Effect of La_2O_3 on the Viscosity, Crystallization, and Structure of Calcium-silicate-based Mold Flux for Continuous Casting La-bearing FeCrAl Alloy

Lei FAN,^{1,2)} Chengjun LIU,^{1,2)*} Jie QI^{1,2)} and Maofa JIANG^{1,2)}

1) Key Laboratory for Ecological Metallurgy of Multimetallurgical Ores (Ministry of Education), Northeastern University, Shenyang, Liaoning Province, 110819 China.

2) School of Metallurgy, Northeastern University, Shenyang, Liaoning, Province, 110819 China.

(Received on March 22, 2021; accepted on May 6, 2021)

The influence of La_2O_3 on the properties and structure of calcium-silicate-based mold flux for continuous casting La-bearing FeCrAl alloy was studied through employing rotating viscometer, SEM-EDS, XRD, and Raman spectroscopy. The results showed that the viscosity of mold fluxes decreased with the increase of La_2O_3 content from 0 mass% to 15 mass%. The apparent activation energy for viscous flow decreased from 108.56 ± 1.96 kJ/mol to 87.29 ± 7.29 kJ/mol with increasing La_2O_3 . Deconvolution Raman analysis showed that with increasing La_2O_3 , the mole fraction of Q^3 units decreased, while that of Q^0 , Q^1 , and Q^2 units increased. Furthermore, the values of NBO/Si increased from 1.27 to 1.83 with the increase of La_2O_3 , which indicated that the degree of polymerization of melt structure was reduced and lead to the decrease of viscosity. During the cooling process, cuspidine ($\text{Ca}_4\text{F}_2\text{Si}_2\text{O}_7$) was the main crystalline phase in calcium-silicate-based mold fluxes. Nevertheless, when La_2O_3 was excessively added, a new phase of $\text{CaLa}_2(\text{SiO}_4)_2$ was formed owing to the charge balance of Ca^{2+} and La^{3+} on the simple structural units Q^0 ($[\text{SiO}_4]^{4-}$). Therefore, with increasing La_2O_3 can increase the break temperature and accelerate the formation of crystalline phases $\text{Ca}_4\text{F}_2\text{Si}_2\text{O}_7$ and $\text{CaLa}_2(\text{SiO}_4)_2$ at high temperature.

KEY WORDS: La_2O_3 ; properties; structure; calcium-silicate-based mold flux.

1. Introduction

FeCrAl alloy is a kind of functional material that converts electric energy into heat energy. The content of Al in FeCrAl alloy is up to 5 mass%, which can form compact Al_2O_3 film to improve oxidation resistance at high temperature. Hence, FeCrAl alloy is widely used in many fields, such as metallurgy, machine manufacturing, household appliances.¹⁾ However, FeCrAl alloy exists some prominent problems, such as low strength at high temperature, poor plastic toughness, and short service life.²⁾ To solve these problems, above 0.1 mass% rare earth La is added into FeCrAl alloy to improve its properties, which can play the role of microalloying.^{3,4)}

During the continuous casting process of FeCrAl alloy, the conventional mold flux $\text{CaO-SiO}_2\text{-Na}_2\text{O-CaF}_2$ was used. The flux-steel reaction between [Al] and (SiO_2) would occur inevitably, but the flux system could still meet the demands for continuous casting. Therefore, the traditional CaO-SiO_2 based mold flux was considered to be used for

continuous casting La-bearing FeCrAl alloy. However, when continuous casting La-bearing FeCrAl alloy, the problem of serious slag layer crust appeared and it was difficult to realize single furnace pouring. Through analyzing the slag phases, the composition of mold flux changed dramatically and a large number of high melting point phases containing La formed. So, the viscosity and crystallization characteristics of mold flux were deteriorated, so that it could not play the vital role of lubrication and heat transfer between the steel and the mold.^{5,6)} Overall, the occurrence of this problem was closely related to La_2O_3 entering into the slag, resulting from the floating of rare earth oxide inclusions and flux-steel reaction. Thus, in order to clarify the mechanism of deterioration of the properties of mold flux, it is of great significance to study the effect of La_2O_3 on the viscosity and crystallization properties of calcium-silicate-based mold flux.

