

Surface adsorption of silicon dioxide in molten silicate systems

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Dedicated to Corresponding Member M. Zikmund, in honour of his 60th birthday

Surface tension of melts in the system $\text{CaSiO}_3\text{—CaMgSi}_2\text{O}_6\text{—Ca}_2\text{MgSi}_2\text{O}_7$ was measured using the maximum bubble pressure method at the temperatures 1400—1650°C. It has been found that the surface tension decreases with the increasing content of SiO_2 . The influence of temperature has not been determined because of experimental error. The surface adsorption of SiO_2 in the ternary system CaO—MgO—SiO_2 was calculated from the experimental values of surface tension. The influence of cations on the value of surface adsorption and on the structure of surface layer is discussed.

Методом максимального давления пузырька было определено поверхностное натяжение расплавов системы $\text{CaSiO}_3\text{—CaMgSi}_2\text{O}_6\text{—Ca}_2\text{MgSi}_2\text{O}_7$ в температурном интервале 1400—1650°C. Было найдено, что значение поверхностного натяжения понижается с повышением содержания двуокиси кремния в указанной системе. Влияние температуры не удалось определить из-за ошибки измерений. По указанным данным поверхностного натяжения были рассчитаны значения поверхностной адсорбции двуокиси кремния в трехкомпонентной системе CaO—MgO—SiO_2 . Обсуждается влияние катионов на значение поверхностной адсорбции и структуры поверхностного слоя.

The surface tension in silicate melts is studied mainly in order to know the surface layer structure of these melts and to gain a better understanding of a number of metallurgical processes, *e.g.* separation of slag from metal, penetration of slag into refractory lining, gas absorption in slages, *etc.* Since the systems in question are multicomponent, the dominant role in the above processes is played by the surface-active component, in the given cases SiO_2 .

The ternary CaO—MgO—SiO_2 system is one of the basic systems from the metallurgical point of view. The surface tension of this system has been little investigated so far. Owing to considerable difficulties at high-temperature physicochemical measurements the corresponding experimental data are scarcely found in literature [1—3]; moreover, these results probably show considerable errors. Comparatively the most correct values are given in [4] for the binary system MeO—SiO_2 .

In the present work the measurement of surface tension of melts of the system $\text{CaSiO}_3\text{—CaMgSi}_2\text{O}_6\text{—Ca}_2\text{MgSi}_2\text{O}_7$ has been carried out in the temperature range 1400—1650°C. The experimental results were used for the calculation of surface adsorption of SiO_2 in the system CaO—MgO—SiO_2 .

Experimental

The maximum bubble pressure method has been used for melt surface tension measurements. The detailed description of the device used is given in [5]. 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 7 mm with an accuracy ± 0.02 mm. Measuring gas (air) was blown into the capillary with a syringe the piston of which was driven by the connected electric motor. The rate of bubble formation ranged within 2—5 min^{-1} . The gas pressure 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 a PtRh20 crucible in the centre of heating space of electrical resistance furnace. The temperature was measured with a PtRh6/PtRh30 thermocouple, immersed into the melt, with an accuracy $\pm 5^\circ\text{C}$. The accuracy of surface tension determination was ± 4 mN m^{-1} .

The samples were prepared using the compounds CaSiO_3 (CS), $\text{CaMgSi}_2\text{O}_6$ (CMS_2), and $\text{Ca}_2\text{MgSi}_2\text{O}_7$ (C_2MS_2). The compounds were prepared by calcination of CaCO_3 and MgCO_3 , both of anal. grade (Lachema, Brno) and by the subsequent melting with SiO_2 , anal. grade (C. Erba, Milan), in the corresponding stoichiometric proportion. Before melting the mixture was kept at the temperature 1200°C for 2 h.

