Liquidus and Phase Equilibrium in $\text{CaO-SiO}_2\text{-Nb}_2\text{O}_5\text{-10\%La}_2\text{O}_3$ System

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(Received on September 28, 2017; accepted on December 13, 2017)

The reserves of niobium and rare earth element in the mineral resources in Bayan Obo ranked the forefront of the world, the thermodynamic information such as liquidus and phase equilibrium relations in the related slag system phase diagram were important to the comprehensive utilization of niobium and rare earth resources. In the current work, the pseudo-melting temperatures were determined by the single-hot thermocouple technique (SHTT) for the specified content of 10 to 50 pct Nb_2O_5 in the $\text{CaO-SiO}_2\text{-Nb}_2\text{O}_5\text{-10\%La}_2\text{O}_3$ phase diagram system. The 1 573 K, 1 623 K, and 1 673 K liquidus were first calculated based on the pseudo-melting temperatures according to thermodynamic equations in the specific primary crystal area. The phase equilibrium relations at 1 573 K and 1 473 K were determined experimentally using the high-temperature equilibrium followed by scanning electron microscope, X-ray diffraction, and energy dispersive X-ray spectroscopy analysis. The liquid phase, SiO_2 phase, CaO-SiO_2 phase, and $2\text{CaO-Nb}_2\text{O}_5$ phase were found in the experiment. Therefore, the phase diagram was constructed for the specified region of the $\text{CaO-SiO}_2\text{-Nb}_2\text{O}_5\text{-10\%La}_2\text{O}_3$ system. The experimental results have practical significance for further research on the related slag system, and for the comprehensive utilization of niobium and rare earth resources.

KEY WORDS: phase diagram; liquidus; phase equilibrium; SHTT; $\text{CaO-SiO}_2\text{-Nb}_2\text{O}_5\text{-10\%La}_2\text{O}_3$.

1. Introduction

China's Bayan Obo REE-Nb-Fe ore deposit in Inner Mongolia is a super large Rare Earth Element-Nb-Fe complex ore deposit, its rare earth reserves ranked first while the niobium reserves ranked second in the world.¹⁾ At present, a large number of valuable metal elements, such as rare earth and niobium, are abandoned to the tailings due to the immaturity of the related smelting process, resource cannot be used effectively.²⁾ So the uncertainty of thermodynamic property of correlative slag system hindered the research and development of the smelting and extracting process of elemental niobium and rare earth, even restricts the development of comprehensive utilization of REE-Nb-Fe ore deposit resources. As the most intuitive thermodynamic tool, the phase diagram contains much important thermodynamic information such as liquidus and phase equilibrium relations. Wilkins A L constructed the $\text{CaO-SiO}_2\text{-Nb}_2\text{O}_5$ phase diagram through experiments, the liquidus was determined basically in addition to the high CaO content area, and a ternary compound that named "Niocalite" was found in the ternary system.³⁾ In the rare earth (with lanthanum as a representative) related slag system, only the $\text{CaO-La}_2\text{O}_3$ and $\text{La}_2\text{O}_3\text{-SiO}_2$ binary phase diagrams can be referred

to. T. L. Barry found that $\text{CaO-La}_2\text{O}_3$ system is a simple binary eutectic phase diagram.⁴⁾ N. A. Toropov found three compounds exist in $\text{La}_2\text{O}_3\text{-SiO}_2$ system, they are La_2SiO_5 , $\text{La}_{4.67}\text{Si}_3\text{O}_{13}$ and $\text{La}_2\text{Si}_2\text{O}_7$ respectively.⁵⁾ However, the guidance of these simple binary or ternary system phase diagrams on the actual melting process of complex slag system is very finite. Until now, there are few studies on the slag system phase diagram contains both elemental niobium and rare earth.

