

DENSITY AND SURFACE TENSION OF SLAG MELTS OF THE SYSTEM $\text{Fe}_2\text{O}_3\text{-FeO-CaO-SiO}_2$

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The effect of SiO_2 on the density and surface tension of $\text{Fe}_2\text{O}_3\text{-FeO-CaO-SiO}_2$ slag melts was studied at concentrations of up to 10 wt.% SiO_2 . The maximum gas bubble pressure method was employed in the measurements. Silica reduces density and surface tension, while increasing the molar volume and statistically mean size of ions present in the ferritic-lime melt. The results showed that the physical properties of slag systems are for the most part influenced by the character of anionic ferric oxide complex compounds. The Fe^{3+} cation can form FeO^+ , FeO_2^- , $\text{Fe}_2\text{O}_5^{4-}$ and FeO_4^{5-} complex compounds with oxygen while possibly also changing oxygen coordination of the iron ions. At the concentrations in question, SiO_2 occurs mostly in the form of SiO_4^{4-} tetrahedrons.

INTRODUCTION

Pyrometallurgical metal production processes involve by-production of slags whose amounts often exceed several times the yield of the metal itself. Slag is a polycomponent system of metallic and non-metallic oxides forming compounds, solutions and eutectic mixtures, and moreover containing metals, sulphides and gases. The main role of slag is to act as collector of the undesirable components of the charge and of the impurities formed in the course of melting or refining of the metals. Correct choice of slag composition affects the total loss of the metal, its quality, the energy demands of the process, the consumption of refractory lining, and thus in general the overall economy and environmental aspects of the pyrometallurgical process.

In non-ferrous metallurgy, the use of ferritic-lime slags was started in Japan in the middle seventies in the continuous copper production process [1] developed on the basis of theoretical work by Yazawa [2]. Such slags may be characterized as a $\text{FeO-Fe}_2\text{O}_3\text{-CaO}$ system, under real technological conditions supplemented with additional components. Takeda et al. [3] studied the thermodynamics of lime-ferritic slags at 1473 K and 1573 K. Their work includes a formula for calculating the concentration of Fe^{3+} and Fe^{2+} in dependence on the content of calcium oxide, the partial pressure of oxygen and the melt temperature.

The density and surface tension of the system $\text{CaO-FeO-Fe}_2\text{O}_3\text{-SiO}_2$ were measured by numerous authors, in particular in connection with steelmaking slags [4-12]. Most of these melts are characterized by a high SiO_2 content and temperatures exceeding 1670 K.

Ličko et al. [13] measured the density of melts in the system $\text{CaO-FeO-Fe}_2\text{O}_3\text{-SiO}_2$ in air at 1540 - 1940 K. Density of the melts increased with increasing content of iron oxides. A change in the oxidation degree of iron was indicated by a non-linear temperature dependence of density and by a decreasing molar volume of the melt in terms of increasing temperature.

There is little data available in the literature on the physical properties of ferritic-calcium slags with a low content of silica (below 15 wt.% SiO_2), and it appeared only in recent years. Hara et al. [14] measured surface tension and density of $\text{FeO-Fe}_2\text{O}_3\text{-CaO}$ and $\text{FeO-Fe}_2\text{O}_3\text{-2CaO.SiO}_2$ melts in the atmosphere of air and carbon dioxide. At the First International Conference on Processing Materials for Properties in 1993, Okamoto et al. [15] presented a paper named Density and Surface Tension in Ferritic Slags. Sumita, Morinaga and Yangase [6] studied the structure of ferritic melts in terms of their chemical composition and temperature. They expressed their findings in the form of plots describing the effect of concentration of CaO on that of O^{2-} , Fe^{2+} , Fe^{3+} and Ca^{2+} ions in the melt.

The present paper gives the results of a study of density and surface tension in pre-oxidized slag melts of the system $\text{Fe}_2\text{O}_3\text{-FeO-CaO-SiO}_2$ at silica contents ranging from 0 to 10 wt.% at 1573 K. On the basis of experimentally established values of density, molar volume, surface tension, statistically mean dimensions of ions in the melt as well as on that of literary data, the present authors proposed their concept of the structure of slag melts in the system $\text{Fe}_2\text{O}_3\text{-FeO-CaO-SiO}_2$ in dependence of its composition, for the temperature of 1573 K.

