



Article Effect of Bubbles on Crystallization Behavior of CaO–SiO₂ Based Slags

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Abstract: Surface longitudinal cracks are a serious problem and particularly prevalent in the casting of peritectic steel (carbon content between 0.10%C and 0.18%C, non-alloyed). It is usually alleviated by controlling the horizontal heat transfer from the steel shell to the mold through increasing the crystallization performance of slags. In the actual continuous casting process, a large number of bubbles are formed in the molten slags, and the crystallization properties of the mold fluxes are affected by bubbles. Therefore, an investigation of the influence of bubbles on the crystallization performance of mold fluxes was carried out by applying the hot thermocouple technique and it is hoped that surface longitudinal cracks can be solved in this way in the peritectic steel casting process. The continuous cooling transformation (CCT) diagrams and time-temperature transformation (TTT) diagrams were constructed for an analysis of the crystallization kinetics. The results showed that the crystallization ability of mold fluxes was enhanced by adding bubbles through shortening the incubation time of crystallization, increasing the critical cooling rate, and decreasing the activation energy of crystallization. As a result, the crystalline fraction, slag film thickness, and surface roughness of the slag films were improved, but the crystalline phase was not affected by bubbles. With an increase of the bubble content remaining in the molten slag, the growth mechanism of the cuspidine crystal phase changed from a low dimension to a high dimension, and the content of the molten slag's structure unit (Q_1) needed for cuspidine in the molten slag was markedly increased.

Keywords: molten slags; bubbles; crystallization property; microstructure; crystallization kinetics

1. Introduction

Mold fluxes are vital functional materials in the continuous casting process and play an indispensable role for preventing oxidation of molten steel, lubricating the steel shell, adsorbing non-metallic inclusions, moderating mold heat transfer, and insulating the molten steel free surface [1,2]. It is well known that crystallization is one of the most important properties of mold flux, as it primarily controls the heat transfer and lubrication performance in the continuous casting mold [3].

Longitudinal cracks have always been a serious problem that influences the steel shell quality in the continuous casting of peritectic steels (carbon content between 0.10%C and 0.18%C, non-alloyed). It is caused by the releasing of thermal stresses formed through the volumetric shrinkage during the δ/γ phase transformation [4]. It can be relieved by regulating the horizontal heat transfer from

the shell to the mold, especially, in the initial stage of solidification, where the peritectic reaction begins to occur [5]. Presently, the common method is to improve the basicity of mold fluxes. However, lubrication of the shell can be deteriorated by high-basicity mold fluxes [6]. In the actual continuous casting process, mold fluxes are composed of base slags, fluxes, and carbon materials. Among them, many carbonate materials, such as CaCO₃, MgCO₃, Na₂CO₃, and Li₂CO₃, are included [7]. Hence, a large number of the bubbles are formed by the decomposition of carbonate materials and even by the interaction of some compositions during the continuous casting process, as shown in equations 1 through 8 [8,9]. In addition, some gases produced by the burning of carbon materials may be captured by molten slags [7]. The bubbles affect the crystallization property of mold fluxes. However, previous studies on the crystallization property of mold fluxes in the laboratory always eliminated the influence of bubbles, which is inconsistent with the actual continuous casting process [3]. Mills et al. [10] indicated that many bubbles were formed in molten slags between the mold and the steel shells during the continuous casting process, as shown in Figure 1. Davis et al. [11] investigated the nucleation of crystals on bubbles in the lithium disilicate system and reported that crystal nucleation efficiency (heterogeneous site "activity") and crystal morphology were related to bubble size and bubble composition. During investigating the influence of the raw material type on the heat transfer and structure properties of mold fluxes, Wen et al. [12] found that some bubbles were formed in the slag films through the decomposition of sodium carbonate, and they even found that the heat transfer performance of mold fluxes was also affected by bubbles. Yang et al. [9] studied the behavior of bubbles, including bubble motion, bubble size distribution, bubble rise velocity, and bubble coalescence, in the molten slag by numerical simulation and indicated that bubbles might influence the conductivity and optical properties of the slag film. From the above studies, it can be deduced that bubbles existed in mold fluxes and affected the physicochemical properties of mold fluxes. However, to the knowledge of the authors, the effect of bubbles on the crystallization properties of mold fluxes has not been reported systematically, especially, regarding kinetics. Therefore, it is of great practical significance to systematically and deeply investigate the influence of bubbles on the crystallization behavior of mold fluxes. Simultaneously, it can provide a theoretical basis for preparing the mold fluxes applied in the continuous casting process of peritectic steels.

