kg·m ⁻³ ·bar ⁻¹)	Physical solubility L_i (mol·m ⁻³ ·Pa ⁻¹)
SO ₂	$3.15 \times 10^{-4} \exp(-26105/T_b)$	0.10	1.56×10^{-5}
O ₂	$1.55 \times 10^{-7} \exp(-9550/T_b)$	$2.31 \exp(-5750/T_b)$	$7.22 \times 10^{-4} \exp(-5750/T_b)$
CO ₂	$1.92 \times 10^{-5} \exp(-21516/T_b)$	$1.67 \times 10^{-2} \exp(3840/T_b)$	/
N ₂	6.5×10^{-12}	$\exp(-11.4-15273/T_b)$	/
KSO_4^{2-}	$2681 \exp(-21670/T) \text{ mol}^{1/2} \cdot \text{m}^{-3/2}$		
CSO_4^{2-}	$0.90 \exp(8100/T) \text{ mol} \cdot \text{m}^{-3}$		
k_r	$5.13 \times 10^{-11} \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-3/2}$		
η	$0.141 \exp(16.49/T) \text{ Pa} \cdot \text{s}$		
σ	$0.35 \text{ N} \cdot \text{m}^{-1}$		

Table 4 Data used in calculations for heat transfer.

Thermal conductivity $W \cdot (m \cdot K)^{-1}$	$1523 < T \leq 1673$	0.50
	$1273 < T \leq 1523$	0.80
	$T \leq 1273$	1.65
Emissivity	Copper detector	0.4
	Inner surface of crucible	0.8
Heat capacity $J \cdot (kg \cdot K)^{-1}$	$2.937 - 0.004T + 1.875 \times 10^{-6}T^2$ $J \cdot (kg \cdot K)^{-1}$	
Thickness of solid slag film (mm)	2.4	
Fluid temperature K	1400 ± 10	

Table 5 Statistical results of pore size distribution.

NO.	Proportion of pores with different sizes (%)					Sauter mean diameter (μm)	Number density (mm^2)
	$< 50 \mu m$	50-100 μm	100-150 μm	150-200 μm	$> 200 \mu m$		
1	82	11	7	0	0	75.9	14.45
2	67	13	11	6	3	127.7	3.16
3	0	25	15	40	20	172.6	0.96
4	0	0	15	47	38	183.2	0.68
5	13	50	38	0	0	106.8	0.38