Crystallization Control for Fluorine-free Mold Fluxes: Effect of Na₂O Content on Non-isothermal Melt Crystallization Kinetics

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There are increasing demands for developing fluorine-free mold fluxes for continuous casting of steel. When removing fluorine from mold flux composition, it is necessary to replace it with oxides, which must maintain the technological parameters, related to viscosity, melting characteristics, and crystallization behavior. For industrial developments in the CaO–SiO₂–Na₂O–Al₂O₃–TiO₂–B₂O₃–MgO (with basicity = 1, Al₂O₃ = 7%, TiO₂ = 5%, B₂O₃ = 3%, MgO = 2%) slag system, it is necessary to know the effect of Na₂O concentration regarding crystallization kinetics. This is especially important for fluorine-free mold fluxes for peritectic steel slab casting. In this work, the crystals' precipitation sequence for this system during cooling was determined, combining Differential Scanning Calorimetry (DSC), X-Ray Diffraction (XRD), and Scanning Electron Microscopy (SEM). The Friedman differential isoconversional method was applied for determining the effective activation energy for non-isothermal crystallization, since it gives relevant information without knowing the form of the kinetic equation. A modified Avrami model was used to calculate the *n* values; it was found that they are near 2.5, for all analyzed samples, which means that it is related to the crystallization mode diffusion controlled, with constant nucleation rate and three-dimensional growth. This agrees with the SEM micrographs, where dendritic structure is observed for all crystalline samples. Additionally, structural information got from Raman spectroscopy, for the samples in vitreous state, was used to interpret crystallization tendency, *i.e.*, the fact that crystallization was enhanced by increasing Na₂O content, due to slag depolymerization. Moreover, computational thermodynamics was used to analyze mold fluxes crystallization behavior.

KEY WORDS: fluorine-free mold fluxes; crystallization; kinetics; peritectic steel; slab casting.

1. Introduction

Mold flux has two main functions during continuous casting of steel. The first one, lubrication, prevents sticking. The second one is the control of horizontal heat transfer rate. It is well known that these functions are strongly dependent on crystallization behavior of mold flux.¹⁾ Crystallization happens in two different ways, since crystals precipitate from liquid slag and from glassy phase. The other functions are to protect steel against oxidation, to absorb inclusions, and thermal insulation.²⁾

Fluorine is usually part of commercial mold fluxes composition, because it is relevant for mold flux performance. This element in traditional CaO–SiO₂–CaF₂ mold fluxes is

important to control their technological parameters, such as: mold slag viscosity, characteristic temperatures, and crystallization kinetics. On the other hand, fluorine in mold fluxes is disadvantageous due to environmental and health concerns. Furthermore, it causes the corrosion of the continuous casting machine, because hydrofluoric acid is generated from mold flux; it increases dramatically the corrosion rate especially below the mold where there is a high amount of water accelerating the process.^{3–7)} This context makes the elimination of fluorine of mold fluxes composition a very important industry demand.

When developing fluorine-free mold fluxes, the technological parameters should be similar when using alternative raw materials. Besides, the cost for these materials must be observed; Li₂O-bearing raw materials, for example, are very expensive. Some oxides as alternatives to replace

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CaF_2 have been tried, mainly TiO_2 , B_2O_3 and Na_2O .⁷⁾ For billet casting, steelmakers frequently use high viscosity mold fluxes to overcome problems such as slag entrapment and submerged entry nozzle (SEN) erosion. In this case, crystallization kinetics does not need to be addressed when developing fluorine-free mold fluxes, since crystallization rate is very low; increase in Na_2O content is a good choice to compensate for fluorine removal.⁸⁾ For low carbon steel slab casting, B_2O_3 can be used as alternative, since crystallization tendency is low for this case. B_2O_3 addition decrease crystallization ability of slags; this was not a problem for industrial tests with a B_2O_3 -bearing F-free mold flux.⁹⁾

However, when it is necessary to reduce horizontal heat transfer rate (mild cooling), crystallization kinetics becomes a very important parameter. For peritectic steel (0.09–0.16 wt% C) slab casting, the crystalline fraction of the solid slag layer along the mold must be high to avoid longitudinal cracking, which in turn happens because of the 4% mismatch in the steel thermal shrinkage coefficients for the δ and γ phases. Regarding crystallization behavior for $\text{CaO-SiO}_2\text{-CaF}_2$ mold slags, the precipitation of cuspidine ($3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{CaF}_2$) is related to heat transfer control. Although the mechanism for heat transfer control has not yet been determined, two ideas have been proposed. An idea is that radiation heat flux decreases by scattering at the boundary between the crystalline and the liquid layers during crystallization from slag. Another idea is that the total heat flux can be decreased by the large thermal resistance of the air gap formed because of the solidification shrinkage of the solidified slag layer, which occurs due to crystallization from glass. In both cases, crystallization of cuspidine happens. When comparing crystallization from melt and crystallization from glass, the first one should be more important, because crystallization from liquid is faster. The heat transfer control function starts to work a few seconds from the casting, therefore crystallization from melt brings the great effect on heat transfer control.¹⁰⁾ Thus, the first crystal should have a special role.