The high-temperature equilibrium experiment is a scientific and effective static-method that commonly used in the determination of silicate system phase diagram.^{6–10)} The single-hot thermocouple technique (SHTT) is a dynamic-method to measure liquidus, the feasibility and accuracy of this method was determined by previous scholars. Junjie Shi applied SHTT to investigate the liquidus of the $\text{CaO-SiO}_2\text{-5 pctMgO-10 pctAl}_2\text{O}_3\text{-TiO}_2$ system.^{11–13)}

In the current work, the single-hot thermocouple technique (SHTT) was used to determine pseudo-melting temperatures of the $\text{CaO-SiO}_2\text{-Nb}_2\text{O}_5\text{-10\%La}_2\text{O}_3$ system, and then the liquidus was calculated according to the thermodynamic equations. Combined with a small number of high-temperature equilibrium experiments at 1 473 K and 1 573 K, the phase diagram for the specific region of the $\text{CaO-SiO}_2\text{-Nb}_2\text{O}_5\text{-10\%La}_2\text{O}_3$ system could be constructed. The results of current work can be helpful for further study on related slag system phase diagram, and for the compre-

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DOI: <http://dx.doi.org/10.2355/isijinternational.ISIJINT-2017-569>

hensive utilization of resources of elemental niobium and rare earth.

2. Experiment

2.1. Sample Preparation

Reagent grade oxides powders (provided by the Sinopharm Chemical Regent Co., Ltd) of CaO (99.99 pct pure), SiO₂ (99.99 pct pure), Nb₂O₅ (99.99 pct pure), and La₂O₃ (99.99 pct pure) were employed to synthesize the slags, which were calcined at 1 273 K for 14 400 seconds to evaporate the moisture and impurities, respectively. 0.015 kg mixtures were carefully weighed, fully mixed and pre-melted in air atmosphere using MoSi₂ furnace. The mixtures were placed inside platinum crucibles which were placed inside the hot zone of the furnace at 1 873 K for 21 600 seconds to completely homogenize the slags. The size of platinum crucibles for pre-melt has an upper diameter 0.04 m, bottom diameter 0.03 m, and height 0.038 m. The samples were then quenched into ice water, dried, crushed, and grinded to 200 meshes for further experiment.

The composition of the pre-melt slag was analyzed by X-Ray diffraction (XRD) and scanning electron microscope (SEM) to ensure the result of pre-melt experiment, the energy dispersive spectrometer (EDS) result was used as the initial composition of pre-melt slag, as listed in **Table 1**. Quenching by ice-water ensured that the quenched slags showed glassy phase, as shown in **Figs. 1** and **2**. The measure results showed that 1 873 K achieved the homogenization of slag samples. In the preparation of the samples, all the compositions have been aimed at in the 10 pct La₂O₃ section in the CaO-SiO₂-Nb₂O₅-10%La₂O₃ system. However, none of the experimental points lies exactly on the 10 pct La₂O₃ section, **Fig. 3** shows the projection of the pre-melted composition on the CaO-SiO₂-Nb₂O₅-10%La₂O₃ pseudo-ternary phase diagram.

Table 1. The EDS measured compositions of pre-melt slags, mass percent.

No.	R	CaO	SiO ₂	Nb ₂ O ₅	La ₂ O ₃
A1	0.57	28.30	49.24	12.24	10.23
B1	0.71	31.35	44.39	12.04	12.21
B2	0.70	26.89	38.52	22.42	12.16
B3	0.73	22.87	31.52	33.18	12.43
B4	0.72	17.98	24.90	45.28	11.84
C1	0.94	36.62	39.03	12.97	11.39
C2	0.95	32.29	34.02	23.02	10.67
C3	0.93	26.90	29.07	32.91	11.12
C4	0.90	22.61	24.99	42.57	9.83
C5	0.92	17.95	19.49	53.47	9.08
D1	1.13	28.36	25.04	36.27	10.34
D2	1.17	22.94	19.66	47.49	9.91
E1	1.51	32.10	21.31	36.10	10.48
E2	1.47	30.74	20.94	38.55	9.76
E3	1.60	25.70	16.05	47.59	10.66

2.2. Pseudo-Melting Temperature Determination

The SHTT technique was used to measure the pseudo-melting temperature of the slags in the current experiments. This method has been proven as an effective method in previous work.^{11–13)} The principle of SHTT technique has been described in detail and is briefly summarized in this study.^{14–16)}

The following method, as illustrated in **Fig. 4**, was used

Fig. 1. XRD result of typical pre-melt slag.