There are some researches on the mold fluxes with different Re_xO_y contents. Cai⁷⁾ found that CeO_2 increased the melting temperature and decreased the viscosity because of the depolymerization of network structure in CaO-SiO_2 -based mold flux containing CaF_2 or B_2O_3 . Zhang⁸⁾

* Corresponding author: E-mail: liucj@smm.neu.edu.cn

investigated that La_2O_3 could increase the crystallization temperature and crystallization ratios of CaO-SiO_2 -4 mass% Al_2O_3 -8 mass% Na_2O -2 mass% Li_2O -4 mass% B_2O_3 slag. In Deng's study,⁹⁾ few contents introduced that high La_2O_3 content would reduce the viscosity of $\text{La}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ slag from the perspective of the changes of viscosity-temperature curves. However, both Zhang and Deng's work only focused on the effect of La_2O_3 on the crystallization and viscosity properties of CaO-SiO_2 based slags, respectively, while ignoring its important impact on the melt structure which affects the properties of mold fluxes greatly. Xi¹⁰⁾ studied the relationship between the content of Re_xO_y and viscosity in $\text{CaO-SiO}_2\text{-MnO-Li}_2\text{O-Ce}_2\text{O}_3$ dephosphorization slags. In recent studies, Qi^{11,12)} has devised $\text{CaO-Al}_2\text{O}_3\text{-Li}_2\text{O-Ce}_2\text{O}_3$ mold flux for continuous casting 253MA heat-resistant steel considering the strong reactivity between Ce and traditional CaO-SiO_2 -based mold flux and found that Ce_2O_3 could decrease the viscosity of slag and depolymerize the aluminate structure. In general, the effect of La_2O_3 on the relationship between structure and properties of calcium-silicate-based mold flux has not been sufficiently studied.

In this work, the influence of La_2O_3 on the viscosity, crystallization, and structure of calcium-silicate-based mold flux was studied in detail, and the results were beneficial to design the appropriate mold flux for continuous casting La-bearing FeCrAl alloy.

2. Experimental Methods

2.1. Sample Preparation

Pure chemical reagents CaO , SiO_2 , Li_2CO_3 , Na_2CO_3 , CaF_2 , La_2O_3 were synthesized and melted at 1 673 K in a graphite crucible for 60 min. During the melting process, Li_2CO_3 and Na_2CO_3 were decomposed to oxides. The molten liquid slag with homogeneous composition would be poured into the ice water to quench immediately. After drying, the as-quenched fluxes were ground into powder for measuring viscosity and structure. The chemical compositions of mold fluxes are listed in Table 1. On the basis of the analytical result of the compositions in S1, 5 mass%, 10 mass%, and 15 mass% La_2O_3 was extra added into the traditional CaO-SiO_2 -based mold fluxes to simulate La_2O_3 entering the slags, which was formed by the floating of rare-earth oxide inclusion or flux-steel reaction. To prove that the pre-melted samples were totally amorphous glassy state, the samples were tested by the X-ray diffraction (X Pertpro, Holland) and the results are shown in Fig. 1. It can be found that all the quenched samples are fully glassy phase and can be used for the detection of melt structure.

2.2. Viscosity Measurement

Viscosity was measured by the rotating cylinder method.¹²⁾ The schematic diagram of the rotating viscometer (RTW-16, China) is shown in Fig. 2. Approximately 140 g pre-melted slag was put into a graphite crucible. Then, the graphite crucible was heated to 1 623 K at the rate of 20 K/min and held for 30 min to obtain a homogeneous liquid slag in an electric resistance furnace under Ar atmosphere. A Mo spindle was inserted into the flux and rotated at the speed of 200 r/min. Meanwhile, the slag was cooled down with a rate of 3 K/

Table 1. The chemical compositions of mold fluxes (mass%).

	CaO	SiO ₂	Li ₂ O	Na ₂ O	CaF ₂	La ₂ O ₃
S1	10.41	41.28	5.65	15.51	27.16	—
S2	9.91	39.31	5.38	14.77	25.86	4.76
S3	9.46	37.52	5.14	14.10	24.69	9.09
S4	9.05	35.89	4.91	13.49	23.62	13.04

Fig. 1. XRD results of the pre-melted samples. (Online version in color.)