$$Na_2CO_3(s) + SiO_2(s) = Na_2SiO_3(s) + CO_2(g)$$
 (1)

$$Na_2CO_3(l) = 2Na(l) + CO_2(g) + 1/2O_2(g)$$
(2)

$$Na_2CO_3(s) = Na_2O(s) + CO_2(g)$$
 (3)

$$CaCO_3(s) = CaO(s) + CO_2(g)$$
(4)

$$Na_2SO_4(l) = Na_2O(l) + SO_2(g) + 1/2O_2(g)$$
(5)

$$Na_2O(s) + CaF_2(s) = 2NaF(g) + CaO(s)$$
(6)

$$SiO_2(s) + 2CaF_2(s) = 2CaO(s) + SiF_4(g)$$
(7)

$$SiO_2(s) + 4NaF(g) = 2Na_2O(s) + SiF_4(g)$$
 (8)



Figure 1. Schematic diagram of mold fluxes at the meniscus region.

2. Materials and Methods

2.1. Material Preparation

Reagent grade powders of CaCO₃ (>99.5 mass percent), SiO₂ (>99.5 mass percent), Al₂O₃ (>99.5 mass percent), Na₂SO₄ (>99.5 mass percent), Na₂CO₃ (>99.5 mass percent), CaF₂ (>99 mass percent), MgO (>99 mass percent), and Na₂O (Na₂CO₃ calcined 10 h in a muffle furnace at 1173 K) were used as raw materials. The composition of the mold flux used in the present study is given in Table 1. 50 g and 350 g samples were prepared and mixed according to the proportions shown in Table 1 and calcined in a muffle furnace at 373 K to remove moisture. The 350-g sample was placed in a HF-200 Heat Flux Simulator made by ourselves group and kept at 1673 K for 10 min to homogenize its chemical composition. A preheated steel bar (Φ 15 mm \times 80 mm) was first stuck into the molten slag for 10 s and then quickly extracted for quenching and subsequent drying. After that, the slag film was obtained by the HF-200 Heat Flux Simulator. Some slag films were polished for the scanning electron microscope (SEM) (VEGA 3 LMH, TESCAN, Brno, Czech Republic) experiment. Some slag films were crushed, ground, and sieved using a 200-mesh screen for X-ray diffraction (XRD) (Shimadzu, Kyoto, Japan) and differential scanning calorimetry (DSC) (NETZSCH-Gerätebau GmbH, Selb, Germany) experiments. The remaining samples were used for the confocal scanning laser microscope (CLSM) (VL2000DX-SVF17SP, Yonekura, Yokohama, Kanagawa, Japan) experiment. The water-quenched samples were used for the Raman spectra (LabRAM HR Evolution, Horiba Jobin-Yvon, France) experiment. The 50-g sample was placed in an electromagnetic pulverizer for 2 min, then placed in a glass beaker (100 mL) with 50 mL absolute alcohol, stirred with a stirrer at 300 rpm for 60 min, and finally placed in a muffle furnace at 373 K for 2 h. The 50-g sample was crushed, ground, and sieved using a 200-mesh screen for the single hot thermocouple technique (SHTT).

Table 1. Chemical compositions of mold fluxes (wt%).