Fig. 2. Backscattered electron image of typical pre-melt slag.

Fig. 3. The projection of pre-melt compositions on CaO-SiO₂-Nb₂O₅-10 wt%La₂O₃ pseudo-ternary phase diagram, mass%.

for the judgements of the melting temperatures. During the experiments, approximately 10^{-5} kg slag was mounted on the tip of B-type thermocouple and heated rapidly at the rate of 5 to 10 K/s to a point about 100 K below the approximate melting temperature. As shown in Fig. 4(a), it was clearly seen that the slag was completely solid at this temperature. Then, the slag was heated continuously with a very slow rate of 0.1 K/s to the temperature shown in Fig. 4(b), at which the slag close to the tip of the thermocouple first became fluidity and transparent while the slag far away from the thermocouple tip was still solid phase, which meant that the slag around the thermocouple tip had already been liquid phase. The temperature of the state in Fig. 4(b) was found reproducible and taken as the melting temperature of the slag, which was called pseudo-melting temperature in this work. With the temperature further increased, the left slag gradually became liquid due to the heat transfer in Fig. 4(c). The whole melting process of the slag was recorded as a video file and the pseudo-melting temperature was then obtained.

Each measurement was performed at least three times to verify the reproducibility. The B-type thermocouple was calibrated against the pure NaF and CaF_2 to ensure the temperature accuracy within ± 1 K.

The problem of superheat and undercooling exist in all dynamic method of determination experiment of phase diagram.¹⁷⁾ In current work, the pseudo-melting temperatures of the slag samples was measured at 0.1 K/s, 0.5 K/s and 1 K/s respectively. And then, the true-melting temperature was obtained by regress the pseudo-melting temperatures measured at different heating rate, as shown in Fig. 5. “k” is the slope of the regression line in the equation “ $T=kx+T_{\text{true}}$ ” while “x” is the heating rate in the SHTT.

2.3. Equilibration Experiments

The MoSi_2 furnace used for the pre-melt was also used for the equilibrium experiments. The pre-melt slag

(0.0015 kg for each slag) was placed in the platinum crucible and placed into the hot zone of the MoSi_2 furnace. The curve of controlled temperature was shown in Fig. 6. The equilibrium temperature in the experiment was 1 473 K

Fig. 5. A schematic diagram of the melting temperature data regression.

Fig. 6. Curve of controlled temperature in high-temperature equilibrium experiment.

Fig. 4. Graphical representation for pseudo-melting temperature determination.

and 1 573 K. The equilibration time lasted 86 400 s based on experiences reported by other studies,^{18–22)} repeat experiments with 172 800 s were performed for some samples to check whether the equilibrium was achieved. There was no significant difference between the equilibrium phases with longer equilibration time. After the equilibrium, the sample was rapidly taken out from the furnace and quenched to 273 K by ice-water, the quenching process was completed in 2 s to ensure that all samples maintained the high temperature equilibrium phase composition. Quenched samples were then dried and embedded in epoxy resin and polished for analysis. Scanning electron microscope (SEM), X-ray diffraction (XRD), and energy dispersive X-ray spectroscopy (EDS) were used to identify the co-exist phase and analyze the composition of each sample.

3. Results and Discussion

3.1. Results of Pseudo-Melting Temperatures and Construction of the Liquidus

Table 2 shows the pseudo-melting temperature and true-melting temperature of each slag in the CaO-SiO₂-Nb₂O₅-10%La₂O₃ slags system.

We assumed the melting liquid phase in this oxide system as an ideal solution, it means that when the mixtures formed into a homogeneous solution, there was no change of enthalpy and volume. Therefore, concentration was used as activity in related calculation. According to the principles of thermodynamics, the melting temperature “*T*” and composition “*x*” in the specific primary crystal area conform to the relationship in Eq. (1).

$$x = \exp\left(\frac{A}{T} + B\right) \dots\dots\dots (1)$$

Table 2. Pseudo-melting temperatures and true-melting temperature of samples, K.