EXPERIMENTAL PART

Density and surface tension were measured by the bubble maximum gas pressure method. The gas was introduced through a capillary into the melt and the increasing gas pressure formed a bubble at the end of the capillary. Up to the point of separation, the bubble has to overcome the hydrostatic pressure and the pressure acting against the formation of a new surface. With capillaries of larger diameters, a corrected calculation of the surface tension has to be used in order to compensate the gravity-induced deviation of the bubble shape from the spherical form [16]. This modified relation replaces the second term (P_σ) of the right-hand side of Equation (2).

The density and surface tension were calculated according to the following equations:

$$\rho = \frac{\Delta P_{\max}}{\Delta h g} = \frac{P_{2\max} - P_{1\max}}{g (h_2 - h_1)} \quad (\text{kg m}^{-3}) \quad (1)$$

where Δh is the difference between the depth of two immersions (m), ΔP_{\max} is the difference between two maximum pressures at two immersions (Pa), g is gravity (m s^{-2}).

$$P_{\max} = P_h + P_\sigma = (\rho - \rho_0')g h + \frac{2\sigma}{r} \quad (\text{N m}^{-1}) \quad (2)$$

where ρ is the density of the melt (kg m^{-3}), ρ_0' is the density of gas in the bubble (kg m^{-3}), P_{\max} is the maximum pressure of gas in the bubble (Pa), P_h is the pressure necessary for overcoming the hydrostatic pressure of the melt (Pa), P_σ is the pressure necessary for overcoming the surface tension of the melt (Pa).

In most instances of density and surface tension calculations, the gas density is neglected if it holds that $\rho \gg \rho_0'$.

The corrected calculation of surface tension after Schroedinger [16]:

$$\sigma = \frac{rP_\sigma}{2} \left[1 - \frac{2}{3} \left(\frac{\rho r g}{P_\sigma} \right) - \frac{1}{6} \frac{(\rho r g)^2}{P_\sigma^2} \right] \quad (\text{N m}^{-1}) \quad (3)$$

The resultant equation for calculating the surface tension was obtained with the use of Equations (2) and (3):

$$\sigma = \frac{r (P_{\max} - \rho g h)}{2} \left[1 - \frac{2}{3} \left(\frac{\rho r g}{(P_{\max} - \rho g h)} \right) - \frac{1}{6} \frac{(\rho r g)^2}{(P_{\max} - \rho g h)^2} \right] \quad (\text{N m}^{-1}) \quad (4)$$

where h is the depth of capillary immersion (m), r is the

capillary radius (m), g is gravity (m s^{-2}), ρ is the melt density (kg m^{-3}).

In order to rule out double separation of the bubble from the internal and external capillary diameter, the end of the capillary was machined into a "blade edge" at an angle of 30 degrees. Use was made of a platinum capillary tube of 1.285 mm ID (at 1573 K). The depth of immersion in the melt was measured with a depth micrometer with an accuracy of ± 0.005 mm, and contact of the capillary with the melt was recorded by an electrical contact. Pure nitrogen was employed as the gaseous medium of the bubbles. The gas flow rate was adjusted to 3 - 5 bubbles a minute and the gas pressure measured by an ÚMK tilt-arm micromanometer. The accuracy of reading the maximum pressure in the bubble amounted to 0.5 of the scale division, which, at an angle of 45 degrees and with the use of distilled water as manometer liquid, represented an error of ± 0.25 mm. The slag samples were melted in a platinum crucible placed, in a protective corundum crucible, in an electric resistance furnace. The melt temperature was measured with two PtRh18 thermocouples, of which one was immersed in the melt (before and after the measurement), and the other rested against the crucible bottom. The temperature was controlled with an accuracy of ± 2.5 K.

In measuring the surface tension and density by the maximum bubble pressure method, the largest errors are caused by inaccurate machining and deviations from circularity of the capillary orifice, by deviations from exactly vertical position of the capillary, and by inaccurate reading of the immersion depth and gas pressure. A critical analysis of the method and of the effects of the separate inaccuracies on the resultant error in measuring the surface tension was presented in [17]. The accuracy of density and surface tension measurements with our experimental equipment was tested with distilled water, methyl alcohol and mercury, and the relative measuring errors established were as follows:

- density, from +1.82% to -1.5 %
- surface tension, from +0.3 % to +3.7 %.

Higher values were obtained in determinations of density and surface tension of mercury, due to the low wetting power of mercury with respect to the material of the capillary [18]. The accuracy of measurement of wettable melts is in agreement with the data specified for the method in [17,18].

The experimental results were used in calculating the density and surface tension of the slag melts. The molar volume of the system at the given temperature was calculated from the chemical analysis and the density.