-	Number	CaCO ₃	CaO	SiO ₂	MgO	Al_2O_3	Na_2SO_4	Na ₂ CO ₃	Na ₂ O	F
	А	0	45.2	33.4	0.8	5.0	0	0	8.0	7.6
	B1	14.4	37.2	33.4	0.8	5.0	0.5	3.1	6.0	7.6
	B2	28.6	29.2	33.4	0.8	5.0	2.0	5.4	4.0	7.6
	B3	42.9	21.2	33.4	0.8	5.0	3.5	7.6	2.0	7.6

2.2. Experimental Methods

SEM and XRD were used to analyze the microscopic morphology and the crystalline phase of the slag films.

DSC was used to analyze the crystalline fraction of the slag films. The principle of DSC has been described in detail in a previous paper [13]. An HF-200 Heat Flux Simulator was used to obtain the water-quenched slags and the slag films [14]. The mean slag film thickness (narrow side and wide side) was obtained by measuring three values using a Vernier caliper. A CLSM was used to analyze the mean surface roughness (R_a) of the slag films, obtained by measuring ten values [4]. The measuring methods are shown in Figure 2.



(a)



Figure 2. Measuring methods of (a) mean slag film thickness and (b) mean surface roughness of slag films.

The microstructure information of the amorphous glassy samples was analyzed through Raman spectroscopy using a Lab-RAM HR Evolution micro-Raman spectrometer (LabRAM HR Evolution, HORIBA Jobin Yvon, France) equipped with a CCD detector at room temperature [15]. The acquired Raman spectra were curve-fitted with Gaussian functions using the Origin 9.0 Microcal Software. The area of deconvoluted peaks was measured to calculate the polymerization of the molten slags.

The time-temperature transformation (TTT) and continuous cooling transformation (CCT) diagrams were constructed using SHTT technology [16,17]. Figure 3a,b shows the schematic diagram of SHTT and a typical image of an in situ observation of the mold flux crystallization process by SHTT, respectively. For the SHTT, the temperature of the molten slag was controlled by a single thermocouple. After setting the temperature profile, a slag sample mixed with raw materials was heated on the tip of the thermocouple. Meanwhile, the temperature measured by the thermocouple was shown on a computer screen. The errors of temperature control can be corrected by measuring the melting point of K_2SO_4 . Figure 4 shows the heat file used in the SHTT experiment. For the TTT tests, the thermocouple, together with the powder sample, was first heated to 1773 K at a rate of 15 K/s, and then samples were cooled down rapidly to different temperatures for isothermal crystallization tests. However, for the CCT tests, the sample was also first heated to 1773 K at a rate of 15 K/s, and then continuous cooling at different cooling rates was used. The TTT and CCT diagrams were constructed by recording the relationship between the temperature, time, and transformation.





(b)

Figure 3. Schematic diagram of the single hot thermocouple technique (SHTT) (**a**) and crystallization process of the molten slag through SHTT (**b**).



Figure 4. Thermal profile for (a) TTT and (b) CCT tests.

3. Results and Discussion

3.1. Microstructure

The microstructures of the A slag and the B1 slag are shown in Figure 5a,b. As can be seen, no pores exist on the surface of the A slag film, while a large number of pores of different sizes are notably formed on the surface of the B1 slag film. The diameter of the pores on the liquid slag side is larger than that on the Cu sensor side, and the number of pores on the sensor side is higher than that on the liquid slag side, according to the left image in Figure 5b. When the sensor immersed into the molten slag, the liquid slag near the sensor side rapidly converted to solid slag at a high cooling rate, and bubbles are fixed in the solid slag. However, bubbles near the liquid side were able to grow and some large bubbles may even have escaped from the molten slag during the gradual cooling process. As for the microstructure, the grain size in the A slag film was larger than that in the B1 slag film. Conversely, the crystal fraction in the A slag film was smaller than that in the B1 slag film. It may due to the occurrence of a large number of nucleation sites in the slag film caused by bubbles, leading to the formation of more crystals and an increase in the crystalline fraction. Wen et al. [12] indicated that the "chilling effect" may be caused by the bubbles in the slag film, and the formation of cuspidine could be promoted by the strong chilling effect. At the same time, the crystals impeded the release of the bubbles. Thereby, the formation of cuspidine, in turn, was promoted by the bubbles. The more crystals generate in the same slag film, the smaller the grain size becomes. Hence, the grain size decreases compared to that of the A slag film.