Fig. 2. The schematic diagram of the rotating viscometer. (Online version in color.)

min and the viscosity was measured. When the viscosity of flux reached 5 Pa·s, the measurement was stopped.

2.3. Crystalline Phases Analysis

To analyze crystalline phases during the solidification process of mold fluxes, slag samples were extracted and quenched with ice water when the viscosity of flux was 5 Pa·s with a large number of phases precipitation. The morphologies and chemical compositions of crystalline phases were analyzed by Scanning Electron Microscope equipped with an Energy spectroscopy microanalyzer (Phenom, Finland) and X-ray Diffractometer (X Pertpro, Holland).

2.4. Structural Analysis Using Raman Spectroscopy

In order to reveal the changes of structural units in mold flux, the as-quenched fluxes were analyzed by Raman spec-

troscopy (HR 800, B&W Tek, America). For the Raman analysis, the spectra concentrated in the range of 400–4 000 cm^{-1} with a resolution of 2 cm^{-1} . The excitation source was the 488 nm laser. Origin 8.5 software was used to deconvolute the Raman spectra.¹³⁾

3. Results and Discussion

3.1. Effect of La_2O_3 on the Viscosity Properties of Mold Fluxes

Viscosity-temperature curves of mold fluxes with different La_2O_3 contents during the cooling process are shown in Fig. 3. It can be observed that with the increase of La_2O_3 , the viscosity of mold fluxes decreases gradually at high temperature range from 1 500 K to 1 623 K. The values of viscosity at characteristic temperature 1 573 K, which can represent the viscosity of mold fluxes at high temperature¹⁴⁾ and the break temperature are listed in Fig. 4. As we can see that with the increase of La_2O_3 , the viscosity at 1 573 K decreases gradually. During the continuous casting process, the reduction of viscosity of mold flux may improve the function of lubricating solidified shell to a certain degree, but also leads to accelerating the crystallization ability of

mold flux.^{14,15)} The correlation will be discussed in section 3.3.

Break temperature is characterized as the temperature at which viscosity changes dramatically during the cooling process. When temperature is lower than the break temperature, the state of mold flux will transform from the fully liquid region to the solid-liquid coexistence region.^{16,17)} The viscosity of mold flux will increase abruptly due to the occurrence of crystallization. From Fig. 4, the break temperature of mold fluxes rises sharply with the increase of La_2O_3 , which suggests that the crystallization ability of mold fluxes is improved.

When temperature is above the break temperature of mold flux, the melt is a Newtonian fluid and follows an Arrhenius-type Eq. (1).^{18–20)}

$$\eta = AT \exp\left(\frac{E_a}{RT}\right) \dots\dots\dots (1)$$

Where η , A , E_a , R , T are the viscosity (Pa·s), constant, apparent activation energy (kJ/mol), gas constant (8.314 kJ/mol/K), and the absolute temperature (K). Furthermore, the activation energy for viscous flow is closely related to the viscosity, which is characterized as when particles in melt move from one equilibrium position to another, the energy required to overcome the resistance.²¹⁾ The apparent activation energy for viscous flow can be expressed by the slope of Eq. (1). The Arrhenius equation can be transformed into the following Eq. (2).

$$\ln\left(\frac{\eta}{T}\right) = \frac{E_a}{RT} + \ln A \dots\dots\dots (2)$$

The calculated values of E_a are shown in Fig. 5 and Table 2. As the increase of La_2O_3 , the apparent activation

Fig. 3. Viscosity-temperature curves of mold fluxes S1 through S4. (Online version in color.)

Fig. 4. Variation of viscosity at 1 573 K and break temperature of mold fluxes S1 through S4. (Online version in color.)

Fig. 5. Temperature dependence of viscosity of mold fluxes. (Online version in color.)

Table 2. The apparent activation energy for viscous flow of slags with different La_2O_3 addition.

Activation energy	S1	S2	S3	S4
E_a (kJ/mol)	108.56 ± 1.96	100.62 ± 2.31	93.85 ± 3.12	87.29 ± 7.29

energy for viscous flow decreases from 108.56 ± 1.96 kJ/mol to 87.29 ± 7.29 kJ/mol, which indicates that the energy barrier of viscous flow decreases. The result is consistent with the decrease of viscosity.