No	T _{0.1}			T _{0.5}			T ₁			T _{true}
	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd	
A1	1 609	1 610	1 611	1 614	1 612	1 613	1 628	1 629	1 633	1 605
B1	1 609	1 610	1 611	1 615	1 616	1 618	1 628	1 635	1 643	1 621
B2	1 575	1 570	1 575	1 578	1 581	1 582	1 586	1 586	1 585	1 573
B3	1 525	1 524	1 525	1 533	1 536	1 533	1 545	1 545	1 544	1 523
B4	1 636	1 634	1 636	1 643	1 644	1 644	1 648	1 647	1 647	1 637
C1	1 694	1 694	1 695	1 696	1 699	1 698	1 707	1 706	1 704	1 692
C2	1 638	1 646	1 637	1 649	1 651	1 650	1 663	1 656	1 659	1 639
C3	1 555	1 556	1 557	1 559	1 561	1 561	1 563	1 564	1 565	1 555
C4	1 557	1 555	1 553	1 559	1 560	1 558	1 570	1 569	1 569	1 553
C5	1 625	1 626	1 627	1 637	1 639	1 638	1 646	1 648	1 647	1 625
D1	1 568	1 565	1 566	1 571	1 569	1 572	1 582	1 585	1 588	1 563
D2	1 578	1 580	1 581	1 587	1 594	1 588	1 606	1 602	1 601	1 576
E1	1 621	1 622	1 621	1 626	1 627	1 628	1 640	1 639	1 639	1 618
E2	1 619	1 620	1 622	1 625	1 623	1 624	1 631	1 629	1 636	1 618
E3	1 621	1 622	1 623	1 631	1 629	1 629	1 644	1 641	1 643	1 619

In the Eq. (1), “*A*” represent $-\frac{\Delta H_{B(fus)}^\theta}{R}$, “*B*” is $\frac{\Delta H_{B(fus)}^\theta}{RT_m}$, “ $\Delta H_{B(fus)}^\theta$ ” is the molar Gibbs energy of pure solid B, “*T_m*” is the melting temperature and “*x*” is the variables of composition of the slag such as *w*(CaO), *w*(SiO₂) and *w*(Nb₂O₅). Based on Eq. (1), we found that

$$w(\text{CaO})/w(\text{SiO}_2) = \exp\left(\frac{A_{\text{CaO}}}{T} - \frac{A_{\text{SiO}_2}}{T} + B_{\text{CaO}} - B_{\text{SiO}_2}\right) \dots (2)$$

$$= \exp\left(\frac{A'}{T} + B'\right)$$

Equation (2) can be used as regression equation for the *w*(CaO)/*w*(SiO₂), while the Eq. (1) can be used for single composition such as *w*(Nb₂O₅). “*A*”, “*B*”, “*A'*” and “*B'*” are constants in the specific primary crystal area. Therefore, the melting temperature of the slag should be a single-valued function of the composition of the slag.

The composition of slag in Table 1 and the true-temperature of slag in Table 2 were combined to calculate the function of the liquidus. Sample B1, B2, B3 and B4 were taken as examples as follow. As shown in Fig. 7, the true-melting temperature changed gradually with the increase of *w*(Nb₂O₅) in the same condition that *w*(CaO)/*w*(SiO₂)=0.71. The melting temperature decreased from 1 621 K to 1 523 K as the *w*(Nb₂O₅) decreased from 33.18% to 12.04%. The melting temperature decreased regularly between B1, B2 and B3. However, the melting temperature of sample B4 increased abnormal as the *w*(Nb₂O₅) decreased gradually. According to the relevant thermodynamic principle,¹¹⁾ it can be confirmed that sample B1, B2 and B3 are in the same primary crystal area. And then, the function of liquidus were fitted by the *w*(Nb₂O₅) and melting temperature under the condition that *w*(CaO)/*w*(SiO₂)=0.71, the result is shown in Eq. (3).

$$w(\text{Nb}_2\text{O}_5) = \exp\left(\frac{24\,356.31}{T} - 12.43\right) \dots\dots\dots (3)$$

The fitting processes at other contents of *w*(Nb₂O₅) and *w*(CaO)/*w*(SiO₂) were done by the same way. Finally, the regressive equations were established for the composition investigated in the present work as shown in Table 3.