(a)



(b)

Figure 5. Overall image (left) and microstructure image (right) of slag films. (a) A slag film; (b) B1 slag film.

3.2. Crystal Phase

The crystalline phases of the four mold flux series at the nose temperatures of 1473 K and 1273 K obtained during the TTT tests are shown in Figure 6a,b, respectively. Gao et al. [17] indicated that each "C" shape of the TTT diagram represents a crystallization process, and the nose temperature in the "C" shape was the best temperature for crystallization including the thermodynamic conditions and kinetic conditions. It can be seen that only wollastonite (CaO·SiO₂) and only cuspidine (CaO·2SiO₂·3CaF₂) were found in the slag films at 1473 K and 1273 K, respectively. It can be concluded that the crystalline phase in the slag film is not affected by the bubbles. Li et al. [18] indicated that CaO·SiO₂ formed at high temperatures, while in the lower temperature region, CaO·SiO₂ converted to 3CaO·2SiO₂·CaF₂. According to the XRD of A, B1, B2, and B3, the characteristic peak area of wollastonite or cuspidine increased with increasing bubbles content of the mold fluxes A, B1, and B2. In the B3 slag, the characteristic peak area of wollastonite or cuspidine fraction in the slag film according to many researches [19,20].



Figure 6. Crystalline phases of the slag films at different temperatures: (a) T = 1473 K and (b) 1273 K.

3.3. Crystalline Fraction, Slag Film Thickness, and Surface Roughness of Slag Film

The crystalline fraction, slag film thickness, and surface roughness results of the slag films are listed in Table 2. It can be seen in Table 2 that the crystalline fraction of B serial slags was larger than that of the A slag. This proves that the crystallization property was enhanced by the bubbles of the molten slags. Accordingly, the slag film thickness and surface roughness increased. It is in very good agreement with the results of Figure 6. Fox et al. [21] illustrated that the surface roughness was mostly formed by the uneven volumetric shrinkage coming from the glass layer converting to the crystal layer ($\rho_{crystal} > \rho_{glass}$), including the liquid slag layer converting to the solid slag layer. In B serial slags, the crystalline fraction first enhanced and then reduced with an increase of the bubble content, and the crystalline fraction of the B2 slag film reached the maximum (89%) with the volume ratio of bubbles being 47%. With the addition of bubbles, the liquid slag flow was converted from a single-phase into a gas-liquid two-phase flow, leading to the homogeneous nucleation process turning into a heterogeneous nucleation process. Meanwhile, it led to a decrease of the crystallization activation energy and the critical radius of crystal nucleus. In addition, it increased the nucleation sites. Therefore, it was easier to form crystals. However, as the bubbles of the molten slag further increased, the distance between each bubble gradually decreased, causing the bubbles to aggregate, grow, and run out of the molten slags more easily. Ultimately, the actual nucleation sites remaining in the molten slags reduced. This negatively impacted the crystallization behavior of the molten slags. Therefore, the

reduction of crystalline fraction of the B3 slag was carried out. Concurrently, the slag film thickness and surface roughness of the B3 slag also reduced.

Sampla Number	Crystalline	Slag Film Th	Surface	
Sample Number	Fraction (%)	Wide Side	Narrow Side	Roughness (um)
А	69.3	2.9	3.2	32.6
B1	80.3	3.3	3.6	47.1
B2	87.1	3.5	3.8	53.4
B3	73.6	3.2	3.5	40.9

Table 2. Crystalline fraction, slag film thickness, and surface roughness of slag films.

