

Surface adsorption of SiO_2 in melts of the system $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$

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Received 20 April 1984

Surface tension of the $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$ melts decreases with the increasing content of SiO_2 . The change of Fe_2O_3 concentration in the melts with the mole ratio $x(\text{CaO})/x(\text{SiO}_2) \approx 1$ has no influence on the surface tension value. The surface adsorption of SiO_2 in the investigated melts increases with the increasing activity of SiO_2 . The positive influence of cations on surface adsorption of SiO_2 increases in the order Fe^{3+} , Fe^{2+} , Ca^{2+} , which is due to the electropositivity of cation and its coordination in the melt.

Поверхностное натяжение расплавов системы $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$ понижается с повышением содержания SiO_2 . Концентрация Fe_2O_3 в расплавах с молярным отношением $x(\text{CaO})/x(\text{SiO}_2) \approx 1$ не влияет на значение поверхностного натяжения. Поверхностная адсорбция SiO_2 в расплавах изучаемой системы повышается с повышением активности SiO_2 в расплаве. Положительное влияние катионов на поверхностную адсорбцию SiO_2 повышается в ряду Fe^{3+} , Fe^{2+} , Ca^{2+} , что связано с электроположительностью катиона и его координацией в расплаве.

The system $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$ is one of the basic systems from the metallurgical point of view. Surface tension of melts of this system is one of the properties which determine a number of metallurgical processes, e.g. separation of slag from metal and penetration of slag into refractory lining. Wide range of composition of metallurgical slags during the steel-making process and the dependence of slag composition on the temperature and on the partial pressure of oxygen make the measurement of physical properties of the melts difficult. That is why the data on surface tension of the $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$ melts are not available in the literature. The single source of information are the data on three-component systems containing FeO [1—8]. The influence of FeO on the silicate melts surface tension is dealt with, in a whole, in the *Richardson's* monograph [9]. The influence of Fe_2O_3 on the surface tension of silicate melts is not discussed in the literature.

In the present work the measurement of surface tension of melts of the system $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$ was carried out in the temperature range 1570—1820 K. The measurements were carried out in the atmosphere of air. An equilibrium between two- and trivalent iron was fixed at each experimental temperature. The equilibrium composition was then dependent on the temperature, the mole ratio $x(\text{CaO})/x(\text{SiO}_2)$, and on the total content of iron oxides. The results of the surface tension measurements were used for the calculation of the surface adsorption of SiO_2 in the system $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$.

Experimental

The maximum bubble pressure method was used for melt surface tension measurements. The detailed description of the device used is given in [10]. A PtRh20 capillary having an inner diameter of 2 mm was used. The tip of capillary was shaped to be conical and sharp. The depth of immersion of the capillary into the melt was adjusted with a micrometer screw in the range from 1 to 5 mm with an accuracy ± 0.01 mm. The pressure of measuring gas (air) in the capillary was measured with the use of tempered water manometer. The height of level in the manometric tube was measured with a kathetometer KM-5, USSR, with an accuracy ± 0.01 mm. The sample was placed in the PtRh20 crucible in the centre of heating space of the electrical resistance furnace. The temperature was measured with a PtRh6—PtRh30 thermocouple with an accuracy ± 5 K. The accuracy of surface tension determination was $\pm 5 \text{ mN m}^{-1}$.

The composition of the investigated melts was chosen to follow, as possible, the change in slag composition in the model system $\text{CaO—Fe}_2\text{O}_3\text{—SiO}_2$ during the steel-making process in the basic oxygen-furnace. The curve is represented in Fig. 1 according to the data given in [11]. The compositions of the investigated samples are also represented in Fig. 1. The points correspond to two sections of the system $\text{CaO—Fe}_2\text{O}_3\text{—SiO}_2$ with the constant mole ratio $k_1 \doteq x(\text{CaO})/x(\text{SiO}_2) = 1$ and $k_2 = x(\text{CaO})/x(\text{Fe}_2\text{O}_3) = 4$.

The samples were prepared by calcination and subsequent melting of CaCO_3 with Fe_2O_3 and SiO_2 (all anal. grade). Before melting the mixtures were kept at 1250 K for 2 h. The mass of sample was about 100 g. The contents of two- and three-valent iron were determined in the quenched samples after surface tension measurements. The analyses were carried out by a titration and by an atomic absorption spectroscopy. The analytical compositions were in good agreement with the calculated ones according to the data taken from [12, 13]. In [12, 13] the equilibrium compositions of melts in the system $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$ dependent on the temperature, the partial pressure of oxygen, and on the composition were investigated. For calculation of the equilibrium mole ratio $x(\text{Fe}_2\text{O}_3)/[x(\text{FeO}) + x(\text{Fe}_2\text{O}_3)] = r$ at the given temperature and the partial pressure of oxygen corresponding to that in the air, the following empirical equation was used in the present work

$$r = 1.7273 - 6.592 \times 10^{-4} T/\text{K} + 0.223k + 0.116x'(\text{Fe}_2\text{O}_3) \quad (1)$$