Fig. 7. The relation of temperature *T* with *w*(Nb₂O₅) for *w*(CaO)/*w*(SiO₂)=0.71.

Table 3. The parameters in the formulas of liquidus under different composition conditions.

Composition condition	Calculation formula	Applicable composition range		r^2
$w(\text{Nb}_2\text{O}_5)=12\%$	$w(\text{CaO})/w(\text{SiO}_2) = e^{\left(\frac{-13\,681.08}{T}+8.03\right)}$	$R_{\min}=0.57$	$R_{\max}=0.94$	0.97
$w(\text{Nb}_2\text{O}_5)=35\%$	$w(\text{CaO})/w(\text{SiO}_2) = e^{\left(\frac{-16\,032.64}{T}+10.31\right)}$	$R_{\min}=0.93$	$R_{\max}=1.51$	0.98
$w(\text{Nb}_2\text{O}_5)=45\%$	$w(\text{CaO})/w(\text{SiO}_2) = e^{\left(\frac{-20\,902.36}{T}+13.39\right)}$	$R_{\min}=0.90$	$R_{\max}=1.60$	0.99
$w(\text{CaO})/w(\text{SiO}_2)=0.71$	$w(\text{Nb}_2\text{O}_5) = e^{\left(\frac{24\,356.31}{T}-12.43\right)}$	$w(\text{Nb}_2\text{O}_5)_{\min}=12.04\%$	$w(\text{Nb}_2\text{O}_5)_{\max}=33.18\%$	0.99
$w(\text{CaO})/w(\text{SiO}_2)=0.94$	$w(\text{Nb}_2\text{O}_5) = e^{\left(\frac{15\,139.28}{T}-6.22\right)}$	$w(\text{Nb}_2\text{O}_5)_{\min}=12.97\%$	$w(\text{Nb}_2\text{O}_5)_{\max}=32.91\%$	0.97

Fig. 8. The phase diagram for the specific area in the CaO-SiO₂-Nb₂O₅-10%La₂O₃ system, mass%.

Based on the regressive equations, the liquidus of 1 573 K to 1 673 K of the CaO-SiO₂-Nb₂O₅-10%La₂O₃ system were calculated, as shown in **Fig. 8**. For example, when the $w(\text{CaO})/w(\text{SiO}_2)$ is 0.71 and T is 1 573 K, the $w(\text{Nb}_2\text{O}_5)$ can be calculated from formula $w(\text{Nb}_2\text{O}_5) = e^{\left(\frac{24\,356.31}{T}-12.43\right)}$, which is 21.20%. And then, combine $w(\text{CaO})/w(\text{SiO}_2)=0.71$ and $w(\text{La}_2\text{O}_3)=10\%$, the composition of liquid point at 1 573 K with $w(\text{CaO})/w(\text{SiO}_2)=0.71$ can be determined. Other liquid points in **Fig. 8** can be calculated in the same way. The liquidus temperature increases when $w(\text{CaO})/w(\text{SiO}_2)$ increases and the shape of liquidus are similar to each other from 1 573 K to 1 673 K.

3.2. Estimation of Equilibrium Phase

Totally 9 samples, as the soft dots in **Fig. 9**, were selected for equilibrium experiment at 1 473 K or 1 573 K to detect the primary crystal phase in the phase diagram. **Table 4** shows the corresponding pre-slag composition. The SEM micrographs are shown from **Figs. 10(a)** to **10(i)** respectively. Three kinds of different two-phase equilibrium were found in the samples.

Sample B2 was selected for the high-temperature experiment at 1 473 K to identify the primary crystal phase in the low Nb₂O₅ content region. According to the SEM microphotograph, as shown in **Fig. 10(a)**, two phases were detected by SEM. Based on the EDS result, as shown in **Table 5**, it is easy to confirm that the black phase is CaO·SiO₂ and

Table 4. The experiment temperature and the EDS composition of equilibrium points.