3.4. Structure of Molten Slags

Raman spectral fragmentation of samples between 400 and 1400 cm⁻¹ is plotted in Figure 7a. Figure 7b shows the typical deconvolution results for the mold fluxes. The bands marked in the ranges 850-880, 900-920, 950-1000, and 1050-1100 cm⁻¹ correspond to Q₀, Q₁, Q₂, and Q₃ units, respectively [15,22-24]. The characteristic peaks in the Raman spectra of the various structural units were obtained by typically fitting until an R^2 value of >99.5% was achieved. The integrated area of the individual deconvoluted peaks provides a semi-quantitative evaluation of the amount of Q_n units. The peak area ratios obtained from the Gaussian deconvolution of Raman spectroscopic data using the above indirect method are listed in Table 3. It can be seen in Table 3 that Q_1 increases with an increase of bubbles. According to Equations (1) and (8), the chain structure of silicate may be destroyed by Na_2CO_3 and CaF_2 , leading to an increase of Q_1 . Therefore, the higher the content of bubbles, the more Q_1 structure is present. Li et al. [18] pointed out that the structure of cuspidine was mainly composed of Q_1 . While, according to Table 2, the content of cuspidine first increased and then decreased with the increase of bubbles, it may be that the nucleation sites were first improved by the bubbles. But the solubility of the bubbles in molten slag is limited with any further increase in bubble content. Some small bubbles may have converted into large bubbles, leading to an easy escape out of the molten slags. Then, in turn, the actual bubble content remaining in the B3 slag decreased to 23%, causing a decrease of the nucleation sites. Davis et al. [11] illustrated that some of the large bubbles did not serve as crystal nucleation sites. Hence, the reduction of the crystalline fraction was carried out. This further verifies the results in Table 2. Further study should be conducted on the relation of bubble size and crystal nucleation sites in future work.



Figure 7. Raman spectra: (**a**) A, B1, B2, and B3 sample Raman spectra ranging from 400 to 1400 cm⁻¹; (**b**) typical deconvolution of the Raman spectra.

Raman Bands	Raman Shift (cm ⁻¹)			Peak Area Ratio (%)				
Ruman Duries	Α	B 1	B2	B3	Α	B1	B2	B3
Symmetric stretching Si-O ^{$-$} of Q ₀	866	860	869	863	10.88	13.68	19.38	21.18
Symmetric stretching Si-O ^{$-$} of Q ₁	905	905	902	909	17.02	20.03	38.84	19.84
Symmetric stretching Si-O ^{$-$} of Q ₂	959	966	953	951	58.99	59.21	36.95	52.41
Symmetric stretching Si-O ^{$-$} of Q ₃	1055	1051	1046	1049	13.11	7.08	4.91	6.57
R^2	0.9981	0.9987	0.9979	0.9985	-	-	-	-

Table 3. Peak analysis of Raman spectra in the mold fluxes.

3.5. TTT and CCT

3.5.1. TTT

The TTT diagrams of A and B series mold fluxes are shown in Figure 8a–d. In the experiment, the temperature corresponding to the occurrence of 5 vol pct of crystallization is defined as the beginning crystallization temperature, and the end crystallization temperature corresponds to the occurrence of 95 vol pct of crystallization [17]. It can be observed from the Figure 8a–d that there are two noses in each of the TTT curves, indicating two crystallization phases are formed. This is in agreement with the XRD result. Incubation time is an important parameter to characterize crystallization properties, and a shorter incubation time suggests a larger speed of crystal precipitation. Figure 8e shows the incubation time of all four series of mold fluxes. It suggests that the incubation time was first reduced and then increased with the increase of bubbles in the mold fluxes, and the same tendency is found in the nose temperature. The heterogeneous nucleation in the slag was promoted by the bubbles, which facilitated crystallization. In addition, according to equations 1 through 7, the polymerization of silicate structures could have been broken through this reaction, leading to a fast transfer of ions. The movement of bubbles also increased the ion transfer [25]. Inevitably, a decrease in incubation time is conducted. When the bubble content further increases (i.e., the B3 slag), the actual bubble content remaining in the molten slag reduced. Correspondingly, the incubation time prolonged.