Results and discussion

Experimental values of surface tension of the melts tested are given in Table 1. Since the temperature coefficient of surface tension is comparable with the experimental error, the values given in Table 1 are valid for the whole temperature range investigated. It has been found that the surface tension of melts in the system $\text{CaSiO}_3\text{—CaMgSi}_2\text{O}_6\text{—Ca}_2\text{MgSi}_2\text{O}_7$ increases with the increasing content of $\text{Ca}_2\text{MgSi}_2\text{O}_7$ (Fig. 1), obviously as a result of the decrease in SiO_2 content. The experimentally found dependence of surface tension on the melt composition in the system CaO—MgO—SiO_2 can be, in the first approximation, described by a simple linear equation

$$\begin{aligned} \gamma &= \gamma_{\text{CaO}} \cdot x_{\text{CaO}} + \gamma_{\text{MgO}} \cdot x_{\text{MgO}} + \gamma_{\text{SiO}_2} \cdot x_{\text{SiO}_2} = \\ &= (726 \cdot x_{\text{CaO}} + 658 \cdot x_{\text{MgO}} + 185 \cdot x_{\text{SiO}_2}) \text{ mN m}^{-1} \end{aligned} \quad (1)$$

$$\Delta\gamma = \pm 3 \text{ mN m}^{-1}$$

Table 1

Surface tension of melts (γ) in the system $\text{CaSiO}_3\text{—CaMgSi}_2\text{O}_6\text{—Ca}_2\text{MgSi}_2\text{O}_7$,
 x_i — mole fractions

x_{CS}	x_{CMS_2}	x_{CaO}	x_{MgO}	$\frac{\gamma_{\text{exp}}}{\text{mN m}^{-1}}$	$\frac{\gamma_{\text{calc}}^*}{\text{mN m}^{-1}}$	k
0	1	0.250	0.250	438	439	1
0.2	0.8	0.278	0.222	437	441	1.25
0.6	0.4	0.333	0.167	443	444	2.5
1	0	0.500	—	458	456	∞
0	0.8	0.286	0.238	453	453	1.2
0	0.6	0.318	0.227	467	465	1.4
0	0.3	0.362	0.213	485	482	1.7
0	0.2	0.375	0.208	486	487	1.8
0	0.1	0.388	0.204	493	492	1.9
0.8	0	0.462	0.077	470	472	6
0.6	0	0.438	0.125	479	482	3.5
0.4	0	0.421	0.158	485	488	2.67
0.3	0	0.414	0.171	491	490	2.42
0.2	0	0.409	0.182	493	493	2.25
0.1	0	0.404	0.191	493	494	2.12
0	0	0.400	0.200	497	496	2
0.48	0.32	0.370	0.160	466	461	2.31
0.2	0.6	0.316	0.211	458	456	1.5
0.2	0.13	0.391	0.188	483	486	2.08

* Calculated according to eqn (1).

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 mole fractions of the oxides. It is obvious that the given equation is valid exactly only for the investigated concentration range of the oxides.

Surface adsorption of SiO_2 in the system CaO—MgO—SiO_2 was calculated for the pseudobinary sections with the constant ratios of the calcium and magnesium oxide contents $x_{\text{CaO}}/x_{\text{MgO}} = k$. For such a section the Gibbs equation in the form

$$d\gamma = -\Gamma_{\text{MeO}} \cdot d\mu_{\text{MeO}} - \Gamma_{\text{SiO}_2} \cdot d\mu_{\text{SiO}_2} \quad (2)$$

can be applied. Γ_{MeO} and Γ_{SiO_2} are the surface adsorptions and μ_{MeO} and μ_{SiO_2} are the chemical potentials of the corresponding components in the system MeO—SiO_2 . The symbol MeO refers to the total amount of the alkaline earth oxides in the given mixture. Supposing that $\Gamma_{\text{MeO}} = 0$ (i.e. we choose such dividing surface where no

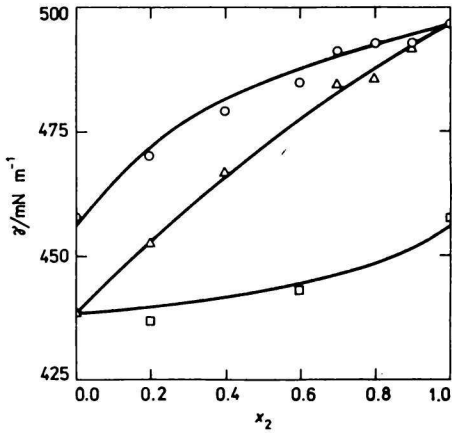


Fig. 1. Surface tension in the investigated systems.
 ○ CS—C₂MS₂; △ CMS₂—C₂MS₂;
 □ CMS₂—CS.
 — calculated according to eqn (1).

