High-Temperature Mass Spectrometric Study of the CaO-TiO_2-SiO_2 System

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ABSTRACT

The CaO-TiO_2-SiO_2 system, containing about 10.5 and 16.5 mole % TiO_2 was examined at temperatures 1850-2200 K using the Knudsen effusion method. Partial pressures of SiO and O over samples were determined by the complete isothermal vaporization method and by the ion current comparison method at 1850 K. The SiO_2 activities in the CaO-TiO_2-SiO_2 system were found to have negative deviations from the ideality for all compositions except the sample with high SiO_2 concentration (CaO/SiO_2=0.6, 16 mole % TiO_2). Replacement of CaO with TiO_2 in slags of relatively high basicity ($x_{CaO}/x_{SiO2}>1$) causes a sharp increase in the SiO_2 activity and activity coefficient. In more acidic slags, addition of TiO_2 to the CaO-SiO_2 system does not have a strong effect on the SiO_2 activity and activity coefficient.

INTRODUCTION

Thermodynamic properties of the CaO-TiO_2-SiO_2 system are important from the viewpoint of smelting of titanium containing iron ores and titanium extraction processes.

According to Frohberg *et al.* /1,2/, addition of TiO_2 to the CaO-SiO_2 system increases the fluidity of slags. The viscosities of CaO-TiO_2-SiO_2 melts are in the range from 0.5 to 4 Pa s at temperatures of about 1800 K. The values of the specific electrical conductivity of this system at 1470-1740 K were found by Mori /3/ to be equal to 0.1-1.0 $Ohm^{-1}cm^{-1}$. It was concluded that these melts have the ionic conductivity, which increases with TiO_2 content at constant $CaO:SiO_2$ ratio and with increasing $CaO:SiO_2$ ratio at constant TiO_2 content.

It has been noted /4/ that various aspects of the behaviour of TiO_2 in slags can be accounted for by the specific structure of the electron shell of a titanium atom and by the high polarizability of the Ti^{+4} cation.

Thermodynamic properties of multi-component slags based on the CaO-TiO_2-SiO_2 system were studied by the gas-slag equilibrium technique with addition of FeO and MnO /4/, and MgO and Al_2O_3 /5/. The following oxides were identified in the condensed phase: Ti_2O, TiO, Ti_2O_3, Ti_3O_5, Ti_4O_7, TiO_2, Ti_5O_9 and $Ti_{10}O_{19}$.

Titanium partitioning between Ti^{3+} and Ti^{4+} valency states in the CaO-SiO_2-TiO_x system as a function of temperature, oxygen potential, titanium oxide content and $CaO:SiO_2$ ratio was examined by Tranell *et al.* /5/. It was found that the Ti^{3+}/Ti^{4} ratio decreases with the increasing CaO/SiO_2 ratio, increasing oxygen potential and decreasing temperature.

Phase equilibria in the CaO-TiO_2-SiO_2 system have been considered in Ref. 6 and in Ref. 7 using microprobe analysis (beam size of 200 μm). Sphene ($CaTiSiO_5$) with the melting point of 1655 K was the only ternary compound identified in the condensed phase of this system.

Literature data on the vaporization and thermodynamic properties of the CaO-TiO_2- SiO_2 system are extremely limited. The nitride capacity of this system, studied by Sakai and Suito /8/ at 1873K was found to be strongly affected by titanium oxide. They reported a significant loss of SiO_2 at low oxygen partial pressures ($\log p_{O2}$ = -11-(-14) atm). The CaO-Ti_2O_3-TiO_2 system was also examined by Tanabe and

Suito /9/ using the gas-slag equilibrium technique, and thermodynamic data on titanium oxides activities and slag nitride capacity were obtained.

Vaporization and thermodynamic properties of titanium oxides by high temperature mass spectrometric method were examined by Semenov /10/ and Gilles *et al.* /11-26/. The high temperature mass spectrometric study of the corresponding binary systems of the ternary CaO-SiO_2-TiO_x system was carried out in the following temperature ranges: for the CaO-SiO_2 system at 1933-2133 K /27/, for the TiO-TiO_2 /28-30/, Ti_2O_3 -TiO_2 /28-30/ and CaO-Ti_2O_3-TiO_2 /31/ systems at 1700-2200 K. These systems were vaporised from molybdenum effusion cells and the following species were identified in the vapour phase: (i) the CaO-SiO_2 system: Ca, CaO, SiO, SiO_2, $CaSiO_3$, and O_2; (ii) TiO-TiO_2, Ti_2O_3 -TiO_2 and CaO-Ti_2O_3-TiO_2 systems: Ti, TiO, TiO_2, and O_2. In both cases vaporization of the MoO_3 and MoO_2 species was also observed. Thus the composition of vapour over the systems studied included the same species as those over individual oxides CaO /27, 32/, SiO_2 /27,32/ and TiO, Ti_2O_3 and TiO_2 /32/. In the CaO-SiO_2 and CaO-Ti_2O_3-TiO_2 systems, negative deviations from the ideality were observed /27, 31/. The sign of deviations from the ideality in the TiO-TiO_2 and Ti_2O_3 -TiO_2 systems changes depending on the concentration of titanium in various oxidation states /28-30/.

The aim of the present study was identification of the vapour composition and determination of thermodynamic properties in the CaO-TiO_2-SiO_2 system using the high-temperature mass spectrometric method.