Reiss, Frisch, Helfand and Lebowitz [19,20] estimated the reversible work required for forming spherical cavities in a melt composed of solid spheres, and derived the following equation of state for these melts:

$$\frac{pV}{RT} = \frac{1 + Y + Y^2}{(1-Y)^3} \quad (5)$$

where p is pressure, and V is the molar volume.

$$Y = \frac{\pi a^3 N}{6V} \quad (6)$$

where a is the diameter of the solid spheres and N is Avogadro's number.

The method was expanded by Vasu [21] to include calculation of transport properties of liquids. The findings were also used by Fellner and Daněk [22] in their calculation of viscosity and electrical conductivity of molten halogenides. Sumita, Morinaga and Yanagase [23] employed the method in deriving an equation for calculation of surface tension. Using Equations (6) and (7), and the known surface tension and molar volume values, it is possible to calculate the mean "statistical" dimension a of ions in the melt:

$$\sigma = \frac{kT}{4\pi a^2} \left[\frac{12Y}{1-Y} + \frac{18Y^2}{(1-Y)^2} \right] - \frac{pa}{2} \quad (7)$$

where T is the temperature (K), σ is the surface tension (N m), N is Avogadro's number (mol^{-1}), V is the molar volume ($\text{m}^3 \text{mol}^{-1}$), p is the pressure (Pa), k is Boltzmann's constant (J K^{-1}).

The value of $pa/2$ is negligible and was not taken into account in the calculations [23].

The synthetic slags were prepared from Fe_2O_3 and CaO of AR purity by Lachema Brno, and SiO_2 , likewise of AR purity, by POCH Gliwice, Poland. Mixtures about 100 g in weight were melted in a platinum crucible in air atmosphere until a steady-state composition was attained. This was determined by monitoring the chemical composition and took 1 - 1.5 hour. In experimental measurements, the melt composition was allowed to equalize for at least 2 hours. In some cases, the partial pressure of oxygen above the melt was reduced by blowing pure nitrogen into the furnace.

Melt samples for chemical analyses were taken with a platinum rod and quenched in water. The samples were analyzed by the AAS method (Fe_{total} , Ca, Si), or by Reinhard-Zimmerman's titration method (Fe^{2+}).

RESULTS AND DISCUSSION

Density and surface tension of melts in the system $\text{Fe}_2\text{O}_3\text{-FeO-CaO-SiO}_2$ were measured at 1573 ± 2.5 K in the high oxidation region, in air atmosphere, up to an SiO_2 content of 10 wt.%. The results of density, surface tension, molar volume and statistical mean ion dimension measurements are listed in Table I. Graphic plots of the

effect of silica on the physico-chemical properties examined are shown in Figures 1 through 8.

In the oxidized system $\text{Fe}_2\text{O}_3\text{-FeO-CaO-SiO}_2$, silicon dioxide reduces the melt density on replacing calcium dioxide or ferric oxide. Substitution for calcium dioxide as well as ferric oxide results in an increase in the molar volume of the melt, and it is possible to observe formation of "levels" in dependence on a constant content of ferric oxide or calcium dioxide. In the case of substitution for calcium dioxide, the effect of silica on the change in molar volume decreases with increasing concentration of ferric oxide in the melt. In substitution for ferric oxide, the increase in molar volume with increasing silicon dioxide content is approximately identical, i.e. the increase is independent of a constant CaO concentration in the melt. Increases of the constant CaO content reduce the absolute value of the molar volume of the system. This is due to a decrease of the overall concentration of trivalent iron in the system. In the melts, silicon dioxide occurs in the form of SiO_4^{4-} tetrahedra which tend to polymerize readily [9,10]. The ions of trivalent iron with oxygen in ferrite-calcium melts form complex compounds in tetrahedral or octahedral coordination, in dependence on the $\text{Fe}^{3+}/\text{O}^{2-}$ ratio. Rising concentrations of oxygen anions promote formation of tetrahedrally coordinated ferric anionic complexes. Tetrahedrally coordinated complexes may link to form polyanionic structures, the polymerization being accompanied by an increase in molar volume. This increase is caused by the existence of free volumes in the tetrahedral polyanionic network. It is obvious that the effect of silicon dioxide on the increase in molar volume is likewise higher at higher concentrations of tetrahedrally coordinated Fe^{3+} anions.