Nakada and Nagata¹⁰⁾ suggested it is worth to investigate the effect of Na_2O addition in $\text{CaO-SiO}_2\text{-TiO}_2$ slags, considering the possibility of using this slag system for tailoring fluorine-free mold fluxes. These slags are expected to have the lubrication function because *liquidus* temperatures and viscosities are similar to slags in the $\text{CaO-SiO}_2\text{-CaF}_2$ system. This suggestion was followed by another work, in which the effect of Na_2O on crystallization kinetics was evaluated with Time-Temperature-Transformation (TTT) and Continuous-Cooling-Transformation (CCT) diagrams, which were built using the Single Hot Thermocouple Technique (SHTT).¹¹⁾ It was found that addition of Na_2O in $\text{CaO-SiO}_2\text{-TiO}_2$ slags dramatically shortens the crystals' incubation times to the range of seconds, with a clear effect of the Na_2O content on the critical cooling rate. Thus, it is possible to control crystallization kinetics in $\text{CaO-SiO}_2\text{-TiO}_2$ slags by changing the Na_2O content. In this study, five samples were analyzed, with binary basicity in the range 0.6–0.8, TiO_2 15.2–18.1 wt%, and Na_2O 0.0–7.1 wt%.¹¹⁾

Based on plant trials, Wen *et al.*¹²⁾ proposed the following composition range for TiO_2 -bearing F-free mold fluxes for peritectic steel slab casting: basicity 0.95–1.15,

TiO_2 4.0–7.0 wt%, Na_2O 5.0–8.0 wt%, Li_2O 1.0–2.0 wt%, MnO 3.0–5.0 wt%, and B_2O_3 4.0–8.0 wt%. They reported that the laboratory technological parameters were like the corresponding traditional F-bearing mold flux. Besides, the industrial trials indicated that the F-free mold flux effectively controlled heat transfer, due to rapid precipitation of perovskite ($\text{CaO} \cdot \text{TiO}_2$), which replaced cuspidine. In terms of crack index, slab surface quality became even better.

In a previous laboratory work,¹³⁾ non-isothermal melt crystallization kinetics for $\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ F-free mold fluxes, for continuous casting of high aluminum steels, through modified Avrami analysis and Friedman differential isoconversional method, was studied. Crystallization mechanisms and effective activation energy of crystallization were determined for different compositions, for the first crystal, which precipitates from melt ($\text{Ca}_3\text{Al}_2\text{O}_6$). It was found for all compositions that effective activation energy is negative, showing anti-Arrhenius behavior, because crystallization is controlled by thermodynamic driving force for nucleation.

Another way to analyze crystallization from melt is from structural data of glasses, considering that structure of quenched glass should be like parent melt. In this way, it is possible to find correlations between structure of quenched glass and crystallization tendency, for different compositions. In a previous work,¹⁴⁾ the effect of TiO_2 content on structure of the glassy $\text{CaO-SiO}_2\text{-CaF}_2\text{-TiO}_2$ system, which is related to the mold slag for continuous casting of titanium-stabilized stainless steel, was investigated through two techniques: Raman spectroscopy, and Nuclear Magnetic Resonance with Magic Angular Spinning spectroscopy (MAS-NMR). It was observed that Q_2 is the predominant silicate species for the studied samples, and that Ti^{4+} mainly exists in the form of $[\text{TiO}_4]$ in silicates, forming TiO_2 -like clusters with Ti^{4+} in tetrahedral coordination, not changing degree of polymerization of the silicate network. Moreover, it was concluded that a small amount of Ti enters the silicate network as the role of network formation, enhancing degree of polymerization of the silicate network. Three samples were studied, with TiO_2 contents of 0, 5, and 10 wt.%, basicity ($w\text{CaO}/w\text{SiO}_2$) ~1.3 and CaF_2 content ~10 wt.%.

Thus, it is important to understand crystallization from mold slag to improve performance of continuous casting process. The objective of the present work is, therefore, to investigate non-isothermal melt crystallization kinetics for F-free TiO_2 -bearing mold fluxes, considering the first crystal, which precipitates during cooling, using the model-free Friedman differential isoconversional method, and modified Avrami analysis. Three samples with different Na_2O contents were studied through Differential Scanning Calorimetry (DSC). Besides, structural information got from Raman spectroscopy was used to interpret crystallization behavior for these samples. Moreover, a thermodynamic analysis was carried out considering the effect of Na_2O addition on thermodynamic driving force for the precipitation of Ca_2SiO_4 during cooling.

2. Experimental

2.1. Preparation of Glassy Samples

Slags were synthesized from reagent grade MgO , Al_2O_3 , Na_2CO_3 , CaO , TiO_2 , SiO_2 and H_3BO_3 . Composition (wt.%)

of the samples investigated in the present work are shown in **Table 1**. CaO was prepared by decomposition of CaCO_3 at 1 000°C overnight. Reagent powders were mixed in an agate mortar and held in a platinum crucible placed in a MoSi_2 furnace at 1 400°C for 2 hours in air. After melting, the samples were quenched in water to obtain glassy cullets. X-Ray Diffraction (XRD) confirmed the glassy state, according to **Fig. 1**.

2.2. DSC Measurements

Glassy cullets were pulverized and subjected to DSC analysis. The runs were performed using a thermal analyzer STA 449 F3 Jupiter from the manufacturer Netzsch-Gerätebau GmbH, with argon acting as purge gas at dynamic conditions. Calibration for the apparatus was performed using $\alpha\text{-Al}_2\text{O}_3$ as the reference material, building a temperature calibration curve and a sensitivity calibration curve with pure substances. After calibration, the glassy samples were heated up to 1 400°C with a heating rate of 20°C/min, and then cooled with different rates (15, 20, 25, and 30°C/min). Platinum crucibles with platinum lids were used to minimize the loss of volatile substances. A new baseline was generated for each heating rate using an empty platinum crucible.