3.2. Effect of La_2O_3 on the Crystalline Phases of Mold Fluxes

Crystallization is one of the most significant properties of mold flux, which can affect the function of lubrication and heat transfer during the continuous casting process.²²⁾ Also, the variety of crystalline phase is an important indicator of the crystallization properties of mold flux. The morphologies of crystalline phases detected by SEM in mold fluxes with different La_2O_3 contents are shown in Fig. 6. The analysis of chemical compositions is listed in Table 3. It can be observed that with the increase of La_2O_3 , cuspidine ($\text{Ca}_4\text{F}_2\text{Si}_2\text{O}_7$) with the block or strip morphology is the main crystalline phase. However, with increasing La_2O_3 from 10 mass% to 15 mass%, the new crystalline phase of $\text{CaLa}_2(\text{SiO}_4)_2$ with light block shape forms at high temperature. The species of crystalline phases can be confirmed by XRD patterns as shown in Fig. 7. In general, increasing La_2O_3 not only accelerates the precipitation of cuspidine,

but also forms the crystalline phase $\text{CaLa}_2(\text{SiO}_4)_2$ at high temperature, indicating that crystallization ability of mold flux gets strong.

3.3. Effect of La_2O_3 on the Structure of Melts

Viscosity and crystalline phases are related to the slag structure. Figure 8 shows the Raman spectra of as-quenched mold fluxes with 0 mass%, 5 mass%, 10 mass%, and 15 mass% La_2O_3 . It can be observed that there are only two obvious peaks at $600\text{--}800\text{ cm}^{-1}$ and $800\text{--}1200\text{ cm}^{-1}$. The Raman wavenumbers between $600\text{--}800\text{ cm}^{-1}$ represent Si–O symmetry stretching vibration^{19,20)} and the wavenumbers between $800\text{--}1200\text{ cm}^{-1}$ correspond to $[\text{SiO}_4]$ -tetrahedral stretching vibration.^{23–26)} Moreover, the characteristic peak from 800 to 1200 cm^{-1} can be deconvoluted into different peaks representing the various silicate structural units.

The deconvoluted Raman spectra at $800\text{--}1200\text{ cm}^{-1}$ are shown in Fig. 9. The deconvoluted Raman peaks are fitted by Gaussian function with the correlation coefficient $R^2 > 99.5\%$. The assignments of different Raman shifts, which represent various structural units Q^i are listed in

Fig. 6. The morphologies and compositions analysis of crystalline phases.

Table 3. EDS analysis of crystallization phases of mold fluxes (atomic ratio%).

Phase	O	Ca	Si	Na	F	La	Estimated phase
P1	47.36	24.70	14.96	–	12.97	–	$\text{Ca}_4\text{F}_2\text{Si}_2\text{O}_7$
P2	47.61	25.48	16.31	–	10.60	–	$\text{Ca}_4\text{F}_2\text{Si}_2\text{O}_7$
P3	50.22	22.51	14.07	–	13.21	–	$\text{Ca}_4\text{F}_2\text{Si}_2\text{O}_7$
P4	45.21	9.17	21.98	–	–	23.64	$\text{CaLa}_2(\text{SiO}_4)_2$
P5	43.06	10.60	22.48	–	–	23.86	$\text{CaLa}_2(\text{SiO}_4)_2$
P6	51.64	21.23	14.70	–	12.43	–	$\text{Ca}_4\text{F}_2\text{Si}_2\text{O}_7$

a) Notice: the atomic number of Li is too small to be detected by EDS.

Fig. 7. XRD patterns of crystalline phases in mold fluxes with different La_2O_3 contents. (Online version in color.)

Fig. 8. Raman spectra for the as-quenched mold fluxes with different La_2O_3 contents. (Online version in color.)

Fig. 9. The deconvoluted Raman spectra of mold fluxes S1 through S4. (Online version in color.)

Table 4. The peak analysis of Raman spectra in the mold flux.