As a complex-forming oxide, silica complicates the structure of oxidic melts. In the pre-oxidized $\text{Fe}_2\text{O}_3\text{-FeO-CaO-SiO}_2$ system, it acts as a surface-active component, i.e. causes reduction of surface tension on replacing calcium dioxide as well as ferric oxide. A different course of changes in surface tension occurs at the lowest constant CaO content (33 mol%), or at the highest Fe_2O_3 content (48 mol%) in the melt. A high value of the $\text{Fe}^{3+}/\text{O}^{2-}$ ratio promotes formation of ferric oxide complexes with a looser octahedral bond (FeO_2). In ferritic melts, these complexes behave as network modifiers, thus tending to increase surface tension of the melt [24]. The effect of silica on surface tension of the slag melts depends on the character of ferric oxygen anions.

On the basis of the calculated values of statistical mean ionic dimension of all ions in the melt, it is not possible to determine the sizes of the individual complex compounds; however, one can examine the effect of an addition of silicon dioxide on the mean dimension. The dependence of the change in the mean ionic dimension

on the content of SiO₂ indicates that increasing the silica content at the expense of calcium oxide is responsible for a mild increase in the mean size of the ions. In the case of substitution of SiO₂ for ferric oxide, the mean dimension decreases with increasing calcium dioxide content, with the exception of the constant CaO content of 33 mol%, when an increase in the dimension was observed. It is assumed that the respective courses are

associated with the type of the oxygen-ferric complex. In the instance of substituting the SiO₄⁴⁻ tetrahedron for the FeO₂⁻ complex, there is an increase in the mean ion size in the melt, whereas the opposite holds for Fe₂O₅⁴⁻ substitution. Herasymenko [5] reports an SiO₄⁴⁻ size of 2.79×10^{10} m, while the mean ionic sizes calculated by us for the system Fe₂O₃-FeO-CaO-SiO₂ were over the interval from 3.5 to 3.9×10^{-10} m.

Table I. Experimental results of density, molar volume, surface tension and statistical mean complex ion diameter in the system Fe₂O₃-FeO-CaO-SiO₂ at a temperature of 1573 K

Chemical composition (mol%)				Density (kg m ⁻³)	Molar volume (m ³ mol ⁻¹ ×10 ⁶)	Surface tension (mN m ⁻¹)	Complex diameter (m×10 ⁻¹⁰)
CaO	Fe ₂ O ₃	FeO	SiO ₂				
37.84	42.19	10.94	9.03	3730	27.315	591.7	3.66
37.84	43.09	9.03	10.02	3600	28.466	590	3.72
43.32	36.32	8.32	12.05	3410	28.008	574.9	3.68
34.91	42.42	17.24	5.42	3724	27.652	605	3.68
41.34	26.1	15.87	16.69	3490	24.737	575.1	3.5
41.12	24.66	16.67	17.54	3450	24.629	570.7	3.49
46.56	21.64	13.69	18.11	3130	26.003	554	3.56
33.95	36.51	22.7	6.84	3840	25.493	618	3.57
42.8	27.4	26.11	3.69	3966	22.376	587.3	3.37
28.84	17.09	48.65	5.42	3870	21.105	572.4	3.28
22.3	10.1	67.61	0	4265	18.12	594	3.09
33.7	49.95	8.66	7.66	3775	29.173	590.5	3.75
33.44	52.3	5.95	8.29	3820	29.203	586.4	3.75
35.26	46.52	2.67	15.55	3570	29.504	583	3.77
31.13	33.14	8.34	27.38	3080	30.14	559.5	3.78
38.78	51.46	3.57	6.18	3740	28.872	580.5	3.73
35.77	49.69	4.35	10.17	3710	29.293	578	3.75
37.22	45.88	5.92	10.97	3630	28.926	573	3.73
39.04	40.64	7.69	12.62	3545	28.184	553.1	3.68
38.41	42.51	2.63	16.43	3437	29.444	535.4	3.73
38.87	39.38	2.95	18.78	3368	29.07	523.9	3.7
39.57	35.73	5.61	19.09	3285	28.859	527.1	3.69
40.37	46.85	3.22	9.54	3710	28.44	558	3.69
42.32	41.87	3.43	12.36	3600	27.90	551.5	3.66
40.0	43.02	2.68	14.3	3560	28.573	546.2	3.69
42.92	38.69	2.13	16.26	3460	28.159	531.3	3.66
42.56	37.92	3.1	16.42	3430	28.122	527.9	3.65
44.21	53.22	2.56	0	3973	28.586	587	3.72
45.55	44.19	2.82	7.44	3742	27.418	553.1	3.64
43.63	46.82	1.71	7.83	3745	28.088	559.1	3.68
45.78	41.72	3.49	9.0	3660	27.385	550.7	3.63
48.22	40.43	0	11.34	3548	27.744	551	3.65
45.25	35.43	1.82	17.5	3300	28.479	520.7	3.67
48.58	29.74	1.8	19.88	3340	27.98	512	3.63
48.89	44.18	1.65	5.27	3730	27.44	558.8	3.64
49.00	45.15	0	5.85	3715	27.76	553.3	3.65
51.45	41	0	7.53	3750	26.35	555.1	3.58