No.	Equilibrium Temperature	CaO	SiO ₂	Nb ₂ O ₅	La ₂ O ₃
B2	1 473 K	26.89	38.52	22.42	12.16
B4	1 573 K	17.98	24.90	45.28	11.84
E1	1 573 K	32.10	21.31	36.10	10.48
E2	1 573 K	30.74	20.94	38.55	9.76
E3	1 573 K	25.70	16.05	47.59	10.66
M1	1 573 K	17.10	29.65	39.80	13.45
M2	1 573 K	20.01	41.64	28.54	9.80
M3	1 573 K	23.84	43.85	21.97	10.34
M4	1 573 K	21.28	40.19	28.48	10.06

Fig. 9. Equilibrium initial points for CaO-SiO₂-Nb₂O₅-10%La₂O₃ system (soft dots), mass%.

the deep gray phase liquid. Therefore, it can be determined that the primary crystals area B2 sample located in was CaO·SiO₂.

After the determination of primary crystal phase in low Nb₂O₅ content region, sample E1, E2 and E3 were selected for the high-temperature experiment at 1 573 K to identify the primary crystal phase in the high Nb₂O₅ content region. According to the SEM microphotograph shows in **Figs. 10(b)**, **10(c)**, and **10(d)**, two phases were detected in these three slags. Based on the EDS result shows in **Table 5**, it can be confirmed that the white phase was composed of

$2\text{CaO}\cdot\text{Nb}_2\text{O}_5$ and the gray phase liquid. At same time the composition of the liquid was obtained by EDS. Therefore, it can be determined that the primary crystal phase in related region area was $2\text{CaO}\cdot\text{Nb}_2\text{O}_5$.

At same time, sample B4, M1, M2, M3 and M4 were selected for research the effect of $w(\text{CaO})/w(\text{SiO}_2)$ on the primary crystal phase in the low and high Nb_2O_5 content regions. According to the SEM microphotograph, as shown

(a) Sample B2 at 1473K

(b) Sample E1 at 1573K

(c) Sample E2 at 1573K

(d) Sample E3 at 1573K

(e) Sample B4 at 1573K

(f) Sample M1 at 1573K

(g) Sample M2 at 1573K

(h) Sample M3 at 1573K

Fig. 10. Continued.

(i) Sample M4 at 1573 K

Fig. 10. SEM microphotographs of equilibrium phases at different temperature. (a) Sample B2 at 1 473 K, (b) Sample E1 at 1 573 K, (c) Sample E2 at 1 573 K, (d) Sample E3 at 1 573 K, (e) Sample B4 at 1 573 K, (f) Sample M1 at 1 573 K, (g) Sample M2 at 1 573 K, (h) Sample M3 at 1 573 K, (i) Sample M4 at 1 573 K.

in Figs. 10(e), 10(f), 10(g), 10(h), and 10(i), the five slags were all two-phase equilibrium at 1 573 K. Based on the EDS result, as shown in Table 5, it is easy to confirm that the black phase is SiO_2 and the gray phase liquid. Therefore, it can be determined that the primary crystals area B2 sample located in was SiO_2 . At same time the composition of the liquid was obtained by EDS. Therefore, it can be determined that the primary crystal phase in related region area became SiO_2 .

3.3. Presentation of the Phase Diagram

The phase co-exist relations in the specified region in previous work²³⁾ and the relative composition position in the current is shown in Fig. 11.

Coupling the equilibrium phase relations with the liquidus, a brief phase diagram of $\text{CaO-SiO}_2\text{-Nb}_2\text{O}_5\text{-10%La}_2\text{O}_3$ system with the predicted phase boundary lines (dashed lines) is depicted in Fig. 12. The higher $w(\text{CaO})/w(\text{SiO}_2)$ and low Nb_2O_5 content region is dominated by the $\text{CaO}\cdot\text{SiO}_2$

Table 5. EDS result of equilibrium phase in samples at different temperature.