From DSC data, CCT diagrams were built, and characteristic temperatures (*liquidus*, crystallization temperature, and undercooling) were determined for each sample.

2.3. SEM-EDS and XRD Analyses

In order to determine the sequence of crystal precipitation in DSC runs, the following thermal cycle was applied,

using muffle furnace. Glassy cullets were heated from room temperature to 1 400°C, with the rate of 5°C/min, and then cooled to target temperatures with the rate of 5°C/min. Then, the slags were quenched in water. The composition, morphology, and nature of crystallization products were identified by Scanning Electron Microscopy with Energy Dispersed Spectroscopy analysis (SEM-EDS), with the working voltage of 25 kV, and by XRD analysis, which was performed with a 18 kW X-ray diffractometer (RIGAKU TTRIII), using $\text{Cu-K}\alpha$ radiation. With this procedure, the sequence of crystal precipitation from melt can be determined.

2.4. Raman Spectroscopy

Raman spectra were recorded at room temperature in the frequency range of 100–2 000 cm^{-1} using a laser confocal micro-Raman spectrometer, LabRAM HR-Evolution (Horiba, Japan). Data collection were performed in room temperature using excitation wavelength of 532 nm and the light source He-Cd laser with power of 100 mW. The spectra were fitted by assuming Gaussian line shapes for peaks of different structural units. Abundances of structural units were calculated in terms of area fraction of peaks.

2.5. Computational Thermodynamic Analysis

The computational thermodynamic tool FactSage 7.3 was used, with FACT oxide database (FToxide) providing the data for solution and stoichiometric solid and liquid oxide phases. In this way, the effect of Na_2O addition on activities of slag components was determined, considering crystallization behavior.

3. Results and Discussion

3.1. Crystals Precipitation Sequence

Figure 2 shows DSC results for Sample 1 (12 wt.% Na_2O), which has the highest content of Na_2O . The thermograms show that the higher the cooling rate is, the bigger the exothermic peaks become. The crystals related to the peaks are indicated in **Fig. 2**; they were identified by XRD. Samples were prepared according to the thermal cycle which was adopted to identify the sequence of crystal precipitation.

Figure 3 shows XRD diffraction patterns for Sample 1. The

Table 1. Chemical composition of the samples investigated in the present work.

Sample	Composition (wt%)							
	CaO	SiO_2	Al_2O_3	MgO	Na_2O	TiO_2	B_2O_3	Basicity
1	35.5	35.5	7	2	12	5	3	1
2	36.50	36.50	7	2	10	5	3	1
3	37.5	37.5	7	2	8	5	3	1

Fig. 1. XRD pattern for Sample 2, which was quenched in water after melting at 1 400°C for 2 hours. All the samples investigated in the present work were prepared in this way. The pattern confirms glassy structure.

Fig. 2. DSC results for Sample 1 (12 wt% Na_2O) at different cooling rates from 1 400°C: 15, 20, 25 and 30°C/min. (Online version in color.)

thermal cycle to determine the sequence of crystal precipitation is: (i) heating glassy cullets from room temperature up to 1 400°C, with a heating rate of 5°C/min; (ii) cooling down to the target temperatures (1 175°C, 1 091°C, and 1 015°C, and room temperature) with a rate of 5°C/min; and water quenching (except for room temperature). Diffraction peaks of CaTiO_3 and Ca_2SiO_4 are found in the patterns quenched at 1 015°C and 1 091°C, while only diffractions peaks of

Fig. 3. XRD diffraction patterns for Sample 1 (12 wt% Na_2O), after going through the thermal cycle which was adopted to identify the sequence of crystal precipitation. (Online version in color.)

Ca_2SiO_4 are found in the pattern quenched at 1 175°C. When cooling to room temperature the crystal NaAlSiO_4 was found in diffraction pattern, together with CaTiO_3 and Ca_2SiO_4 . Thus, the first crystal for Sample 1 is Ca_2SiO_4 , followed by CaTiO_3 , and finally NaAlSiO_4 , as slag is gradually cooled.

The sequence of crystal precipitation for Sample 1 was also confirmed by SEM-EDS. For the sample quenched from 1 175°C, **Fig. 4(a)** shows some dark grey crystals, whose elemental composition corresponds to Ca_2SiO_4 , indicated by number 1. When quenching from 1 091°C, **Fig. 4(b)** shows grey crystals (Ca_2SiO_4) and some light grey crystals, indicated by number 2 (CaTiO_3); moreover, the Ca_2SiO_4 crystals are bigger because quenching temperature is lower. **Figure 4(c)** shows that the number and size of Ca_2SiO_4 and CaTiO_3 crystals increase further when quenching from 1 015°C. For the sample cooled down to room temperature at the rate 5°C/min, in addition to crystals of Ca_2SiO_4 and CaTiO_3 , which are still bigger, there are also NaAlSiO_4 crystals, according to **Fig. 4(d)**. Thus, the SEM-EDS results confirms the XRD results, regarding precipitation sequence.