EXPERIMENTAL

Two series of samples were studied. In the first series, the titanium oxide content was 10.5 mole % and CaO/SiO_2 ratio was between 0.82 and 1.30. The second series of samples contained 16-17 mole % TiO_2 at CaO/SiO_2 ratio from 0.60 to 1.30. Preparation of samples was described elsewhere /5/. Chemical compositions of the samples, determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy, are presented in Table 1. The content of titanium in the reduced state (in the form of Ti_2O_3) in all samples was no more than 0.5 mole %.

This study was carried out using the MS1301 magnetic mass spectrometer, designed for Knudsen effusion high-temperature mass spectrometry of low volatile inorganic substances and manufactured by the Institute of Analytical Instrumentation of Russian Academy of Sciences, St Petersburg. The experimental set-up is described in detail in Ref. 33. The mass resolution (k 0.1) of the MS1301 mass spectrometer on the lines intensities level of 10% is 600. Experiments were carried out at the ionization energy of 12 and 25 eV. The sensitivity of the mass-spectrometer determined for the gold vapour was not less than 10^{-9} atm. A molecular beam from the Knudsen effusion cell was perpendicular to the electron beam from the ion source. The mass spectrometer was separated from the Knudsen effusion cell by a moving shutter to filter background peaks appearing in the mass spectrometer from the molecular beam. The experimental set-up included a special transmission mechanism, which allowed two effusion cells

Table 1

Chemical composition of samples of the CaO-TiO_2-SiO_2 system*

No of sample	Concentration, mole fraction		
	TiO_2	CaO	SiO_2
1	0.105	0.505	0.388
2	0.105	0.462	0.431
3	0.106	0.400	0.489
4	0.157	0.475	0.365
5	0.166	0.429	0.401
6	0.165	0.370	0.458
7	0.160	0.311	0.520

* Ti_2O_3 content in all samples studied was less than 0.5 mole %

to be held in the same block simultaneously, and therefore, to study two samples under the same experimental conditions. The samples were vaporised in the molybdenum effusion cell with the ratio of the vaporization area to the effusion orifice of 100:1. The effusion cells were put into molybdenum block and heated by the electron beam. The temperature was measured by the optical pyrometer EOP-66 with the vanishing glow lamp filament /33/, produced by the Kharkov Optical Plant, Ukraine. The temperature gradient between the top and bottom of the effusion cells was 10±5 K at the temperature 2000 K.

The experimental installation was calibrated using gold (99.999 wt%) and anhydrous CaF_2 (99.9 wt%).

RESULTS AND DISCUSSION

Calculation of partial pressures of species and thermodynamic properties

The vapour partial pressure (p_i), sublimation enthalpy $\Delta H_{s,T,i}$ and thermodynamic activity a_i of a component i at temperature T were calculated as follows /33-35/:

$$p_i = b\Sigma_j I_{ij} T/\sigma_i , \tag{1}$$

$$p_i = p_s I_{ij} T_i \sigma_s \gamma_s / I_s T_s \sigma_i \gamma_j , \tag{2}$$

$$p_i = (q_i/stL)(2\pi RT/M_i)^{-1/2} , \tag{3}$$

$$d\ln K_p/dT - H^o{}_{s,T,i}/RT^2 , \tag{4}$$

$$a_i = p_i/p_i^o , \tag{5}$$

where I_{ij} is the value of the j-ion current resulting from ionization of the i-component of the gaseous phase; σ_i is the ionization cross-section of vaporizing molecule; b is the device sensitivity constant; q_i is the mass of the substance vaporized from the surface area s in time t through the effusion orifice of the Knudsen cell with the Clausing coefficient L; M_i is the molecular mass of the i-component; R is the gas constant; K_p is the equilibrium constant for the reaction of vapourisation; H^o is the enthalpy of vaporization; index "o" corresponds to the component in the standard state. The ionization cross-section of molecules in Eqn.2, were calculated from the atomic ionization cross-sections /36,37/. Partial pressures were obtained by the ion current comparison method (Eqn. 2), and by the complete isothermal vaporization method (Eqn. 3).

Vaporization of standard samples of Au and CaF_2

Vaporization of gold (99.999 wt%) from molybdenum effusion cell was carried out in accordance with the recommendations of IUPAC (Division of Inorganic Chemistry Commission on High Temperatures and Refractory Materials) as a standard for measuring the vapour pressure and enthalpy of sublimation of materials /38/.

Data on the vapour pressure of gold were obtained by the complete isothermal vaporization method (Eqn. 3), from both molybdenum cells as a function of the complete vaporization time of gold at 1744 K (Fig. 1). The Au partial pressure was found to be $(4.3 \pm 0.6)\cdot 10^{-5}$ atm, which is in a good agreement with data recommended by Paule and Mandel /38/.

A CaF_2 sample was used as an additional standard. Data on thermodynamic properties of CaF_2 are summarized in Refs. 39,40. Vaporization of CaF_2 was studied by the Knudsen effusion mass spectrometric method in works /41,42/. The main ion species, identified in the vapour mass spectra of CaF_2, were Ca^+, CaF^+, which are the fragment ions, and CaF_2^+, which is the molecular ion. The fragment ion CaF^+ was the most intensive in the vapour mass spectra of CaF_2. At the ionization energy 25 eV and temperature 1613 K the ratio of intensities of Ca^+:CaF^+:CaF_2^+ in the CaF_2 vapour mass spectra was (0.0014 ± 0.0003): 1: (0.031±0.002). Vaporization isotherms at 1658 K used for the determination of CaF_2 partial pressures (Eqn. 3) are shown in Fig.2 . The further temperature increase is also indicated in Fig.2, which was done with the aim of vaporizing the substance completely from the cell. The calculated partial pressure of CaF_2 as a function of temperature is plotted in Fig.3. It agrees well with reference data /40/ also presented in Fig. 3. The sublimation enthalpy of CaF_2, calculated using plot of log ($T\ I_{CaF+}$) vs $1/T$ and Eqns. 1 and 4, was found to be (389.3±5.4) kJ/mole. Thus, CaF_2 partial pressure as a function of temperature is described by the following equation in the temperature range of 1600-1690 K :