Figure 8. Cont.



Figure 8. TTT curves of mold fluxes: (a) A, (b) B1, (c) B2, (d) B3, (e) incubation time of mold fluxes.

3.5.2. CCT

Figure 9a–d shows the CCT curves of the four mold fluxes. It can be noticed that the crystallization temperatures for all samples decreased with an increase in the continuous cooling rate. Gao et al. [17] indicated that the nucleation and growth rate of crystals were functions of the viscosity and the degree of undercooling of molten slag. As the viscosity increased during cooling, a stronger driving force was needed to initiate the mold flux nucleation. Therefore, the crystallization temperature decreased with an increasing continuous cooling rate. The critical cooling rate of the four mold fluxes is shown in Figure 9e. As can be found in Figure 9e, the critical cooling rate increased first and then decreased with the increase in bubble content. The reason is the same as that in Figure 8.



Figure 9. Cont.





Figure 9. CCT curves of mold fluxes. (a) A, (b) B1, (c) B2, (d) B3, and (e) critical cooling rate of mold fluxes.

3.6. Crystalline Kinetics

The kinetics are closely related to the crystallization process involving nucleation and growth of mold fluxes. Therefore, the Johnson–Mehl–Avrami (JMA) model [3] was adopted to investigate the kinetics of mold flux isothermal crystallization. According to the JMA model, the volume fraction of crystals X(t) is given by

$$X(t) = 1 - \exp(-kt^n) \tag{9}$$

where X(t) is the relative degree of crystallinity at a given time t and at a certain temperature, which can be obtained through the equation $X(t) = A_C/A_T$, where A_C is the area of crystal and A_T is the total area of mold flux in the thermocouple. The values of A_C and A_T were obtained by image analysis. t is time, including the incubation and crystallization process. n is the Avrami exponent, which is associated with the nucleation and growth mechanism, and k is the effective crystallization rate constant, which is dependent on temperature and rate of nucleation and crystal growth.

The values of *n* and *k* can be obtained by fitting the double logarithmic form as follows:

$$\ln\{-\ln[1 - X(t)]\} = \ln k + n \ln t$$
(10)

The double logarithmic plots of $\ln\{-\ln[1 - X(t)]\}$ vs. $\ln t$ for mold fluxes at different temperatures are shown in Figure 10. Because cuspidine was formed mainly in the lower part of the four series TTT diagrams, the isothermal crystallization processes at temperatures ranging from 1173 K to 1323 K were chosen for the kinetic study. Values of the Avrami exponent *n* and effective crystallization rate constant *k* can be obtained from the slope and the intersection of the plots, as summarized in Table 4.



Figure 10. Plots of $\ln\{-\ln[1 - X(t)]\}$ versus $\ln t$ for isothermal crystallization of the four series of mold fluxes (**a**) A, (**b**) B1, (**c**) B2, and (**d**) B3.

Table 4. Results of *n* and *k* analyses for isothermal crystallization of mold fluxes under different temperatures.

Mold Fluxes	Temperature/K	n	lnk
	1173	1.54	-5.12
٨	1223	2.01	-4.71
А	1273	2.10	-4.18
	1323	2.11	-4.98
	1173	2.28	-3.68
D1	1223	2.44	-2.41
B1	1273	2.61	-2.22
	1323	2.62	-1.59
	1173	2.99	-2.49
DO	1223	3.02	-2.13
D2	1273	3.08	-1.86
	1323	3.09	-1.18
	1173	2.11	-4.74
D 2	1223	2.17	-4.26
D3	1273	2.26	-3.77
	1323	2.28	-4.31

It can be seen in Table 4 that the effective crystallization rate increased with the rise of hold temperature and bubble content of the mold fluxes. With rising temperature, the viscosity of the mold fluxes decreased, increasing the ion transfer rate. Concurrently, the nucleation sites increased due to the occurrence of bubbles. As for the B3 slag, the actual bubble content remaining in the molten slag reduced. Consequently, the fall in the crystallization rate was carried out.