For Sample 2 (10 wt.% Na_2O), DSC results are in **Fig. 5**. The thermogram shows two peaks, one for Ca_2SiO_4 , and the other for NaAlSiO_4 . XRD diffraction patterns and SEM micrographs are in **Figs. 6** and **7**, respectively. The analyzed samples were also submitted to the same thermal cycle: heating glassy cullets up to 1 400°C with a heating rate of 5°C/min, then cooling down to the target temperatures at 5°C/min–990°C and 950°C for this sample –, followed

Fig. 4. SEM micrographs for Sample 1 (12 wt% Na_2O), after going through the thermal cycle which was adopted to identify the sequence of crystal precipitation. Phases: 1 - Ca_2SiO_4 , 2 - CaTiO_3 , and 3 - NaAlSiO_4 . (a) quenching from 1 175°C, (b) quenching from 1 091°C, (c) quenching from 1 015°C, and (d) cooling down to room temperature at the rate 5°C/min. (Online version in color.)

by water quenching. Even with these relatively low target temperatures, only Ca_2SiO_4 was found. Thus, the first crystal is Ca_2SiO_4 , and it should be related to the first peak of the thermograms. For Sample 2 the precipitation sequence is the

Fig. 5. DSC results for Sample 2 (10 wt% Na_2O) at different cooling rates: 15, 20, 25 and 30°C/min. (Online version in color.)

Fig. 6. XRD diffraction patterns for Sample 2 (10 wt% Na_2O), after going through the thermal cycle which was adopted to identify the sequence of crystal precipitation. Quenching temperatures: 990°C and 950°C. (Online version in color.)

same: Ca_2SiO_4 , CaTiO_3 , and NaAlSiO_4 , as slag is cooled. Besides, it can be observed, when comparing Sample 1 (12 wt.% Na_2O) with Sample 2 (10 wt.% Na_2O), that crystallization temperature decreased.

For Sample 3 (8 wt.% Na_2O), which has the lowest content of Na_2O , Fig. 8 shows DSC results. Only one peak can be seen for all the cooling rates in the thermograms, in the range ~1 000–1 150°C. According to SEM and XRD data, Figs. 9 and 10, it is assumed that this peak is related to the primary crystallization of Ca_2SiO_4 . A possible explanation for the absence of the other peaks is the fact that the sample with lower Na_2O content will have lower tendency to crystallization, and consequently lower thermal effect, because reduction of the Na_2O content increases slag viscosity. It was reported in a previous study, with the Single Hot Thermocouple Technique, that it is possible to control crystallization kinetics in $\text{CaO-SiO}_2\text{-TiO}_2$ slags by changing the Na_2O content.¹¹⁾ It was observed that the incubation time for crystallization for $\text{CaO-SiO}_2\text{-TiO}_2\text{-Na}_2\text{O}$ slags is dramatically shortened by Na_2O addition; however, in that case, the analyzed slags had different TiO_2 and Na_2O contents, and lower basicity.

The glassy samples were submitted to the same adopted thermal cycle, with the target temperatures 996°C and

Fig. 8. DSC results for Sample 3 (8 wt% Na_2O) at different cooling rates: 15, 20, 25 and 30°C/min. (Online version in color.)

Fig. 7. SEM micrographs for Sample 2 (10 wt% Na_2O), after going through the thermal cycle which was adopted to identify the sequence of crystal precipitation. Quenching temperatures: (a) 990°C, and (b) 950°C. Phases: 1 - glass, 2 - Ca_2SiO_4 . (Online version in color.)

905°C, and then water quenching. At 996°C (end of precipitation according to Fig. 8), Ca_2SiO_4 and CaTiO_3 were found. At 905°C, NaAlSiO_4 was detected, but the thermal effect was not enough to form a peak in DSC curve.

The SEM images (Figs. 4, 7, and 10) show that the primary crystal – Ca_2SiO_4 – precipitates as dendrite. This reflects the fact that growth of Ca_2SiO_4 is controlled by diffusion from bulk slag to slag-crystal interface.¹⁵⁾

The diffusion coefficient of ions in a slag can be calculated from its viscosity according to the Stokes-Einstein equation:¹⁶⁾

$$D = \frac{k_B T}{6\pi r \eta} \dots\dots\dots (1)$$

where D is the diffusion coefficient of the ion in the slag, k_B is the Boltzmann constant, T is the absolute temperature, r is the radius of the ion in the slag, and η is the viscosity.

Viscosity for $\text{CaO-SiO}_2\text{-Na}_2\text{O}$ melts was measured;¹⁷⁾ it was found that increase of Na_2O content leads to a gradual decrease of viscosity. A similar conclusion was got when studying crystallization kinetics in $\text{CaO-SiO}_2\text{-TiO}_2$ slags, *i.e.*, increase of Na_2O content decreases viscosity; besides,

Fig. 9. XRD diffraction patterns for Sample 3 (8 wt% Na_2O), after going through the thermal cycle which was adopted to identify the sequence of crystal precipitation. (Online version in color.)

it was experimentally found that increase of Na_2O content decreases incubation times in TTT diagrams, and also raised the critical cooling rate.¹¹⁾ Moreover, in another work,¹⁸⁾ in which the fluorine-free system $\text{CaO-SiO}_2\text{-Na}_2\text{O-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-TiO}_2\text{-MgO-Li}_2\text{O}$ was studied, for a fixed CaO/SiO_2 ratio and nearly constant values of B_2O_3 , Al_2O_3 , TiO_2 , MgO and Li_2O , the content of Na_2O varied in the range 5.0–11.0 wt%; then, the effect of Na_2O content on crystallization behavior was discussed. It was found that the increase of Na_2O content raised the critical cooling rate and shortened the incubation time in TTT diagrams, promoting in this way the crystallization tendency for the analyzed slags.