$$\log p_{CaF2\ (atm)} = -(20422 \pm 283)/T + (13.99 \pm 0.03) \tag{6}$$

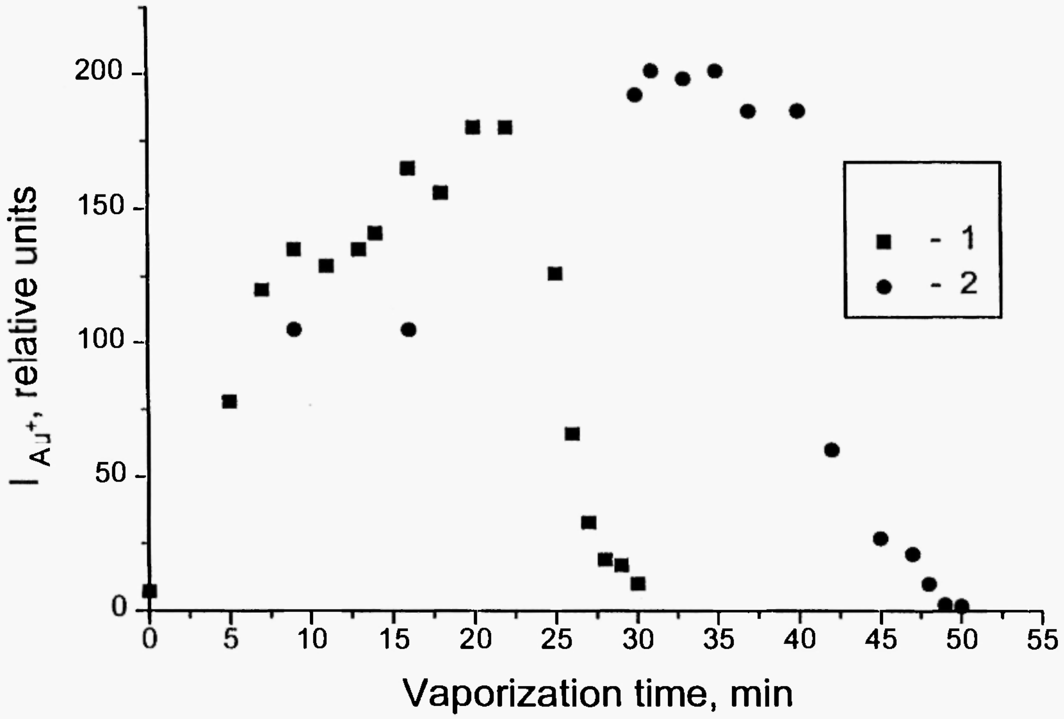

Fig. 1: Au$^+$ ion current from two molybdenum cells as a function of vaporization time of gold at 1744 K in calibration experiments: 1 - data obtained during vaporization from cell 1 and 2 - data from cell 2 .