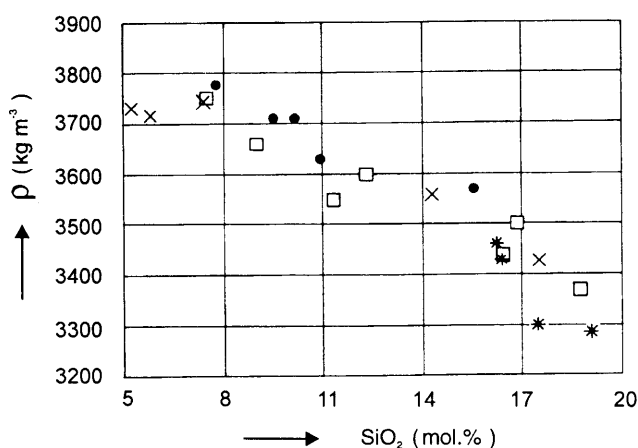


Figure 1. The effect of SiO₂ on density in the system Fe₂O₃-FeO-CaO-SiO₂ at a constant content of 37, 41, 44 and 48 mol.% Fe₂O₃ at a temperature of 1573 K
* - 37 Fe₂O₃; □ - 41 Fe₂O₃; × - 44 Fe₂O₃, ● - 48 Fe₂O₃

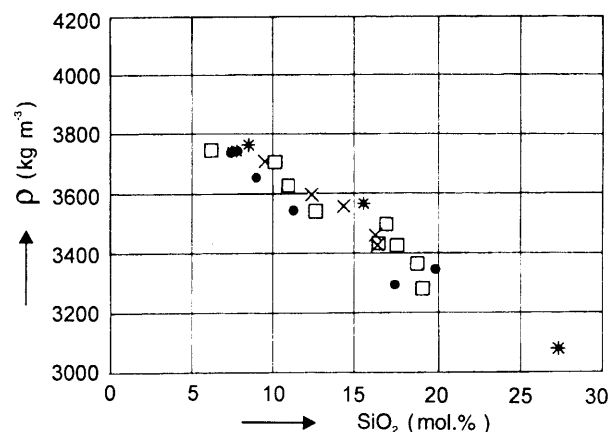


Figure 3. The effect of SiO₂ on density in the system Fe₂O₃-FeO-CaO-SiO₂ at a constant content of 33, 37.5, 41.5 and 46 mol.% Ca at a temperature of 1573 K
* - 33 CaO; □ - 37.5 CaO; × - 41.5 CaO, ● - 46 CaO

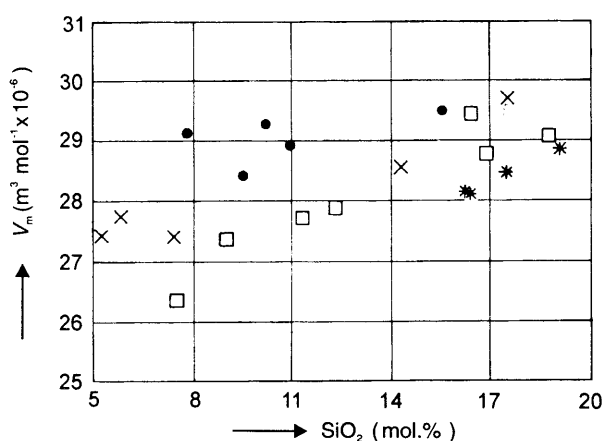


Figure 2. The effect of SiO₂ on molar volume of the system at a constant content of 37, 41, 44 and 48 mol.% Fe₂O₃, at a temperature of 1573 K
* - 37 Fe₂O₃; □ - 41 Fe₂O₃; × - 44 Fe₂O₃, ● - 48 Fe₂O₃