No.	Temperature	Equilibrium phase	CaO	SiO ₂	Nb ₂ O ₅	La ₂ O ₃
B2	1 473 K	L	26.95%	37.74%	22.48%	12.83%
		$\text{CaO}\cdot\text{SiO}_2$	47.56%	52.44%	—	—
E1	1 573 K	L	32.76%	24.58%	30.63%	12.03%
		$2\text{CaO}\cdot\text{Nb}_2\text{O}_5$	26.82%	—	73.18%	—
E2	1 573 K	L	33.37%	23.48%	31.63%	11.52%
		$2\text{CaO}\cdot\text{Nb}_2\text{O}_5$	23.82%	—	76.18%	—
E3	1 573 K	L	25.54%	23.51%	39.60%	11.35%
		$2\text{CaO}\cdot\text{Nb}_2\text{O}_5$	27.17%	—	72.83%	—
B4	1 573 K	L	18.52%	25.17%	46.31%	10.00%
		SiO_2	—	100%	—	—
M1	1 573 K	L	19.95%	28.43%	40.60%	11.03%
		SiO_2	—	100%	—	—
M2	1 573 K	L	22.57%	34.22%	32.40%	10.80%
		SiO_2	—	100%	—	—
M3	1 573 K	L	25.38%	41.97%	22.05%	10.60%
		SiO_2	—	100%	—	—
M4	1 573 K	L	22.54%	35.22%	30.89%	11.34%
		SiO_2	—	100%	—	—

phase, while the domination phase changes $2\text{CaO}\cdot\text{Nb}_2\text{O}_5$ phase when Nb_2O_5 content decreases. As a comparison, the $\text{CaO}\cdot\text{SiO}_2$ phase and $2\text{CaO}\cdot\text{Nb}_2\text{O}_5$ phase becomes the SiO_2 phase as the decrease of $w(\text{CaO})/w(\text{SiO}_2)$ whether in high or low Nb_2O_5 content region.

From the independent region that constructed by $\text{CaO}\cdot\text{SiO}_2$, $\text{CaO}\cdot\text{Nb}_2\text{O}_5$, $2\text{CaO}\cdot\text{Nb}_2\text{O}_5$, and $\text{La}_2\text{O}_3\cdot\text{Nb}_2\text{O}_5$ determined in the previous work and the tendency of the liquidus of $\text{CaO}\cdot\text{SiO}_2$ and $2\text{CaO}\cdot\text{Nb}_2\text{O}_5$ in the $\text{CaO-SiO}_2\text{-Nb}_2\text{O}_5\text{-10%La}_2\text{O}_3$ pseudo-ternary phase diagram in present work, it can be confirmed that the liquidus proved to be out-

Fig. 11. Phase co-exist relations and the relative composition position in the $\text{CaO-SiO}_2\text{-Nb}_2\text{O}_5\text{-La}_2\text{O}_3$ system, mass%.

Fig. 12. Brief phase diagram for CaO-SiO₂-Nb₂O₅-10%La₂O₃ system, mass%.

side of the independent region, that means a single temperature gradient will exist on the eutectic line of 2CaO·Nb₂O₅ and CaO·SiO₂ in the specified region on CaO-SiO₂-Nb₂O₅-10%La₂O₃ pseudo-ternary plane. This leads to it the liquidus will not cross at a eutectic point in current experiment temperature, and a reasonable judgment is that the temperature range of eutectic line on the 10%La₂O₃ pseudo-ternary plane is below 1 473 K, at same time it will not lower than 1 373 K due to the previous work.

4. Conclusion

The pseudo-melting temperatures were determined by the SHTT for the specified content of 10%–50% Nb₂O₅ in the CaO-SiO₂-Nb₂O₅-10%La₂O₃ phase diagram system, the 1 573 K, 1 623 K and 1 673 K liquidus was calculated respectively according to thermodynamic equations in the specific primary crystal area. The equilibrium phase relations at 1 473 K and 1 573 K were experimentally determined using the high-temperature equilibrium followed by XRD, SEM and EDS analysis. The liquid phase, SiO₂ phase, CaO·SiO₂ phase, and 2CaO·Nb₂O₅ phase were found in experiment. Therefore, the phase diagram was constructed for the specified region of the CaO-SiO₂-Nb₂O₅-10%La₂O₃ system.

Acknowledgements

This work was financially supported by the National Key R&D Program of China (No. 2017YFC0805105), National Natural Science Foundation of China (No. 51774087), the Fundamental Research Funds for the Central Universities of China (No. N162506002).

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