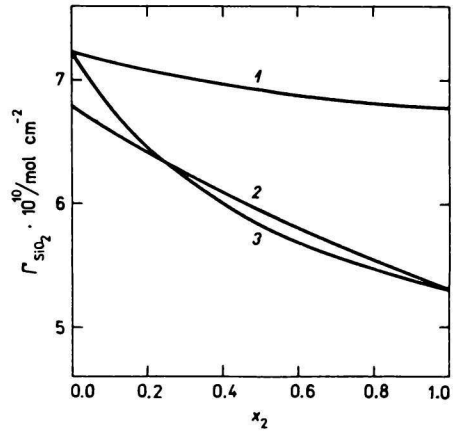


Fig. 2. Calculated SiO₂ surface adsorption in the investigated systems as a function of the second component mole fraction.
 1. CS—CMS₂; 2. CMS₂—C₂MS₂;
 3. CS—C₂MS₂.

excess of MeO is present), we get

$$\begin{aligned} \Gamma_{\text{SiO}_2} &= -\frac{d\gamma}{d\mu_{\text{SiO}_2}} = -\frac{a_{\text{SiO}_2}}{RT} \cdot \frac{d\gamma}{da_{\text{SiO}_2}} = \\ &= -\frac{a_{\text{SiO}_2}}{RT} \cdot \frac{d\gamma}{dx_{\text{SiO}_2}} \cdot \frac{dx_{\text{SiO}_2}}{da_{\text{SiO}_2}} \end{aligned} \quad (3)$$

The expression $d\gamma/dx_{\text{SiO}_2}$ can be obtained by the differentiation of eqn (1) with respect to x_{SiO_2} . Since $dx_{\text{CaO}}/dx_{\text{MgO}} = k$ and $dx_{\text{CaO}} + dx_{\text{MgO}} + dx_{\text{SiO}_2} = 0$, we get

$$\frac{d\gamma}{dx_{\text{SiO}_2}} = (\gamma_{\text{SiO}_2} - \gamma_{\text{CaO}}) + \frac{1}{k+1} (\gamma_{\text{CaO}} - \gamma_{\text{MgO}}) \quad (4)$$

In paper [6] it has been found that the activity of arbitrary component in CaO—MgO—SiO₂ melts can be expressed, with a good approximation, using the Haase approach to activity calculation [7, 8]. The activity of SiO₂ can be then calculated according to the equation

$$a_{\text{SiO}_2} = \frac{x_{\text{Si}^{4+}}}{x_{\text{Si}^{4+}}^0} \left(\frac{x_{\text{O}^-}}{x_{\text{O}^-}^0} \right)^2 = \left(\frac{3x_{\text{SiO}_2}}{2 + x_{\text{SiO}_2}} \right)^3 \quad (5)$$

where $x_{\text{Si}^{4+}}$, $x_{\text{Si}^{0+}}$, $x_{-\text{O}-}$, and $x_{-\text{O}^0-}$ are the ionic fractions of silicon and of shared oxygens in the melt and in the pure molten silica and x_{SiO_2} is the mole fraction of SiO_2 in the melt. The way of activity calculation is given in [6]. The expression

$$\frac{dx_{\text{SiO}_2}}{da_{\text{SiO}_2}} = \frac{(2 + x_{\text{SiO}_2})^4}{162 \cdot x_{\text{SiO}_2}^2} \quad (6)$$

can be obtained by the differentiation of eqn (5). Substituting eqns (4–6) in eqn (3) we obtain the final expression for surface adsorption of SiO_2 in the system under investigation

$$\Gamma_{\text{SiO}_2} = -\frac{1}{RT} \left[(\gamma_{\text{SiO}_2} - \gamma_{\text{CaO}}) + \frac{1}{k+1} (\gamma_{\text{CaO}} - \gamma_{\text{MgO}}) \right] \cdot \frac{x_{\text{SiO}_2} (2 + x_{\text{SiO}_2})}{6} \quad (7)$$

The dependences of SiO_2 surface adsorption on the composition in the systems CaSiO_3 — $\text{CaMgSi}_2\text{O}_6$, CaSiO_3 — $\text{Ca}_2\text{MgSi}_2\text{O}_7$, and $\text{CaMgSi}_2\text{O}_6$ — $\text{Ca}_2\text{MgSi}_2\text{O}_7$, calculated according to eqn (7), are represented in Fig. 2. It is evident that the surface adsorption of SiO_2 increases with its increasing concentration in the melt.