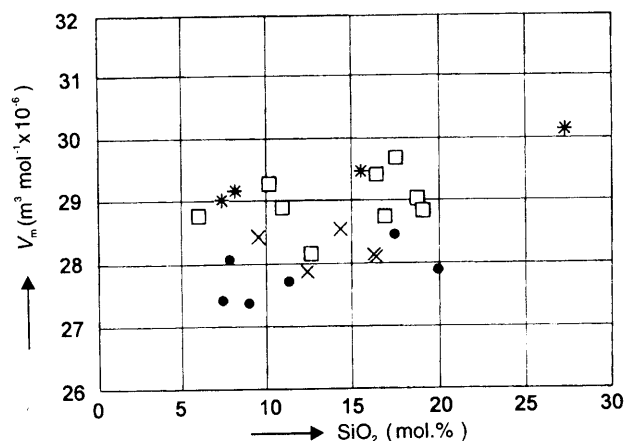
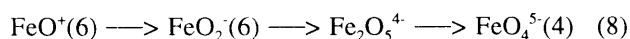


Figure 4. The effect of SiO₂ on molar volume in the system Fe₂O₃-FeO-CaO-SiO₂ at a constant content of 33, 37.5, 41.5 and 46 mol.% CaO, at a temperature of 1573 K
* - 33 CaO; □ - 37.5 CaO; × - 41.5 CaO, ● - 46 CaO

From the relationships described it follows that the physico-chemical properties of ferric-lime slags depend to a decisive degree on the concentration of ferric anionic complexes and on their coordination in the system. The authors assume that in complex anions of trivalent iron the coordination of the Fe³⁺ cation with the O²⁻ anion changes steplessly from octahedral to tetrahedral according to the schematic formula



(the coordination numbers of Fe³⁺ are given in brackets).

The FeO⁺ anion corresponds to molten ferric oxide which has octahedral coordination [26] and whose

existence is assumed by Esin [27] and Yazawa [28]. The FeO₂⁻ complex may arise by dissociation of calcium ferrite (CaO·Fe₂O₃): according to Petzold and Hinz [29] the coordination of trivalent iron in this anion is octahedral. The octahedrally coordinated Fe³⁺ ions act in oxidic melts as network modifiers [24]. The theory of chemical bonds shows that in the FeO₂⁻ anion there must be one double bond with a higher share of covalency. Substances with covalent bonds exhibit lower surface tension, and the mutual effects between particles in substances with mixed bonds is likewise weaker. Kozakevitch [8] reports that the electric field around the FeO₂⁻ ion is weaker than that around the Fe₂O₅⁴⁻ one. Various authors characterize the FeO₂⁻ ion in various

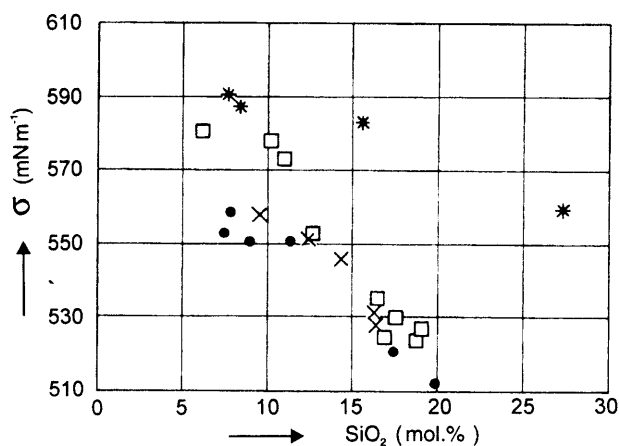


Figure 5. The effect of SiO_2 on surface tension in the system $\text{Fe}_2\text{O}_3\text{-FeO-CaO-SiO}_2$ at a constant content of 33, 37.5, 41.5 and 46 mol.% CaO , at a temperature of 1573 K
 * - 33 CaO ; \square - 37.5 CaO ; \times - 41.5 CaO , \bullet - 46 CaO

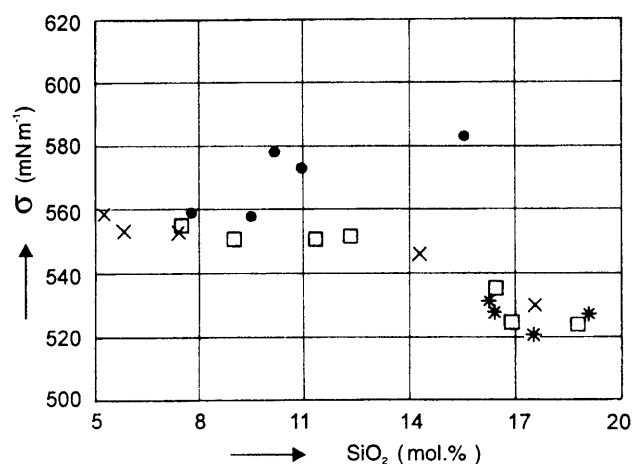


Figure 7. The effect of SiO_2 on surface tension in the system $\text{Fe}_2\text{O}_3\text{-FeO-CaO-SiO}_2$ at a constant content of 37, 41, 44 and 48 mol.% Fe_2O_3 , at a temperature of 1573 K
 * - 37 Fe_2O_3 ; \square - 41 Fe_2O_3 ; \times - 44 Fe_2O_3 , \bullet - 48 Fe_2O_3