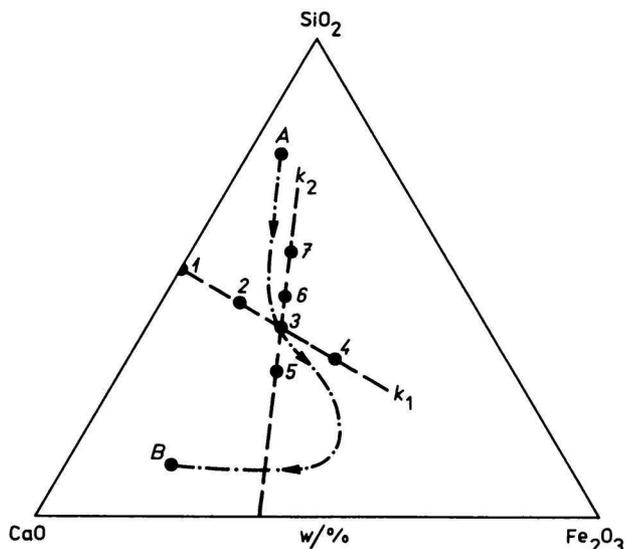


Fig. 1. The investigated sections in the system CaO—Fe₂O₃—SiO₂.
 1—7: the compositions of the investigated samples;
 A—B: the change in the slag composition during the steel-making process.

where T is the temperature (K), $k = x(\text{CaO})/x(\text{SiO}_2)$, and $x'(\text{Fe}_2\text{O}_3)$ is the mole fraction of Fe₂O₃ in the weighed mixture.

Results and discussion

Experimental values of surface tension of the investigated melts are given in Table 1. Since the temperature coefficients of surface tension are comparable with the experimental error, the values of surface tension are given for the average experimental temperature 1723 K. The equilibrium compositions of melts, corresponding to this temperature, are also included in Table 1. It was found that the surface tension in the system CaO—FeO—Fe₂O₃—SiO₂ increases markedly with the increasing content of CaO. The influence of the iron oxides is less significant and the surface tension of melts having a constant mole ratio $x(\text{CaO})/x(\text{SiO}_2) = 1$ is of roughly constant value 458 mN m⁻¹. The experimentally found dependence of surface tension on the melt composition was, in the first approximation, described by a linear equation

$$\begin{aligned} \gamma &= \gamma(\text{CaO}) \cdot x(\text{CaO}) + \gamma(\text{FeO}) \cdot x(\text{FeO}) + \gamma(\text{Fe}_2\text{O}_3) \cdot x(\text{Fe}_2\text{O}_3) + \gamma(\text{SiO}_2) \cdot x(\text{SiO}_2) = \\ &= [689x(\text{CaO}) + 502x(\text{FeO}) + 467x(\text{Fe}_2\text{O}_3) + 223x(\text{SiO}_2)] \text{ mN m}^{-1} \\ \sigma &= 1 \text{ mN m}^{-1} \end{aligned} \quad (2)$$

Table 1

Surface tension of melts in the system CaO—FeO—Fe₂O₃—SiO₂ at 1723 K (x_i — mole fractions)

No.	$x(\text{CaO})$	$x(\text{FeO})$	$x(\text{Fe}_2\text{O}_3)$	$x(\text{SiO}_2)$	$\frac{\gamma}{\text{mN m}^{-1}}$
1	0.500	—	—	0.500	457
2	0.472	0.010	0.046	0.472	456
3	0.444	0.019	0.092	0.444	458
4	0.412	0.030	0.146	0.412	460
5	0.517	0.009	0.120	0.353	495
6	0.383	0.022	0.074	0.521	423
7	0.312	0.023	0.055	0.610	389

where γ_i are hypothetical values of the surface tension of the pure oxides at the experimental temperature obtained by the multiple linear regression analysis and x_i are the equilibrium mole fractions of the oxides at the average experimental temperature 1723 K. The calculated values of surface tension for pure oxides are real and they are comparable with the literature data. For the surface tension of the pure supercooled CaO and SiO₂, respectively, the values of 726 mN m⁻¹ and 185 mN m⁻¹, respectively, were found in the previous work [14]. By the extrapolation of the concentration dependences of the surface tension in binary melts [9] the value of 270 mN m⁻¹ for SiO₂ can be obtained. For FeO the value of 585 mN m⁻¹ is given in [9]. Surface tension of molten Fe₂O₃ has not so far been published, but it is obvious from the properties and behaviour of this oxide that it will be lower than for FeO, but higher than for SiO₂.