Avrami exponent n is an effective kinetic parameter to determine the crystallization mechanism. Several researchers [26,27] have summarized the general corresponding crystallization mechanism, as can be seen in Table 5.

Grow Mode	Crystallization Mode				
Giow mode	Diffusion Controlled	Interface Reaction Controlled			
Constant nucleation rate	-	-			
3-dimensional growth	2.5	4			
2-dimensional growth	2	3			
1-dimensional growth	1.5	2			
Instantaneous nucleation	-	-			
3-dimensional growth	1.5	3			
2-dimensional growth	1	2			
1-dimensional growth	0.5	1			
Surface nucleation	0.5	1			

Table 5. Values of *n* for different nucleation and growth mechanisms.

Compared with the values of n in Tables 4 and 5, it can be concluded that the growth mechanism of the cuspidine crystal phase changes from a low dimension to a high dimension. The increase of the actual bubble content remaining in the molten slag is in the temperature range from 1173 K to 1323 K.I In A slag, the slag's nucleation model is homogeneous nucleation at a constant rate and n is approximately 2, indicating the growth style of cuspidine may be one-dimensional growth with the interface reaction controlled or two-dimensional growth, with the diffusion controlled. However, in the B2 slag, the slag's nucleation model is instantaneous nucleation and n is close to 3, indicating the growth style of cuspidine is three-dimensional growth, with the interface reaction controlled. With the increase in bubbles, crystals grow around the bubbles in different directions.

Crystallization activation energy (*Ea*) is an energy barrier that hinders crystals from precipitating from the molten slags, reflecting the crystallization performance of mold fluxes. The larger the crystallization activation energy is, the more difficult it is for the crystals to precipitate It can be calculated by the Arrhenius formula [28], as shown in Equation (11):

$$k = A\exp(-Ea/RT) \tag{11}$$

where *Ea* is the activation energy of crystallization, *A* is the pre-exponential factor, *R* is the gas constant, and *T* is the absolute temperature (note that the unit is K). Rearranging Equation (11), the value of *Ea* could also be determined by plotting $\ln k$ versus 1/(RT), as in Equation (12):

$$\ln k = \ln A - Ea/RT \tag{12}$$

Figure 11a shows the plots of ln*k* vs 1/RT for the four series of mold fluxes. *Ea* is calculated from the slopes of the linear fits to the experimental data, as indicated in Equation (12), as shown in Figure 11b. It can be found that the crystallization activation energy of the four series of molten slags first increased and then decreased with the increase of the bubble content. The results are also mainly associated with the nucleation sites in the molten slag. The more nucleation sites of heterogeneous nucleation there are, the lower *Ea* is.



Figure 11. Plots of lnk vs. 1/RT for mold fluxes (a) and Ea of the four series of mold fluxes (b).

4. Conclusions

The effect of bubbles on the crystallization behavior of mold fluxes including the crystallization kinetics (isothermal and non-isothermal processes) was studied. Compared to the B series slag, the grain size of the A slag was larger. Concurrently, the crystalline fraction increased, causing an increase of the slag film thickness and the surface roughness of the slag film. However, the crystal phase was not affected by the bubble content. For the four series of slags, the crystalline fraction first increased and then decreased with an increase of the bubble content. The crystalline fraction of B2 slag reached a maximum of 87% with the volume ratio of bubble content being 47%, which is much higher than that of the A slag at 69.3%. As for the crystallization kinetics, with the increase of the actual bubble content remaining in the molten slags, the growth mechanism of cuspidine crystal phase changed from a low dimension to a high dimension, and the crystallization activation energy and crystallization rate of the molten slags decreased. The crystallization activation energy of B2 slag obtained a minimum of 15 kJ·mol⁻¹, much smaller than that of the A slag at 29 kJ·mol⁻¹.

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