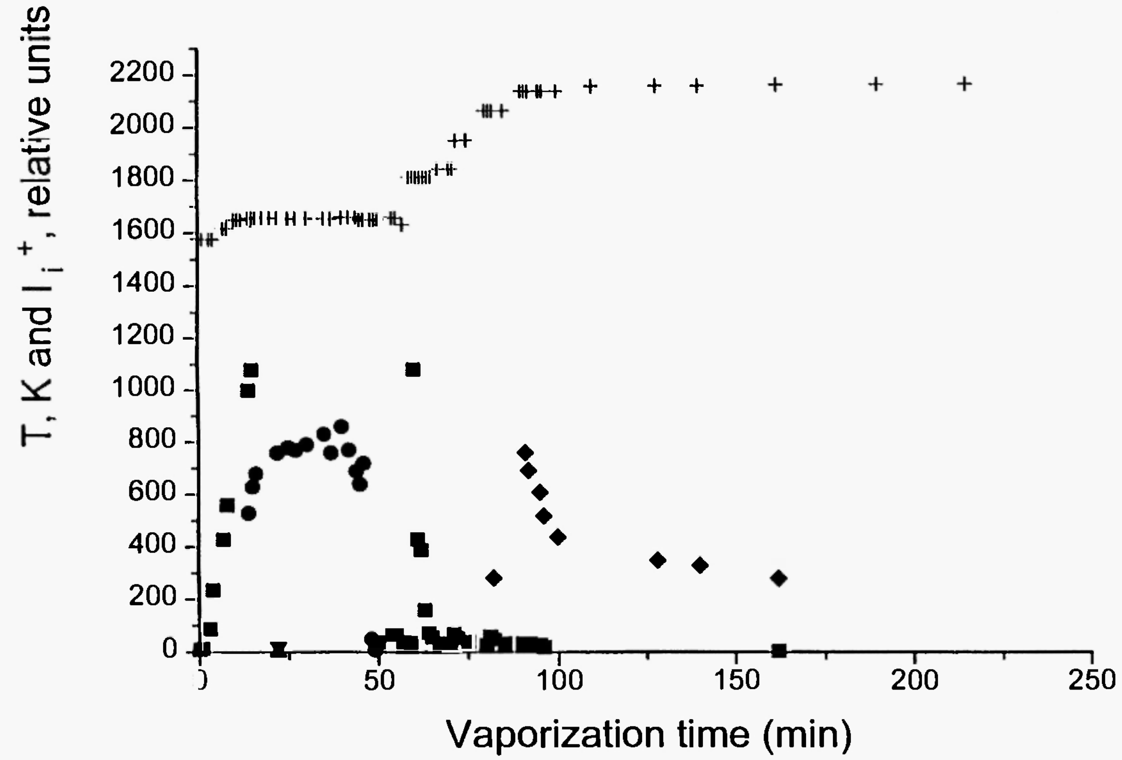

Fig. 2: Ca$^+$ (◆ - cell 1, ∇ - cell 2), CaF$^+$ (■ - cell 1, ● - cell 2), CaF$_2^+$ (Δ - cell 2) ion currents from two molybdenum cells as functions of the vaporization time of CaF$_2$ at 1658 K in calibration experiments. + - temperature change.

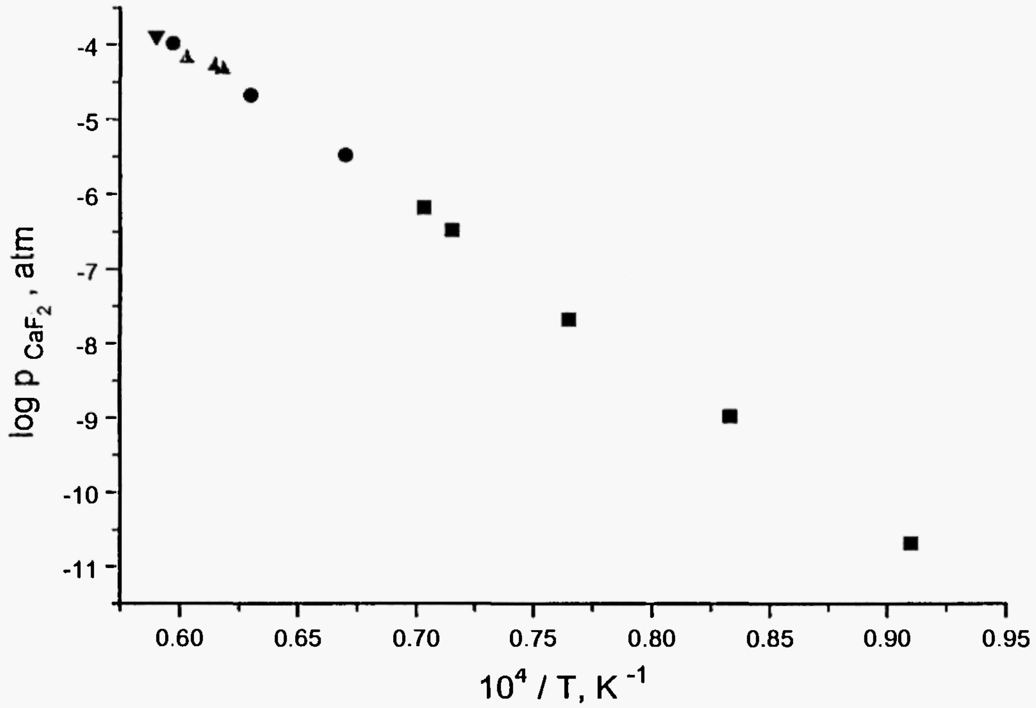

Fig. 3: Partial pressure of CaF_2 over pure CaF_2 as a function of temperature obtained in the present study (Δ) and recommended in Ref. 44: ■ the temperature range is 1100-1424 K; • -1424-1691 K; ∇ temperature is higher than 1691 K.

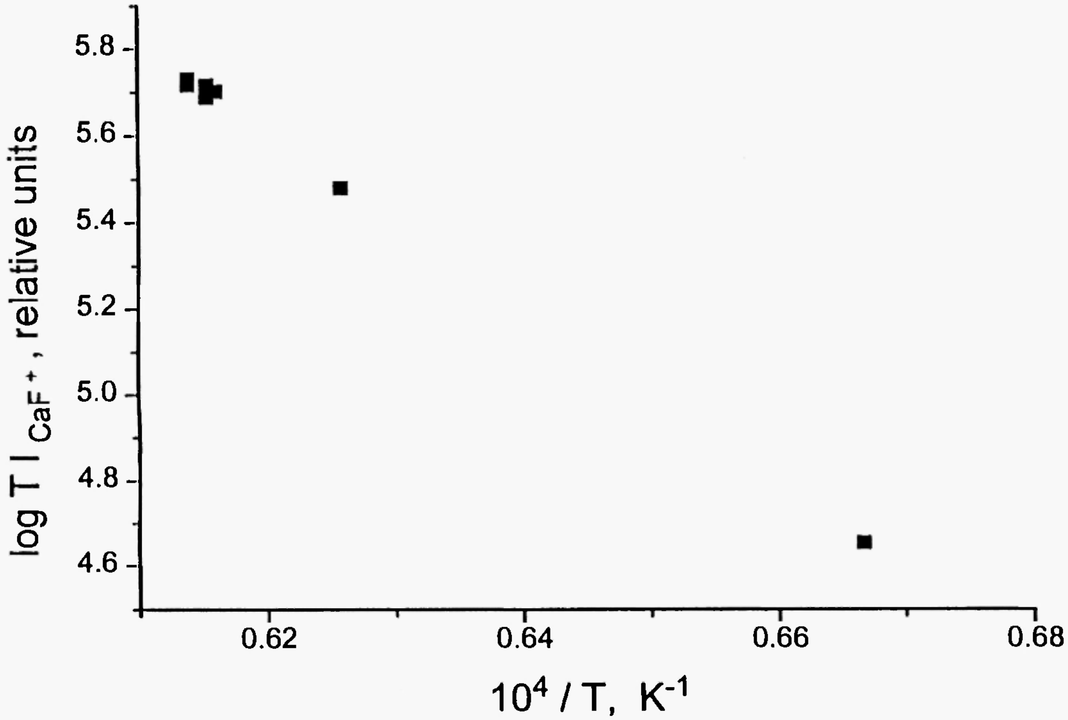

Fig. 4: Temperature dependence of the CaF^+ ion current in mass spectra of vapour over CaF_2 for the determination of vaporization enthalpy using Eqns. 1,4.