Sample	La ₂ O ₃ Concentrations (mass%)				Raman bands
	0	5	10	15	
Raman shift (cm ⁻¹)	—	—	858	860	Q ⁰ (Si) symmetric stretching ^{19,20,23,24}
	—	919	920	918	Q ¹ (Si) symmetric stretching ^{19,20,23,24}
	974	979	977	977	Q ² (Si) symmetric stretching ^{19,20,23,24}
	1 048	1 043	1 044	1 044	Q ³ (Si) symmetric stretching ^{19,20,23,24}

Table 4. The positions of the peaks around 860, 918, 977, and 1 044 cm⁻¹ represent Q⁰ ([SiO₄]⁴⁻) monomers, Q¹ ([Si₂O₇]⁶⁻) dimers, Q² ([SiO₃]²⁻) rings or chains, and Q³ ([Si₂O₅]²⁻) sheets (0, 1, 2, 3 represent the number of bridge oxygens in [SiO₄]-tetrahedral structural units)^{15,27} respectively. It can be observed obviously that the relative area of Q³ (Si) decreases, while that of Q⁰ (Si) and Q¹ (Si) increase, which implies that the network structure is depolymerized.

In order to analyze the silicate structural units quantitatively, the mole fraction of the [SiO₄]-tetrahedral structural units Qⁱ can be calculated by Eq. (3).^{28–31}

$$X_i = \frac{\left(\frac{A_i}{S_i}\right)}{\left(\sum_{i=0}^3 \frac{A_i}{S_i}\right)} \dots\dots\dots (3)$$

where X_i is the mole fraction of Qⁱ, A_i is the relative area fraction of Qⁱ, S_i is the Raman scattering coefficient and S_0 , S_1 , S_2 , and S_3 is 1, 0.514, 0.242, and 0.09, respectively.

In addition, the degree of polymerization of calcium-silicate-based mold fluxes can be expressed by the non-bridging oxygen per silicon NBO/Si.^{19,23,28} With the increase of NBO/Si, the number of non-bridging oxygen

Fig. 10. The mole fraction of Qⁱ and non-bridging oxygen per silicon (NBO/Si). (Online version in color.)

increases, resulting in the decrease of the degree of polymerization. The values of NBO/Si can be calculated through using the mole fraction of structural units Qⁱ as shown in Eq. (4).

$$\text{NBO/Si} = 4X_0 + 3X_1 + 2X_2 + X_3 \dots\dots\dots (4)$$

Figure 10 shows the calculation results of X_i and NBO/Si. As we can see that Q³ units are the main structural units in mold flux S1 with 0 mass% La₂O₃, which indicates that the network structure of the original mold flux is more polymerized. With the increase of La₂O₃ from 0 mass% to 15 mass%, the polymerized Q³ units have a significant decrease and the little-polymerized Q⁰, Q¹, and Q² units increase gradually. Meanwhile, the values of NBO/Si increase from 1.27 to 1.83 with increasing La₂O₃. Therefore, due to the decline of the degree of polymerization,^{19,32} the particles in melt need lower energy to overcome the movement resistance, indicating that the activation energy for viscous flow and the viscosity is reduced. In general, to further analyze the reasons for the depolymerization of melt structure, it can be found that the common properties of La₂O₃ include the melting point of 2 580 K,⁸ the boiling point of 4 473 K, and the density of 6.5 g/cm³. Also, the La–O bonds in La₂O₃ are prone to dissociate in the molten slag at high temperature, and since there is no 4 f electron layer in the La atom, it stably forms La³⁺ and O²⁻.^{33,34} The free O²⁻ ions released by La₂O₃ can break the bridge oxygen bonds (Si–O–Si) in the network structure, which decreases the degree of polymerization of CaO–SiO₂ based mold flux. So, La₂O₃ mainly plays the role of network modifier in this study. **Figure 11** shows the schematic illustration of the changes of structural units. When the content of La₂O₃ is 5 mass%, the portion of the Si–O–Si bonds in Q³ units are destroyed by free O²⁻ ions to form little-polymerized Q¹ and Q² units as shown in Figs. 11(a) and 11(b). With the increase of La₂O₃ from 5 mass% to 15 mass%, more free O²⁻ ions enter into molten slags, resulting in the reduction of Q³ units and the increase of Q⁰, Q¹, Q² units.