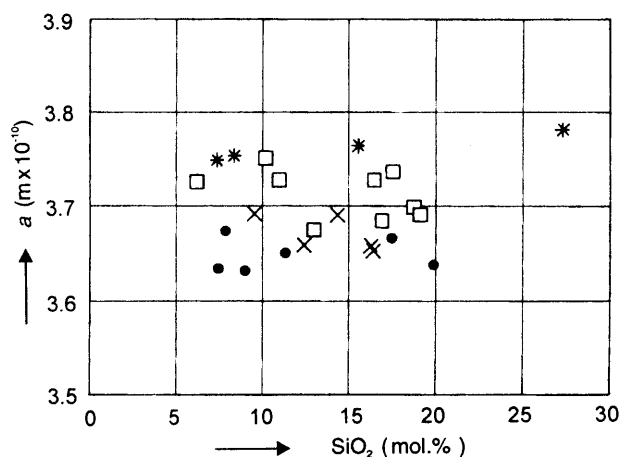


Figure 6. The effect of SiO_2 on statistical mean size of ions in the system $\text{Fe}_2\text{O}_3\text{-FeO-CaO-SiO}_2$ at a constant content of 33, 37.5, 41.5 and 46 mol.% CaO , at a temperature of 1573 K
 * - 33 CaO ; \square - 37.5 CaO ; \times - 41.5 CaO , \bullet - 46 CaO

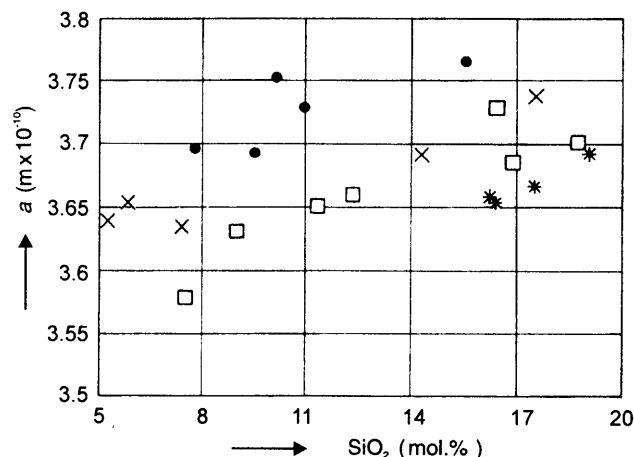


Figure 8. The effect of SiO_2 on statistical mean size of ions in the system $\text{Fe}_2\text{O}_3\text{-FeO-CaO-SiO}_2$ at a constant content of 37, 41, 44 and 48 mol.% Fe_2O_3 , at a temperature of 1573 K
 * - 37 Fe_2O_3 ; \square - 41 Fe_2O_3 ; \times - 44 Fe_2O_3 , \bullet - 48 Fe_2O_3

ways. Our experimental results show that in the ferritic melts studied, absorption of FeO_2^- ions into the melt surface layer increases its surface tension. The $\text{Fe}_2\text{O}_5^{4-}$ anionic complexes may be formed by dissociation of dicalcium ferrite whose structure contains trivalent iron ions in both octahedral and tetrahedral coordination [29]. Experimental results have confirmed that the presence of $\text{Fe}_2\text{O}_5^{4-}$ ions in the melt will be revealed by a decrease of melt surface tension. Additional raising of the concentration of O^{2-} ions in the melt, or reduction of the $\text{Fe}^{3+}/\text{O}^{2-}$ ratio, supports formation of FeO_4^{5-} complexes in the melt. The formally negative charge of the central iron atom in the FeO_4^{5-} tetrahedron is compensated by Ca^{2+} and Fe^{2+} cations, or possibly by another Fe^{3+} cation which,

however, is in a higher coordination [13]. In the FeO_4^{5-} anionic complex, the oxygen atoms are firmly bound by tetrahedral coordination, and the surface activity of FeO_4^{5-} is higher than that of the $\text{Fe}_2\text{O}_5^{4-}$ anion [31]. Formation of the tetrahedrally coordinated FeO_4^{5-} complex causes the melt surface tension to decrease. These findings are in a good agreement with the results of studies [25,27], concerned with measuring the surface tension of the system $\text{Fe}_2\text{O}_3\text{-FeO-CaO}$.