Table 2

Partial pressures of vapour species over pure SiO_2 as a function of temperature (vaporization from Mo- cells).

Vapour species	Temperature (K)	$\log p_i = -A/T + B$ (atm)		References
		A	B	
SiO	1805-1995	27525±833	10.53±0.43	Present study
	2000-2038	25680±2105	9.61±1.04	Present study
	1600-1800	23802±2110	6.58±1.73	Ref. 46
	1601-1754	18266±1617	3.66±0.96	Ref. 45
O	1805-1995	26972±971	5.62±0.43	Present study
	2000-2038	25822±1032	5.93±0.66	Present study
	1600-1800	25250±2140	6.55±1.03	Ref. 46
	1601-1754	29992±2539	9.63±1.51	Ref. 45
SiO_2	1833-1995	30710±510	8.46±0.47	Present study
	2000-2038	28771±669	7.60±0.64	Present study
	1996-2300	28834± 35	8.27±0.02	Ref. 40

Vaporization of pure silica

In the mass spectra of vapour over pure SiO_2, the following ions were identified at the ionization energy 25 eV in the temperature range 1700-2350 K: SiO^+, Si^+, SiO_2^+, MoO_3^+, and MoO_2^+. The ratio of currents of SiO^+:Si^+ ions was 1:0.14. This vapour mass spectra is in agreement with our previous results /27,43,44/ and the data from Ref. 32. The SiO^+ and SiO_2^+ ions are the parent ones and Si^+ is the result of fragmentation. Silica vaporizes according to the following reactions:

$$[SiO_2] = (SiO) + (O), \tag{7}$$

$$[SiO_2] = (SiO_2), \tag{8}$$

$$2(O) = (O_2). \tag{9}$$

The MoO_3^+ and MoO_2^+ ions in the vapour phase were formed as a result of interaction of Mo-cell with oxygen:

$$[Mo] + 3/2\ O_2 = (MoO_3)$$
$$(MoO_3) = (MoO_2) + (O). \tag{10}$$

(Throughout the paper, chemical formulae in round brackets correspond to components in the gas phase, while those in square brackets refer to the condensed phase.) Partial pressures of vapour species over SiO_2 were obtained by the complete isothermal vaporization method (equation 3), and by the ion current comparison method (equation 2) with the use of gold as a standard. The data on silica partial pressure as a function of temperature are presented in Table 2 in comparison with literature data /45, 46/, obtained under similar conditions, when vaporization was carried out from Mo-cells. Partial pressures of SiO_2 obtained at the present study are in agreement with data recommended in Ref. 40.

Vaporization of the CaO-TiO_2-SiO_2 system

Samples of 3-8 mg of the CaO-TiO_2-SiO_2 system were vaporized from the Knudsen cell. The standard sample of CaF_2 was vaporized simultaneously from the second effusion cell for determination of partial pressures of vapour species by the ion current comparison method (Eqn. 2) and to control the sensitivity of the mass spectrometer during experiments. At temperatures up to 1900 K the main vapour

Table 3

Partial pressures of SiO and O over samples of the $CaO-SiO_2-TiO_2$ system at 1850 K, obtained by the complete isothermal vaporization method, Eqn. 3, (I) and by the ion current comparison method, Eqn. 2, (II).

No of sample	Partial pressure, atm		
	$SiO*10^5$	$SiO*10^5$	$O*10^9$
	(I)	(II)	(II)
1	0.463	0.283	1.14
2	0.701	0.690	1.71
3	0.830	0.878	2.60
4	0.368	0.299	1.04
5	0.537	0.716	1.94
6	1.020	1.490	2.11
7	1.830	2.770	3.67

species in vapour were SiO, MoO_3 and MoO_2. Table 3 presents partial pressures of SiO over samples No 1-7 at 1850 K, obtained by the complete isothermal vaporization method (Eqn. 3), and by the ion current comparison method (Eqn. 2). Partial pressures of oxygen, presented in this table, were calculated from a ratio of MoO_3^+ and MoO_2^+ ion currents (I_{MoO3+}, I_{MoO2+}) using equilibrium (10):

$$pO = K_{o10} [I_{MoO3+} * \sigma (MoO_2)/I_{MoO2+} * \sigma (MoO_2)], \quad (11)$$

where K_{o10} is the equilibrium constant of reaction (10), calculated using data from Ref. 40. Partial pressures of Ca, TiO and TiO_2 evaluated by the ion current comparison method (Eqn. 2) at 1900 K were lower than 10^{-8} atm.

As a result of significant difference in the volatility between SiO, Ca, TiO and TiO_2 at 1850 K, initial compositions of the system changed during isothermal vaporization of samples. For example, Fig. 5 illustrates changes in concentrations of TiO_2 and SiO_2 in samples No 3 and No 5 of the $CaO-TiO_2-SiO_2$ system relative to the initial concentrations as a result of the selective vaporization of components in the temperature range 1500-2200 K, which was calculated by the complete isothermal vaporization method /47,48/.