During the continuous cooling process, the crystalline phases of mold flux are related to the melt structure. With the increase of La₂O₃, more free O²⁻ ions break the polymerized Q³ units to form more Q⁰, Q¹, and Q² units, then

Fig. 11. The schematic illustration for the variation of structural units. (Online version in color.)

Table 5. Information of the unit cell in $\text{Ca}_4\text{F}_2\text{Si}_2\text{O}_7$.

System	Space Group	a	b	c	Z	Ref.
Monoclinic	P2 ₁ /c (no. 14)	10.93	10.57	7.57	4	36

the degree of polymerization of melt structure decreases. Therefore, it is more possible for cations (Ca^{2+} , La^{3+} , etc.) to migrate and collide with the simple silicate structural units to form crystals.¹⁵⁾ From the results of Figs. 6, 10, and 11, the degree of polymerization of melt structure decreases and Q^1 units are the main little-polymerized structural units when the content of La_2O_3 increases from 0 mass% to 15 mass%. Nagata³⁵⁾ reported that the CaF^+ ion pair improved by CaF_2 would combine with the non-bridging oxygen to form $\text{Ca}_4\text{F}_2\text{Si}_2\text{O}_7$ in silicate glass. In this paper, it can be observed that the CaF^+ incorporate with little-polymerized Q^1 ($[\text{Si}_2\text{O}_7]^{6-}$) units to form $\text{Ca}_4\text{F}_2\text{Si}_2\text{O}_7$. To clearly describe the phenomenon, the information of the unit cell in $\text{Ca}_4\text{F}_2\text{Si}_2\text{O}_7$ is listed in **Table 5** and the crystal structure of $\text{Ca}_4\text{F}_2\text{Si}_2\text{O}_7$ is depicted by the software Materials Studio 8.0 as shown in **Fig. 12**. It can be seen that the crystal structure of $\text{Ca}_4\text{F}_2\text{Si}_2\text{O}_7$ is mainly composed by Ca^{2+} , F^- and Q^1 ($[\text{Si}_2\text{O}_7]^{6-}$) structural units, which demonstrates that CaF^+ formed by Ca^{2+} and F^- may balance the charges required by Q^1 ($[\text{Si}_2\text{O}_7]^{6-}$) structural units, thus combining to form $\text{Ca}_4\text{F}_2\text{Si}_2\text{O}_7$ phase. Moreover, when the content of La_2O_3 increases from 10 mass% to 15 mass%, the simpler structural units Q^0 ($[\text{SiO}_4]^{4-}$) increase gradually. The $[\text{SiO}_4]^{4-}$ -tetrahedral structural unit is stable, in which the four electrons in the outermost layer of the Si atom combine with the electrons of four oxygen atoms to form Si–O bonds. Since the Q^0 ($[\text{SiO}_4]^{4-}$) structural unit has four negative charges, more positively charged cations are needed to balance the charges and maintain electric neutrality. Hence, Ca^{2+} and La^{3+} will be easy to combine with the simple structural units Q^0 ($[\text{SiO}_4]^{4-}$) to form the crystalline

Fig. 12. Crystal structure of $\text{Ca}_4\text{F}_2\text{Si}_2\text{O}_7$. (Online version in color.)

phase $\text{CaLa}_2(\text{SiO}_4)_2$ at high temperature. In summary, with the increment of La_2O_3 in molten slag, the degree of polymerization of melt structure decreases and the crystallization ability is improved.

4. Conclusions

The effect of La_2O_3 on the viscosity, crystallization, and structure of calcium-silicate-based mold flux for continuous casting La-bearing FrCrAl alloy was studied. The main findings are summarized as follows:

(1) With the increase of La_2O_3 content, the apparent activation energy for viscous flow of mold fluxes decreases from 108.56 ± 1.96 kJ/mol to 87.29 ± 7.29 kJ/mol and the values of NBO/Si increase from 1.27 to 1.83, which is consistent with the decrease of viscosity.

(2) The results of XRD and SEM-EDS show that

$\text{Ca}_4\text{F}_2\text{Si}_2\text{O}_7$ is the main crystalline phase in calcium-silicate-based mold fluxes. Excessive addition of La_2O_3 can accelerate the formation of the new phase of $\text{CaLa}_2(\text{SiO}_4)_2$ at high temperature.