3.2. Characteristic Temperatures

Crystallization temperatures and *liquidus* temperatures for the studied slags were got from thermograms. Crystallization temperature is defined as the onset temperature of the first exothermic peak, during cooling. With these temperatures, CCT curves were built and shown in Fig. 11. The higher the cooling rate is, the lower the crystallization temperature becomes; this fact can be explained considering that nucleation and growth rate of crystals are functions of viscosity (kinetics) and undercooling (thermodynamics). At higher cooling rate, more time is needed for initiating nucle-

Fig. 11. CCT curves for the investigated samples. (Online version in color.)

(a) quenching from 996°C

(b) quenching from 905°C

Fig. 10. SEM micrographs for Sample 3 (8 wt% Na_2O), after going through the thermal cycle which was adopted to identify the sequence of crystal precipitation. Quenching temperatures: (a) 996°C, (b) 905°C. Phases: 1 - glass, 2 - Ca_2SiO_4 , 3 - CaTiO_3 , 4 - NaAlSiO_4 . (Online version in color.)

ation and subsequent crystal growth. Therefore, the crystallization temperature correspondingly decreases.¹⁹⁾ Sample 1 has the highest crystallization temperatures for any cooling rate. It can be seen that crystallization temperature decreases when decreasing Na₂O content.

Liquidus temperatures were also determined from the thermograms, considering the peak temperature for the last endothermic peak when heating the samples. Moreover, undercooling for onset crystallization (ΔT) was calculated; it is defined as the difference between *liquidus* temperature (T_L) and crystallization temperature (T_C). The characteristic temperatures and undercooling values are in Table 2, for the higher cooling rate.

Undercooling for Sample 1 and Sample 2 are similar; this result indicates that the crystallization ability for them is near. However, undercooling for Sample 3 is much higher; this sample presents the lowest crystallization ability.

3.3. Relative Crystallinity of Ca₂SiO₄ as a Function of Temperature

To investigate the non-isothermal melt crystallization kinetics, the heat released during crystallization was measured through DSC. The first crystal of the precipitation sequence should have a special role related to heat transfer control, during continuous casting of steel. Because of that, crystallization kinetics of Ca₂SiO₄ was considered in the following part. Values of relative crystallinity as a function of temperature, $\alpha(T)$, were obtained from the thermograms through the Eq. (2). The kinetic curves for the investigated samples, at different cooling rates, are shown in Fig. 12.

$$\alpha(T) = \frac{\int_{T_0}^T (dH/dT) dT}{\int_{T_0}^{T_c} (dH/dT) dT} \dots\dots\dots (2)$$

where T , T_0 , and T_c are the instantaneous, onset, and end crystallization temperatures, respectively, and dH/dT is the heat flow rate determined by DSC.

3.4. Effective Activation Energy for Crystallization of Ca₂SiO₄

In Avrami equation, which holds for isothermal transformation, the crystallization rate constant has the overall nature because the macroscopic crystallization rate is generally determined by the rates of two processes, nucleation and nuclei growth. Because these two processes are likely to have different activation energies, the temperature dependence of the overall rate constant k can rarely be fit by a single Arrhenius equation, like Eq. (3), in a wide temperature range:

$$k = A \exp\left(\frac{-E}{RT}\right) \dots\dots\dots (3)$$

Table 2. Characteristic temperatures and undercooling values at the cooling rate of 30 K/min for the investigated samples. T_L : *liquidus* temperature, T_C : crystallization temperature, ΔT : undercooling.

	T_L (°C)	T_C (°C)	ΔT (°C)
Sample 1	1 155.3	1 125.9	29.4
Sample 2	1 132.7	1 102.2	30.5
Sample 3	1 137.8	1 003.7	134.1

where R is the gas constant, A is the preexponential factor, and E is the activation energy.

Nevertheless, Eq. (3) should hold reasonably well for a relatively narrow temperature interval that permits estimating the effective value of the activation energy. Therefore, by splitting the temperature region of non-isothermal crystallization into smaller regions, it is possible to determine the temperature dependence of the effective activation energy for non-isothermal crystallization.²⁰⁾

The differential isoconversional method recommended by Brown *et al.*,²¹⁾ which was originally proposed by Friedman,²²⁾ was employed to obtain the effective activation

Fig. 12. Relative crystallinity of Ca₂SiO₄ as a function of temperature for the investigated samples, at different cooling rates. (a) Sample 1 (12 wt% Na₂O), (b) Sample 2 (10 wt% Na₂O), and (c) Sample 3 (8 wt% Na₂O). (Online version in color.)

energy for crystallization (E_α) of Ca_2SiO_4 , at a given crystallization fraction, through the following equation:

$$\ln\left(\frac{d\alpha}{dt}\right)_\alpha = -\frac{E_\alpha}{RT_\alpha} + C \quad (4)$$

where $(d\alpha/dt)_\alpha$ is the instantaneous crystallization rate at the relative crystallinity α , T_α is the temperature at the relative crystallinity α , and C is a constant.

Plotting $\ln(d\alpha/dt)$ against $1/T_\alpha$ should give a straight line with slope $-E_\alpha/R$. The relation between relative crystallinity and E_α of Ca_2SiO_4 is shown in **Fig. 13**. By this method, E_α can be determined without knowing the form of the kinetic equation.