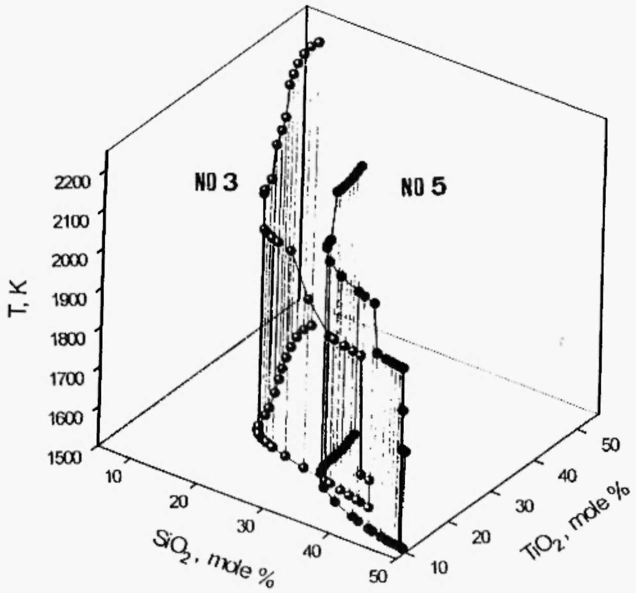

Fig. 5: Changes in concentrations of TiO_2 and SiO_2 in samples No 3 and No 5 of the $CaO-TiO_2-SiO_2$ system as a result of the selective vaporization of components in the temperature range 1500-2200 K determined by the complete isothermal vaporization method.

Experimental data for samples of changing composition were treated by the following method. The change in the composition of a sample after vaporization of some quantity of SiO$_2$ in the form of SiO, O and SiO$_2$ species was calculated as:

$$q_1 = q_o\,(1 - s_1/s_o), \qquad (12)$$

where q_1 is the fraction of the substance (SiO$_2$) evaporated by time t_1 from the initial sample; q_o is the quantity of this substance (SiO$_2$) in the sample before vaporisation; s_o is the area under the plot of the SiO$^+$ ion current as a function of time for the time of complete evaporation t; s_1 is the area under the same plot for time t_1. It was assumed that vaporization of a sample (SiO$_2$) eventually goes to completion as a result of gradually increasing temperature.

The quantity of remaining CaO and TiO$_2$ in the residual sample was calculated from the ratio of the areas s'_0 and s'_1 for CaO and TiO$_2$ from the ratio of the areas s''_0 and s''_1 by the same way. A sample for the experiment was taken of such a mass, to have the rate of change in the sample composition not greater than 0.01-0.04 mole fractions/hour, as required for the complete isothermal vaporization method /47,48/.

The accuracy of such calculation of partial pressures of vapour species in oxide systems was found to be satisfactory in an earlier study /49,50/ of the B$_2$O$_3$-SiO$_2$ and B$_2$O$_3$-Al$_2$O$_3$ systems.

Fig. 6 summarizes changes in concentrations of SiO$_2$ and TiO$_2$ in samples No 1-7 of the CaO-TiO$_2$-SiO$_2$ system during the selective vaporization of components, when the temperature of vaporization increased from 1550 to 2175 K. Enrichment of the condensed phase of the CaO-TiO$_2$-SiO$_2$ system with CaO and TiO$_2$ during vaporization is also presented on the phase equilibrium diagram /6/ for the all samples studied (Fig. 7). These data on the distillation of the CaO-TiO$_2$-SiO$_2$ system during vaporization can be useful in various high-temperature processes.

In the vapour mass spectra of the CaO-TiO$_2$-SiO$_2$ system (samples No 1-7, Table 1) the following ions were identified at the ionizing-electron energy of 25 eV in the temperature range of 1700-2350 K: Ca$^+$, TiO$^+$, TiO$_2^+$, Ti$^+$, SiO$^+$, SiO$_2^+$, Si$^+$, MoO$_2^+$, and MoO$_3^+$. The ratio of SiO$^+$/Si$^+$ ions was the same as in the mass spectra of vapour over pure SiO$_2$. The