(3) The deconvoluted Raman spectra analysis indicates that the free O^{2-} ions dissociated from La_2O_3 break the network formed by Si–O–Si bonds in $[\text{SiO}_4]$ -tetrahedral structure. The changes of melt structural units from polymerized Q^3 units to little-polymerized Q^0 , Q^1 , and Q^2 results in the decrease of the degree of polymerization. Therefore, the viscosity decreases and the crystalline phases $\text{Ca}_4\text{F}_2\text{Si}_2\text{O}_7$ and $\text{CaLa}_2(\text{SiO}_4)_2$ are accelerated to form owing to the charge balance of cations.

Acknowledgements

This work was supported by the Natural Science Foundation of China (grant number U1908224, 51874082, 51904064) and China Postdoctoral Science Foundation (grant number 2019M661114). The authors gratefully acknowledge the supports.

REFERENCES

- 1) W. J. Quadakkers, A. Elschner, W. Speier and H. Nickel: *Appl. Surf. Sci.*, **52** (1991), 271. [https://doi.org/10.1016/0169-4332\(91\)90069-V](https://doi.org/10.1016/0169-4332(91)90069-V)
- 2) Z. B. Teng: New Edition Manual of Metal Materials, Science Press, Beijing, (1994), 5.
- 3) E. Grundy: *Mater. Sci. Technol.*, **3** (1987), 782. <https://doi.org/10.1179/mst.1987.3.9.782>
- 4) X. Ma, Z. An, L. Chen, T. Mao, J. Wang, H. Long and X. Hongyan: *Mater. Des.*, **86** (2015), 848. <https://doi.org/10.1016/j.matdes.2015.07.156>
- 5) W. Yan, G. Zhang and J. Li: *Ceram. Int.*, **46** (2020), 14078. <https://doi.org/10.1016/j.ceramint.2020.02.208>
- 6) S. Zhang, M. Li, L. Zhu, Q. Wang, S. He and Q. Wang: *Ceram. Int.*, **45** (2019), 11296. <https://doi.org/10.1016/j.ceramint.2019.02.206>
- 7) Z. Cai, B. Song, Z. Yang and L. Li: *ISIJ Int.*, **59** (2019), 1242. <https://doi.org/10.2355/isijinternational.ISIJINT-2018-760>
- 8) F. Zhang, Y. Chen, Y. Wang, F. Dong and M. Wu: *J. Rare Earth.*, **29** (2011), 173. [https://doi.org/10.1016/S1002-0721\(10\)60426-7](https://doi.org/10.1016/S1002-0721(10)60426-7)
- 9) Y.-c. Deng, S.-l. Wu, Y.-j. Jiang and S.-q. Jia: *Metall. Mater. Trans. B*, **47** (2016), 2433. <https://doi.org/10.1007/s11663-016-0711-0>
- 10) X. Xi, S. Yang, C. Lai, J. Li and F. Wang: *Ironmaking Steelmaking*, **46** (2019), 968. <https://doi.org/10.1080/03019233.2018.1464284>
- 11) J. Qi, C. J. Liu, D. P. Yang, C. Zhang and M. F. Jiang: *Steel Res. Int.*, **87** (2016), 890. <https://doi.org/10.1002/srin.201500259>
- 12) J. Qi, C. Liu, C. Zhang and M. Jiang: *Metall. Mater. Trans. B*, **48** (2017), 11. <https://doi.org/10.1007/s11663-016-0850-3>
- 13) J. Qi, C. Liu and M. Jiang: *ISIJ Int.*, **58** (2018), 186. <https://doi.org/10.2355/isijinternational.ISIJINT-2017-252>
- 14) T. Wu, Q. Wang, S. He, J. Xu, X. Long and Y. Lu: *Steel Res. Int.*, **83** (2012), 1194. <https://doi.org/10.1002/srin.201200092>