The E_α values for all samples and all crystalline fractions are negative, indicating that crystallization becomes slower with increasing temperature. That is to say, the crystallization of Ca_2SiO_4 during cooling follows anti-Arrhenius behavior, which was found in crystallization of polymers,²⁰⁾ traditional mold fluxes,²³⁾ and F-free mold fluxes.¹³⁾

For Sample 1, the one with the highest Na_2O content, E_α takes greater negative values at lower values of relative crystallinity, corresponding to temperatures closer to *liquidus*. The E_α increases as the extent of conversion rises and the temperature decreases. A physical explanation could be given in terms of the nucleation theory proposed by Turnbull and Fisher.²⁴⁾ According to this theory, the temperature dependence of the nucleation rate is given by

$$I = A \exp\left(-\frac{E_D}{k_B T}\right) \exp\left(-\frac{\Delta G^*}{k_B T}\right) \quad (5)$$

where I is the nucleation rate *i.e.* the number of nuclei per unit volume formed per unit time, A is the pre-exponential factor, E_D is the activation energy for diffusion across the phase boundary, and ΔG^* is the thermodynamic barrier to nucleation.

The E_D and ΔG^* exponential terms have opposing effects on the nucleation rate. The value of ΔG^* is inversely proportional to the degree of undercooling as follows:

$$\Delta G^* \sim \frac{1}{(T_L - T)^2} \quad (6)$$

At temperatures close to *liquidus*, E_D is nearly constant and ΔG^* can be very high. In this situation, the overall crys-

tallization rate is determined by the nucleation rate, and its temperature dependence is determined by Eq. (6).²⁰⁾ Once ΔG^* drops, the nucleation rate becomes controlled by the transport process, whose temperature dependence is determined by the E_D exponential term. This reasoning explains the increase of E_α with relative crystallinity for Sample 1.

For Sample 2, E_α values also increases as the extent of conversion rises and the temperature decreases. This sample has intermediate content of Na_2O (10%), intermediate values of E_α , and presents undercooling value 1.1°C higher than Sample 1. Thus, ΔG^* for Sample 2 should be lower than that for Sample 1.

Regarding Sample 3, the one with the lowest Na_2O content and the highest undercooling, E_α values remain nearly constant with relative crystallinity. Due to the very high undercooling this sample has relatively low value of ΔG^* , according to Eq. (6), thus the nucleation rate should be controlled mainly by the transport process. Assuming E_D as approximately constant, this would explain the shape of the curve for Sample 3.

Another expression for the nucleation rate I is the Eq. (7), which shows that the lower the viscosity is, the higher the nucleation rate becomes. Equation (8) states a similar dependence, since the crystal growth rate U is also inversely proportional to the viscosity η .²⁵⁾ Thus, by decreasing viscosity (through Na_2O addition for example), I and U increase.

$$I = \frac{Ah}{3\pi\lambda^3\eta} \exp\left(\frac{-W^*}{k_B T}\right) \quad (7)$$

where λ is the atomic jump distance, and h is Planck's constant.

$$U = \left(\frac{k_B T}{3\pi a_0^2 \eta}\right) \left[1 - \exp\left(\frac{\Delta G}{k_B T}\right)\right] \quad (8)$$

where a_0 is the interatomic separation distance, and ΔG is the thermodynamic barrier to crystal growth.

3.5. Modified Avrami Equation

Crystallization kinetics for isothermal transformations is described by the Avrami equation²⁶⁾ in double logarithm form (see Eq. (7)). Values of n corresponding to different nucleation and growth mechanisms can be seen in **Table 3**.

$$\ln(-\ln(1-\alpha)) = \ln Z_t + n \ln t \quad (9)$$

where α is the relative crystallinity, t is the crystallization time, Z_t is the crystallization rate constant, and n is the parameter which indicates crystallization mechanism.

However, Avrami equation cannot be directly used for non-isothermal crystallization. The parameter related to crystallization kinetics is corrected according to Eq. (10).

$$\ln Z_c = \ln Z_t / \beta \quad (10)$$

where β is the cooling rate.

This correction, which is based on the approximate theory formulated by Ziabicki (apud Jeziorny²⁷⁾), enables the characterization of non-isothermal crystallization kinetics, since Z_c should be constant for each material. Thus, the modified Avrami equation becomes Eq. (11).

$$\ln(-\ln(1-\alpha)) = \beta \ln Z_c + n \ln t \quad (11)$$

Half crystallization time ($t_{1/2}$) is calculated using Z_c and n

Fig. 13. Effective activation energy for crystallization (E_α) of Ca_2SiO_4 as a function of relative crystallinity for the investigated samples. (Online version in color.)

according to Eq. (12). The calculated Z_t , Z_c , n and $t_{1/2}$ values for the analyzed samples are in Table 4.

$$t_{1/2} = \left(\frac{\ln 2}{Z_c} \right)^{1/n} \dots \dots \dots (12)$$

As already mentioned in section 3.1, the SEM images show that the primary crystal precipitates as dendrite; this reflects the fact that growth of Ca_2SiO_4 is controlled by diffusion from bulk slag to slag-crystal interface. Therefore, the crystals grow three-dimensionally. From Table 3, the n value of 2.5 is related to the crystallization mode diffusion controlled, for constant nucleation rate and three-dimensional growth. It can be seen in Table 4 that the calculated values are near the value of 2.5.