Surface adsorption of SiO₂ in the system CaO—FeO—Fe₂O₃—SiO₂ was calculated in a similar manner as in the previous work [14]. The sections with the constant mole ratio $x(\text{CaO})/x(\text{Fe}_2\text{O}_3) = k_3$ and $x(\text{FeO})/x(\text{Fe}_2\text{O}_3) = k_4$ were chosen. For such sections the Gibbs equation in the form

$$d\gamma = -\Gamma(\text{M}_x\text{O}_y) \cdot d\mu(\text{M}_x\text{O}_y) - \Gamma(\text{SiO}_2) \cdot d\mu(\text{SiO}_2) \quad (3)$$

can be written. $\Gamma(\text{M}_x\text{O}_y)$ and $\Gamma(\text{SiO}_2)$ are the surface adsorptions and $\mu(\text{M}_x\text{O}_y)$ and $\mu(\text{SiO}_2)$ are the chemical potentials of the corresponding components in the system M_xO_y —SiO₂. The symbol M_xO_y refers to the total amount of all the oxides in the given melt, excepting SiO₂. Supposing $\Gamma(\text{M}_x\text{O}_y) = 0$, we get

$$\Gamma(\text{SiO}_2) = -\frac{d\gamma}{d\mu(\text{SiO}_2)} = -\frac{a(\text{SiO}_2)}{RT} \cdot \frac{d\gamma}{da(\text{SiO}_2)} = -\frac{a(\text{SiO}_2)}{RT} \cdot \frac{d\gamma}{dx(\text{SiO}_2)} \cdot \frac{dx(\text{SiO}_2)}{da(\text{SiO}_2)} \quad (4)$$

The expression $d\gamma/dx(\text{SiO}_2)$ can be obtained by the differentiation of eqn (2) with respect to $x(\text{SiO}_2)$. Since $dx(\text{CaO})/dx(\text{Fe}_2\text{O}_3) = k_3$, $dx(\text{FeO})/dx(\text{Fe}_2\text{O}_3) = k_4$, and

$dx(\text{CaO}) + dx(\text{FeO}) + dx(\text{Fe}_2\text{O}_3) + dx(\text{SiO}_2) = 0$, we get

$$\frac{d\gamma}{dx(\text{SiO}_2)} = \frac{k_3}{A} [\gamma(\text{SiO}_2) - \gamma(\text{CaO})] + \frac{k_4}{A} [\gamma(\text{SiO}_2) - \gamma(\text{FeO})] + \frac{1}{A} [\gamma(\text{SiO}_2) - \gamma(\text{Fe}_2\text{O}_3)] \quad (5)$$

where $A = k_3 + k_4 + 1$.

In paper [15] it has been found that the activity of arbitrary component in $\text{CaO}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ melts can be expressed, with a good approximation, using the Haase approach to activity calculation [16]. The activity of SiO_2 can be then calculated according to the equation

$$a(\text{SiO}_2) = \frac{27x_s \left[3x_s + \frac{2(1-x_s)}{A} - 1 \right]^2}{4 \left[2 + \frac{3(1-x_s)}{A} + x_s \right]^3} \quad (6)$$

where x_s is the mole fraction of SiO_2 in the melt. In derivation of eqn (6) it was supposed, in accordance with [15], that a half of Fe^{3+} cations present in the melt is coordinated tetrahedrally and it behaves as a network former. The expression

$$\frac{da(\text{SiO}_2)}{dx(\text{SiO}_2)} = \left\{ \frac{1}{x_s} + 2 \left[\frac{3 - \frac{2}{A}}{\frac{2}{A} - 1 + \left(3 - \frac{2}{A}\right) x_s} \right] - 3 \left[\frac{1 - \frac{3}{A}}{\frac{3}{A} + 2 + \left(1 - \frac{3}{A}\right) x_s} \right] \right\} \cdot \frac{27x_s \left[\frac{2}{A} - 1 + \left(3 - \frac{2}{A}\right) x_s \right]^2}{4 \left[\frac{3}{A} + 2 + \left(1 - \frac{3}{A}\right) x_s \right]^3} \quad (7)$$

can be obtained by the differentiation of eqn (6) with respect to x_s . Surface adsorption of SiO_2 was then calculated substituting eqns (5–7) in eqn (4).