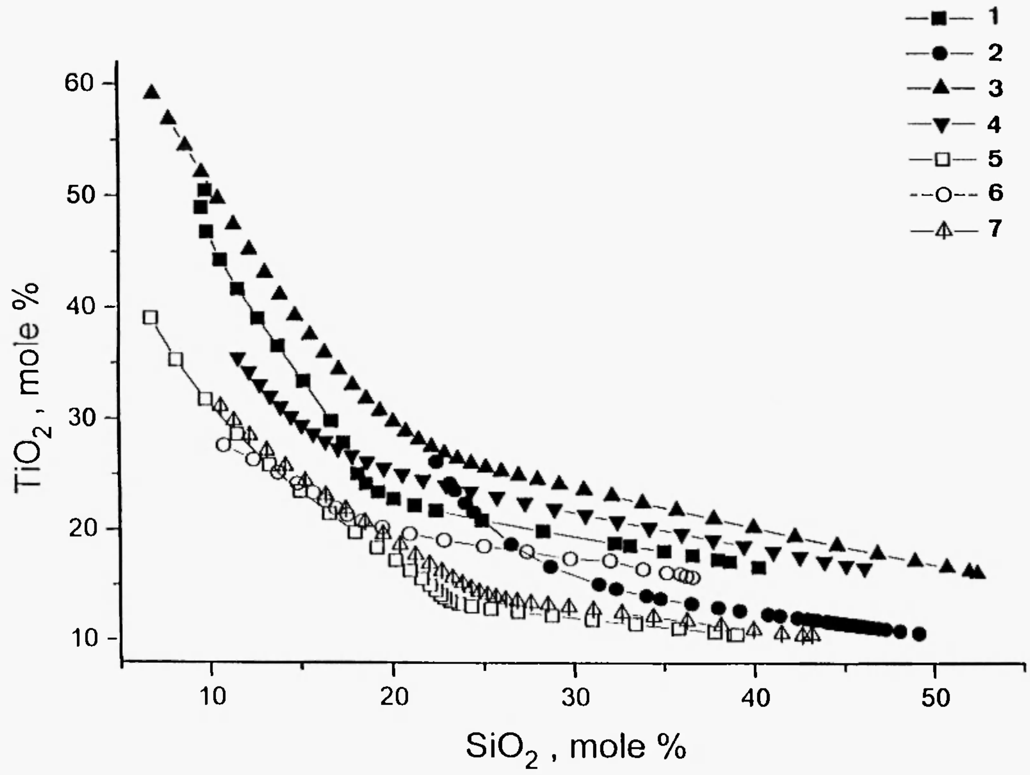

Fig. 6: Changes in concentration of SiO$_2$ and TiO$_2$ in samples No 1-7 of the CaO-TiO$_2$-SiO$_2$ system during the selective vaporization of components, when the temperature of vaporization increased from 1750 to 2175 K.

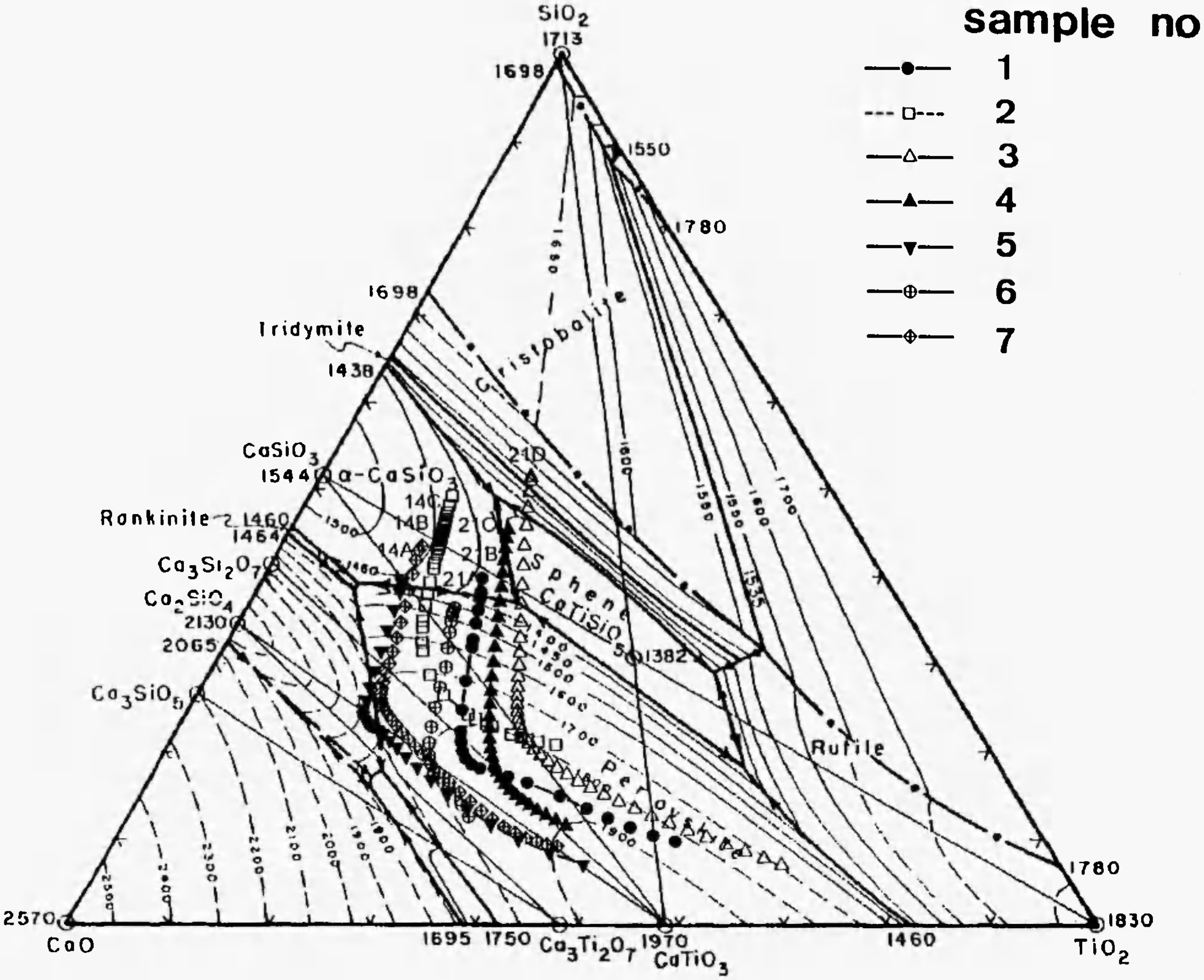

Fig. 7: Phase equilibrium diagram for the CaO-TiO_2-SiO_2 system from Ref. 10 with an indication of the changes in composition of samples No 1-7 during selective vaporization of components, when the temperature of vaporization increased from 1750 to 2175 K.