The cationic influence upon the SiO_2 surface adsorption is shown in Fig. 3. The SiO_2 surface adsorption has been calculated on the assumption that the validity of eqn (1) can be, in a rough approximation, extended for the whole concentration region of the system CaO — MgO — SiO_2 . The calculation has been carried out for the boundary binary systems CaO — SiO_2 ($k = \infty$) and MgO — SiO_2 ($k = 0$). For comparison, the dependence of Γ_{SiO_2} on the silica activity in the FeO — SiO_2 system, found in [9], is also represented in Fig. 3. It can be seen from the figure that the SiO_2 surface adsorption increases with the increasing electropositivity of cation,

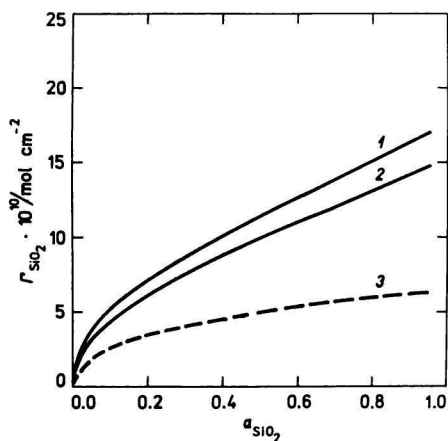


Fig. 3. Calculated SiO_2 surface adsorption as a function of the SiO_2 activity in the systems MeO — SiO_2 .

1. CaO — SiO_2 ; 2. MgO — SiO_2 (both in this work); 3. FeO — SiO_2 (Ref. [9, 11], 1420°C).

while the character of the dependences is the same in all cases. From the results of X-ray diffraction study in the molten MeO—SiO₂ system (Me = Ca, Mg, Fe) it follows that the mean statistical coordination number of the cation in these melts decreases in the order Ca > Mg > Fe [10, 11]. Cations attempt to be coordinated as high as possible with negatively charged unshared oxygens of silicate groups. Consequently, the excess of SiO₄ tetrahedron is formed in the melt surface region. By the weaker attraction between the cations and SiO₄ tetrahedrons and thus by higher coordination number of cation the higher concentration of SiO₄ tetrahedrons in the melt surface in the case of more electropositive cation can be explained.

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References

1. King, T. B., *J. Soc. Glass Technicians* 35, 241 (1951).
2. Ermolaeva, E. V., *Ogneupory* No. 5, 221 (1955).
3. Panov, A. S., Kulikov, P. S., and Tsylev, L. M., *Zh. Fiz. Khim.* 37, 169 (1963).
4. King, T. B., in *The Physical Chemistry of Melts*, p. 35. *Symposium, Inst. Min. Metall.*, London, 1953.
5. Daněk, V. and Ličko, T., *Silikáty* 25, 153 (1981).
6. Pánek, Z. and Daněk, V., *Silikáty* 21, 97 (1977).
7. Haase, R., in *Physical Chemistry*, Vol. 1, p. 352. (Eyring, H., Henderson, D., and Jost, W., Editors.) Academic Press, New York, 1971.
8. Saboungi, M. L. and Blander, M., *J. Amer. Ceram. Soc.* 58, 1 (1975).
9. Richardson, F. D., *Physical Chemistry of Melts in Metallurgy*, Vol. 2, p. 441. Academic Press, London, 1974.
10. Waseda, Y. and Toguri, J. M., *Met. Trans.* 8B, 563 (1977).
11. Waseda, Y. and Toguri, J. M., *Met. Trans.* 9B, 595 (1978).

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