- 15) L. Zhang, W. Wang and I. Sohn: *J. Non-Cryst. Solids*, **511** (2019), 41. <https://doi.org/10.1016/j.jnoncrysol.2019.01.035>
- 16) L. Zhang, W. Wang, S. Xie, K. Zhang and I. Sohn: *J. Non-Cryst. Solids*, **460** (2017), 113. <https://doi.org/10.1016/j.jnoncrysol.2017.01.031>
- 17) W. Wang, H. Shao, L. Zhou, H. Luo and H. Wu: *Ceram. Int.*, **46** (2020), 26880. <https://doi.org/10.1016/j.ceramint.2020.07.164>
- 18) J. Qi, C. Liu and M. Jiang: *J. Non-Cryst. Solids*, **475** (2017), 101. <https://doi.org/10.1016/j.jnoncrysol.2017.09.014>
- 19) M. S. Seo and I. Sohn: *J. Am. Ceram. Soc.*, **102** (2019), 6275. <https://doi.org/10.1111/jace.16456>
- 20) G. H. Kim and I. Sohn: *J. Am. Ceram. Soc.*, **102** (2019), 6575. <https://doi.org/10.1111/jace.16526>
- 21) D. Yang, F. Zhang, J. Wang, Z. Yan, G. Pei, G. Qiu and X. Lv: *J. Mater. Res. Technol.*, **9** (2020), 14673. <https://doi.org/10.1016/j.jmrt.2020.10.061>
- 22) C.-B. Shi, M.-D. Seo, J.-W. Cho and S.-H. Kim: *Metall. Mater. Trans. B*, **45** (2014), 1081. <https://doi.org/10.1007/s11663-014-0034-y>
- 23) J. Gao, G. Wen, T. Huang, P. Tang and Q. Liu: *J. Non-Cryst. Solids*, **435** (2016), 33. <https://doi.org/10.1016/j.jnoncrysol.2016.01.001>
- 24) G.-H. Kim, C.-S. Kim and I. Sohn: *ISIJ Int.*, **53** (2013), 170. <https://doi.org/10.2355/isijinternational.53.170>
- 25) Q. Gao, Y. Min and M. Jiang: *Metall. Mater. Trans. B*, **49** (2018), 1302. <https://doi.org/10.1007/s11663-018-1207-x>
- 26) J. Yang, J. Zhang, O. Ostrovski, C. Zhang and D. Cai: *Metall. Mater. Trans. B*, **50** (2019), 291. <https://doi.org/10.1007/s11663-018-1467-5>
- 27) J. Yang, Q. Wang, J. Zhang, O. Ostrovski, C. Zhang and D. Cai: *Metall. Mater. Trans. B*, **50** (2019), 2794. <https://doi.org/10.1007/s11663-019-01711-z>
- 28) L. Wang, C. Zhang, D. Cai, J. Zhang, Y. Sasaki and O. Ostrovski: *Metall. Mater. Trans. B*, **48** (2017), 516. <https://doi.org/10.1007/s11663-016-0816-5>
- 29) K. Zheng, J. Liao, X. Wang and Z. Zhang: *J. Non-Cryst. Solids*, **376** (2013), 209. <https://doi.org/10.1016/j.jnoncrysol.2013.06.003>
- 30) B. O. Mysen and J. D. Frantz: *Am. Mineral.*, **78** (1993), 699.
- 31) L. Zhang, W. Wang, B. Zhai and I. Sohn: *J. Am. Ceram. Soc.*, **103** (2020), 112. <https://doi.org/10.1111/jace.16714>
- 32) E. Gao, W. Wang and L. Zhang: *J. Non-Cryst. Solids*, **473** (2017), 79. <https://doi.org/10.1016/j.jnoncrysol.2017.07.029>
- 33) N. Elkhoshkhany, R. Essam and E. S. Yousef: *J. Non-Cryst. Solids*, **536** (2020), 119994. <https://doi.org/10.1016/j.jnoncrysol.2020.119994>
- 34) H. Doweidar and Y. B. Saddeek: *J. Non-Cryst. Solids*, **356** (2010), 1452. <https://doi.org/10.1016/j.jnoncrysol.2010.04.036>
- 35) K. Nagata and H. Fukuyama: *Steel Res. Int.*, **74** (2003), 31. <https://doi.org/10.1002/srin.200300158>
- 36) A. Van Valkenburg and G. F. Rynders: *Am. Mineral.*, **43** (1958), 1195.