The dependences of SiO_2 surface adsorption on the concentration for both sections in the system $\text{CaO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$, calculated according to eqn (4), are represented in Fig. 2. For the section $x(\text{CaO})/x(\text{Fe}_2\text{O}_3) = 4$, the surface adsorption of SiO_2 increases with the increasing SiO_2 content. For the section $x(\text{CaO})/x(\text{SiO}_2) = 1$, i.e. for the compatibility join $\text{CaSiO}_3-\text{Fe}_2\text{O}_3$ (Fig. 1), the surface adsorption of SiO_2 is roughly constant in the investigated concentration range. This fact, according to [15], can be explained by the double-dealing behaviour of Fe^{3+} cations. A half of Fe^{3+} cations is coordinated tetrahedrally, it behaves as a network former and makes the decrease in the surface adsorption of SiO_2 . The other half of Fe^{3+} cations is coordinated more highly, it behaves as a network modifier and, consequently, it causes the increase in the SiO_2 surface adsorption. It

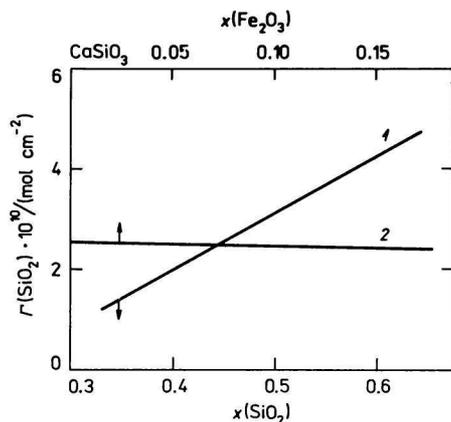


Fig. 2. Surface adsorption of SiO_2 in the investigated sections of the system $\text{CaO}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$.
 1. The section $x(\text{CaO})/x(\text{Fe}_2\text{O}_3) = 4$;
 2. the section $x(\text{CaO})/x(\text{SiO}_2) = 1$.

is obvious that the dependences in Fig. 2 are the projections of real curves into the concentration triangle of the system $\text{CaO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$.

Fig. 3 shows the cationic influence on the surface adsorption of SiO_2 . The SiO_2 surface adsorption was calculated on the assumption that eqn (2) can be, in a rough approximation, extended for the whole concentration region of the system $\text{CaO}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$. The calculation was then carried out for the boundary systems $\text{CaO}-\text{SiO}_2$ ($k_3 = \infty$, $k_4 = 0$), $\text{FeO}-\text{SiO}_2$ ($k_3 = 0$, $k_4 = \infty$), and $\text{Fe}_2\text{O}_3-\text{SiO}_2$ ($k_3 = k_4 = 0$). It is obvious that the SiO_2 surface adsorption in the systems $\text{CaO}-\text{SiO}_2$ and $\text{FeO}-\text{SiO}_2$ increases with the increasing activity of SiO_2 and with the increasing electropositivity of the cations. Since the calculations were carried out on a great number of the assumptions, the results may be considered only as the semiquantitative ones. In spite of this, a good agreement with literature data was achieved. For comparison, the SiO_2 surface adsorptions in the systems $\text{FeO}-\text{SiO}_2$ [9] and $\text{CaO}-\text{SiO}_2$ [14] are also represented in Fig. 3. The surface adsorption of SiO_2 can be, similarly as in [14], qualitatively correlated with the chemical nature of the cations. The more electropositive the cation, the more polar

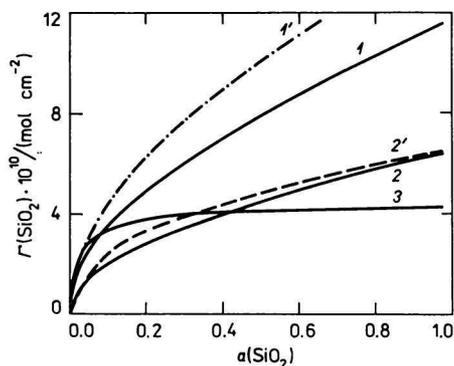


Fig. 3. Surface adsorption of SiO_2 in the boundary binary systems.
 1. $\text{CaO}-\text{SiO}_2$; 1'. $\text{CaO}-\text{SiO}_2$, Ref. [14];
 2. $\text{FeO}-\text{SiO}_2$; 2'. $\text{FeO}-\text{SiO}_2$, Ref. [9];
 3. $\text{Fe}_2\text{O}_3-\text{SiO}_2$.

the bond between the cation and negatively charged unshared oxygen atom and, consequently, the stronger the attempt of the silicate anions to escape from the bulk to the melt surface. The higher adsorption of more complex silicate anions having a larger nonpolar part (*i.e.* having more SiO_4 tetrahedrons per one negative elementary charge) may also be supposed. As a consequence, the concentration of SiO_4 tetrahedrons is relatively increased in the melt surface region.

Different character of the dependence of SiO_2 surface adsorption on the SiO_2 activity was observed in the system Fe_2O_3 — SiO_2 . The positive influence of Fe^{3+} cations upon the SiO_2 surface adsorption is shown only in the region of high concentrations of Fe_2O_3 . The double-dealing coordination of Fe^{3+} cations causes the surface adsorption of SiO_2 to be constant practically in the whole concentration region of the system Fe_2O_3 — SiO_2 . The Fe^{3+} cations are present to the same extent in the bulk and in the surface region of the melt.

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Translated by T. Ličko