intensity of the Ti^+ ion current was evaluated to be about 7 % of the value of the TiO^+ ion current. Further experiments were carried out at the ionizing-electron energy of 12 eV to be sure that ionization of TiO_2 and TiO species in accordance with reactions

$$TiO_2 + e = TiO' + O' + 2\,e, \qquad (13)$$

$$TiO_2 + e = Ti' + O_2 + 2\,e, \qquad (14)$$

$$TiO + e = Ti' + O + 2e. \qquad (15)$$

could be neglected. The ionization processes in vapour over TiO_2 and TiO oxides were studied by Banon *et al.* /29/ who showed that at low ionizing electron energies (12.2 eV), the TiO^+ ion may be considered as the parent. (Ionization energy of Ti and TiO is (6.3±0.3)eV and (6.8±0.5)eV respectively /51/). The vapour mass spectra over the samples of the CaO-TiO_2-SiO_2 system of different compositions showed the same ion species as in the mass spectra of vapour over individual oxides /32/ CaO, TiO_2, and SiO_2 and over the CaO-SiO_2 /27/, CaO-TiO_2 -Ti_2O_3 /31/ systems. The main vaporization processes for the CaO-TiO_2-SiO_2 system in the temperature range 1700-2350 K were presented by reactions (7-10) and (16)-(18):

$$[CaO] = (Ca) + (O), \tag{16}$$

$$[TiO_2] = (TiO_2), \tag{17}$$

$$[TiO_2] = (TiO) + (O). \tag{18}$$

Thermodynamic activity of SiO_2 in the CaO-TiO_2-SiO_2 system

The SiO_2 activity in the CaO-TiO_2-SiO_2 system at 1850 K was calculated using experimental data on vapour pressure of SiO and O (reaction 7) measured by the values of corresponding ion currents, over the samples of the CaO-TiO_2-SiO_2 system and pure SiO_2. It follows from Equation (5), that

$$a_{SiO2} = (p_{SiO}/p^{o}_{SiO}) * (p_{O}/p^{o}_{O}), \tag{5a}$$

where p_i and p^o_i are the values of ion currents of vapour species over the samples of the CaO-TiO_2-SiO_2 system and over SiO_2, respectively. Calculated partial pressures of SiO and O are given in Table 3. In Table 4, the activity of SiO_2 in the ternary CaO-TiO_2-SiO_2 system is presented in comparison with data for the binary CaO-SiO_2 system also obtained by the Knudsen mass-spectrometric method.

SiO_2 activities and activity coefficients in the binary CaO-SiO_2 system decrease with decreasing bacisity (x_{CaO}/x_{SiO2} ratio). The same trend is observed for the ternary CaO-SiO_2-TiO_2 system. Replacement of CaO with TiO_2 in the slag of basicity x_{CaO}/x_{SiO2}=1.07 with about the same SiO_2 concentration (x_{SiO2}=0.431-0.434) results in sharp increase in SiO_2 activity and activity coefficient. This could be expected because TiO_2 is regarded as an acidic oxide, while CaO is a basic oxide. However, the effect of TiO_2 on the SiO_2 activity and activity coefficient in slags of low basicity is rather small, which could be an indication that in the acidic slag TiO_2 behaves as a basic oxide. To determine accurately the thermodynamic activities of CaO and TiO_2 in the CaO-TiO_2-SiO_2 system, much higher temperatures are required, as vapour pressures of species in the vaporization of these oxides are much lower than of SiO. However, at high temperatures SiO_2 would be about completely vaporised. Because of this limitation, activities of CaO and TiO_2 were not determined.

CONCLUSIONS

The CaO-TiO_2-SiO_2 system, containing about 10.5 and 16.5 mole% TiO_2 was examined at temperatures of 1850-2200 K using the Knudsen effusion method. In the vapour mass spectra of this system the following ions were identified at the ionizing-electron energy of 25 eV in the temperature range of 1700-2350 K: Ca^+, TiO^+, TiO_2^+, Ti^+, SiO^+, SiO_2^+, Si^+, MoO_2^+ and MoO_3^+. As a result of

Table 4

SiO_2 activity and activity coefficient in ternary CaO-SiO_2-TiO_2 and binary CaO-SiO_2 systems

Ternary CaO-SiO_2-TiO_2 system					Binary CaO-SiO_2 system		
x_{TiO2}*	x_{CaO}	x_{SiO2}	a_{SiO2}	γ_{SiO2}	x_{CaO}	x_{SiO2}	γ_{SiO2}
0.105	0.505	0.388	0.07	0.189			
0.105	0.462	0.431	0.15	0.348	0.564	0.434	0.035
0.106	0.400	0.489	0.27	0.552	0.517	0.483	0.455
0.157	0.475	0.365	0.05	0.137			
0.166	0.429	0.401	0.13	0.324			
0.165	0.370	0.458	0.27	0.590			
0.160	0.311	0.520	0.84	1.615	0.342	0.658	1.490

* The balance is Ti_2O_3

significant difference in the volatility between SiO, Ca, TiO and TiO_2 initial compositions of the system changed during isothermal vaporization of samples.

Using experimental data on vapour pressure of SiO and O over the CaO-TiO_2-SiO_2 system, the thermodynamic activity of SiO_2 was calculated and compared with the SiO_2 activity in the binary CaO- SiO_2 system. Replacement of CaO with TiO_2 in the slag of basicity x_{CaO}/x_{SiO2}=1.07 with about the same SiO_2 concentration results in a sharp increase in SiO_2 activity. However, this has little effect on the SiO_2 activity in slags of low basicity. This indicates that TiO_2 could be regarded as an acidic oxide in a basic slag and as a basic oxide in the acidic slag.

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