It may be assumed that substitution of ferric oxide in the presence of ferrous oxide in the system $\text{Fe}_2\text{O}_3\text{-FeO-CaO-SiO}_2$, which dissociates into Fe^{3+} and O^{2-} ions, will result in increased density and surface tension of the system, and/or reduction of the molar volume

and of the mean size of ions in the melt. The Fe^{2+} and Ca^{2+} are network modifiers and in the system $\text{Fe}_2\text{O}_3\text{-FeO-CaO-SiO}_2$ are responsible for increasing the surface tension.

CONCLUSION

The results obtained have clarified the effect of low concentrations of silicon dioxide on the density, molar volume, statistical mean size of ions and surface tension of ferritic-calcium slags at the temperature of 1573 K. It may be assumed that in ferritic-calcium slags, the FeO^+ and FeO_2^- complexes act as network structure modifiers. FeO_4^{5-} and to a lesser degree also $\text{Fe}_2\text{O}_5^{4-}$ can be ranked among surface-active ferric-oxidic anionic complexes. Activity of $\text{Fe}_2\text{O}_5^{4-}$ depends on the prevailing coordination in this anion. The slag system being studied very probably contains simple cations Ca^{2+} , Fe^{2+} , and more complex anionic groupings of FeO_2^- , $\text{Fe}_2\text{O}_5^{4-}$ and SiO_4^{4-} .

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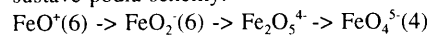
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HUSTOTA A POVRCHOVÉ NAPÄTIE TROSKOVÝCH TAVENÍN SÚSTAVY $\text{Fe}_2\text{O}_3\text{-FeO-CaO-SiO}_2$

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Metódou maximálneho tlaku plynu v bublinke sa merala hustota a povrchové napätie troskovej taveniny $\text{Fe}_2\text{O}_3\text{-FeO-CaO-SiO}_2$ vo vzdušnej atmosfére. Koncentrácia oxidu kremičitého bola v intervale 0 až 10 hmot. % a teplota taveniny 1573 K. Na základe experimentálnych výsledkov merania hustoty a chemického zloženia taveniny sa vypočítal mólový objem taveniny. Použitím vzťahov z literatúry [22,23], ktoré dávajú do súvislosti mólový objem, povrchové napätie a štruktúru tavenín, sa iteračnou metódou vypočítal štatistický priemerný rozmer iónov v tavenine. Oxid kremičitý v preoxidovanej troskovej sústave $\text{Fe}_2\text{O}_3\text{-FeO-CaO-SiO}_2$ pri nahradzovaní oxidu vápenatého aj oxidu železitého znižuje hustotu a povrchové napätie a naopak zvyšuje mólový objem taveniny. Pri nahradzovaní oxidu vápenatého v sústave rastie priemerný rozmer iónov v tavenine. Odlišný vplyv SiO_2 je možno sledovať pri závislostiach s najvyšším konštantným obsahom oxidu železitého resp. minimálneho obsahu oxidu vápenatého. Získané výsledky potvrdili, že fyzikálno-chemické vlastnosti feritickovápenatých troskových tavenín sú v najväčšej miere ovplyvňované charakterom železito kyslíkových aniónových komplexov. V týchto komplexných aniónoch trojmocného železa sa mení koordinácia iónu Fe^{3+} s kyslíkom z oktaédrickej na tetraédrickú v závislosti od koncentrácie aniónov kyslíka v taveninovej sústave podľa schémy:



(v zátvorke sú uvedené koordinačné čísla iónov Fe^{3+})

Rast obsahu oxidu železnatého v sústave $\text{Fe}_2\text{O}_3\text{-FeO-CaO-SiO}_2$ spôsobuje zvyšovanie hustoty a povrchového napätia sústavy resp. zníženie mólového objemu a štatistického priemerného rozmeru iónov v tavenine.

Pri sledovaných koncentráciách oxid kremičitý vytvára vo feritickovápenatých taveninách tetraédre SiO_4^{4-} [9]. V taveninovej sústave $\text{Fe}_2\text{O}_3\text{-FeO-CaO-SiO}_2$ je pravdepodobná existencia jednoduchých katiónov Ca^{2+} a Fe^{3+} ako aj zložitejších aniónových komplexov SiO_4^{4-} , FeO_2^- a $\text{Fe}_2\text{O}_5^{4-}$.