3.6. Mold Slags Structure

Raman spectra for the investigated glassy samples are in Fig. 14. It is assumed that the structure for the vitreous samples at room temperature is like the structure of the molten mold slags. Before deconvolution, spectra backgrounds were subtracted. Then, for bands in the range 600–1 200 cm^{-1} , Gaussian deconvolution was applied, using a method

Table 3. Values of n for different nucleation and growth mechanisms.⁴⁰⁾

	Crystallization Mode	
	Diffusion controlled	Interfacial reaction controlled
<i>Constant nucleation rate</i>		
Three-dimensional growth	2.5	4
Two-dimensional growth	2	3
One-dimensional growth	1.5	2
<i>Instantaneous nucleation</i>		
Three-dimensional growth	1.5	3
Two-dimensional growth	1	2
One-dimensional growth	0.5	1
<i>Surface nucleation</i>	1	1

Table 4. Modified Avrami analysis results.

Sample	Cooling rate	n	Z_t	Z_c	$t_{1/2}$ (min)
Sample 1	15°C/min	2.64	0.48	0.95	0.89
	20°C/min	2.76	0.41	0.96	0.89
	25°C/min	2.23	1.21	1.01	0.85
	30°C/min	2.32	1.40	1.01	0.85
Sample 2	15°C/min	2.82	1.45	1.03	0.87
	20°C/min	2.48	1.52	1.02	0.86
	25°C/min	2.82	2.79	1.04	0.87
	30°C/min	2.16	4.01	1.05	0.83
Sample 3	15°C/min	2.78	0.05	0.82	0.94
	20°C/min	2.51	0.10	0.90	0.90
	25°C/min	2.60	0.21	0.94	0.89
	30°C/min	2.30	0.35	0.97	0.87

proposed in literature,^{28,29)} with correlation coefficient $r^2 \geq 0.999$. The envelope in the range 600–1 200 cm^{-1} is fitted by considering six Gaussian peaks. Deconvolution results are in Fig. 15.

The band around 700 cm^{-1} reflects the deformation vibration of O–Ti–O bonds and vibration of $[\text{TiO}_6]$ structural units.^{30–33)} The band in the range 826–836 cm^{-1} is attributed to the vibration of monomer or chainlike $[\text{TiO}_4]$ unit.^{30–32)} The bands around 860 cm^{-1} , 910 cm^{-1} , 960 cm^{-1} and 1 050 cm^{-1} reflect the vibration of Q^0 monomer unit (SiO_4^{4-}), Q^1 dimer unit ($\text{Si}_2\text{O}_7^{6-}$), Q^2 chain unit (SiO_3^{2-}), and Q^3 sheet unit, respectively.^{28–35)} Assignments for the Raman bands are summarized in Table 5.

The molar fraction of a silicate structural unit Q^i is estimated in the following way:

$$X_{Q^i} = \frac{A_{Q^i}}{\sum_{i=0}^3 A_{Q^i}} \dots \dots \dots (13)$$

where X_{Q^i} is the molar fraction of Q^i , and A_{Q^i} is the area of the Gaussian peak which corresponds to Q^i .

Molar fractions of Q^i for the investigated slags are in Table 6. Molar fractions of Q^0 and Q^1 increases and molar fractions of Q^2 and Q^3 decreases with increase of Na_2O content in slag, indicating that the degree of polymerization decreases with increase of Na_2O content.

The average number of bridging oxygen per silicate tetrahedron (Q) can be used to quantify the degree of polymerization of slags. The value of Q is also shown in Table 6; it is calculated with Eq. (14).

$$Q = \sum_{i=0}^4 X_{Q^i} \cdot i \dots \dots \dots (14)$$

Thus, the value for Q decreases with increase of Na_2O content.

The role of Na_2O in borosilicate melts varies with chemical composition. When $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ molar ratio is less than 0.5, Na_2O act as a charge compensator to BO_4 tetrahedron.^{38,39)} When $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ molar ratio is larger than 0.5, Na_2O would behave as a network modifying oxide and enter into the silicate and borate network causing the depolymer-

Fig. 14. Raman spectra for Sample 1 (12 wt.% Na_2O), Sample 2 (10 wt.% Na_2O), and Sample 3 (8 wt.% Na_2O). All the samples in glassy state and room temperature. (Online version in color.)

Fig. 15. Deconvolution results for the analyzed samples (glassy state and room temperature). (a) Sample 1 (12 wt% Na₂O), (b) Sample 2 (10 wt% Na₂O), and (c) Sample 3 (8 wt% Na₂O). (Online version in color.)

ization of silicate and borate network.^{38,39)}

Since Na₂O/B₂O₃ content in the present fluxes is larger than 2, additional Na₂O should act in a role of network modifying oxide. Accordingly, the increase of Na₂O content in slag would lead to the decrease of degree of polymerization and lead to more simple structural units such as Q⁰ and Q¹.

As discussed in previous sections, crystallization for the investigated samples was controlled mainly by diffusion from bulk slag to the slag-crystal interface. The increase of Na₂O content decreases the degree of polymerization, facilitating ions diffusion. Accordingly, crystallization was

Table 5. Assignments for Raman bands for the analyzed samples.

Raman shift (cm ⁻¹)	Raman assignments
~700	mixing of the [TiO ₆] structure unit and O–Ti–O deformation
~870	SiO ₄ ⁴⁻ stretching in monomer structure unit (Q ⁰), or Q ⁴ (4Al) structure unit
830–860	Vibration of monomer or chainlike [TiO ₄] unit
~860	SiO ₄ ⁴⁻ stretching with no bridging oxygen in monomer structure unit (Q ⁰)
~910	Si ₂ O ₇ ⁶⁻ stretching with one bridging oxygen in dimer structure unit (Q ¹)
~960	SiO ₃ ²⁻ stretching with two bridging oxygen in chain-like structure unit (Q ²)
~1 050	stretching with three bridging oxygen in sheet-like structure unit (Q ³)

Table 6. Distribution of structural units Qⁿ (n = 0, 1, 2, and 3) for Sample 1 (12 wt.% Na₂O), Sample 2 (10 wt.% Na₂O), and Sample 3 (8 wt.% Na₂O).

wt.% Na ₂ O	x(Q ⁰)	x(Q ¹)	x(Q ²)	x(Q ³)	Q
12	0.110	0.272	0.552	0.066	1.574
10	0.096	0.235	0.598	0.070	1.641
8	0.076	0.198	0.606	0.121	1.773

enhanced when adding Na₂O.

3.7. Computational Thermodynamic Analysis

For the simplified CaO–SiO₂–Al₂O₃–Na₂O system, which includes the main components of the mold fluxes samples of Table 1 (in this simplification, mass of each component not included in the system was not considered in the calculations), the calculated CaO and SiO₂ activities are shown in Table 7.

For rising Na₂O levels (up to 12 wt.%) an increase in CaO activity in the liquid slag phase is noticed while SiO₂ activity is simultaneously reduced. The precipitation reaction for Ca₂SiO₄ could be represented as:

where parentheses mean the component in slag. Accordingly, the thermodynamic driving force for Ca₂SiO₄ crystallization ΔG should be represented by supersaturation Π :⁴¹⁾

$$\Delta G = RT \left[\frac{a_{\text{CaO}}^2 a_{\text{SiO}_2}}{\frac{1}{K}} \right] \quad \dots\dots\dots (16)$$

where a_{CaO} and a_{SiO_2} denote the activity of CaO and SiO₂ respectively; K is the equilibrium constant for reaction (15); R is gas constant; T is temperature in Kelvin.

Therefore, the value of $(a_{\text{CaO}})^2 a_{\text{SiO}_2}$ could be calculated to investigate the thermodynamic driving force for Ca₂SiO₄ precipitation. As seen in Table 7, the value of $(a_{\text{CaO}})^2 a_{\text{SiO}_2}$ increases as Na₂O content rises. Accordingly, the thermodynamic driving forces for Ca₂SiO₄ precipitation increase with increase of Na₂O content in slag. From viewpoint of thermodynamics, the addition of Na₂O would be beneficial

Table 7. Results for the simplified system CaO–SiO₂–Al₂O₃–Na₂O, for Sample 1, Sample 2, and Sample 3 (analyzed compositions in Table 1), at 1 250°C.

Sample number	1 (12% Na ₂ O)	2 (10% Na ₂ O)	3 (8% Na ₂ O)
CaO activity in slag (a_{CaO})	2.03 E-3	1.48 E-3	1.35 E-3
SiO ₂ activity in slag (a_{SiO_2})	1.04 E-2	1.95 E-2	2.27 E-2
$(a_{\text{CaO}})^2 a_{\text{SiO}_2}$	4.28 E-7	4.27 E-8	4.137 E-8

to the nucleation and growth of Ca₂SiO₄ crystals.

4. Conclusions

Non-isothermal melt crystallization kinetics for F-free TiO₂-bearing mold fluxes was investigated, for three samples, with wt.% Na₂O of 12% (Sample 1), 10% (Sample 2), and 8% (Sample 3). The following conclusions can be drawn:

(1) During continuous cooling from melt, the crystals' precipitation sequence is Ca₂SiO₄, followed by CaTiO₃, and finally NaAlSiO₄, as slag is gradually cooled.

(2) The effective activation energy for non-isothermal crystallization E_a , as a function of relative crystallinity, for the first crystal which precipitates (Ca₂SiO₄), was experimentally determined with the Friedman differential isoconversional method. This method, which can be used without knowing the form of the kinetic equation, shows that the higher the Na₂O content is, the lower the E_a values become *i.e.* crystallization is enhanced.

(3) With the modified Avrami equation, the n value near 2.5 was calculated for all samples; this value is related to the crystallization mode diffusion controlled, with constant nucleation rate and three-dimensional growth. It agrees with the SEM micrographs, where dendritic structure is observed.

(4) Raman spectra study for the samples in glassy state shows that the increase of Na₂O content decreases the degree of polymerization, facilitating ions diffusion. This confirms the fact that crystallization was enhanced when adding Na₂O.

(5) For the simplified CaO–SiO₂–Al₂O₃–Na₂O base system, thermodynamic analysis shows that Na₂O addition causes an increase in CaO activity in the liquid slag while SiO₂ activity is reduced; The value of $(a_{\text{CaO}})^2 a_{\text{SiO}_2}$ increases with addition of Na₂O, which indicates that the thermodynamic driving force of Ca₂SiO₄ increases. From the viewpoint of thermodynamics, the addition of Na₂O would promote the precipitation of Ca₂SiO₄ crystals.

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