

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

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The densities of melts in the system $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$ in air were measured in the temperature range 1540—1910 K. The densities of the investigated melts increase with the increasing content of the iron oxides. The change of the oxidation state of iron with temperature results in nonlinear dependence of density on the temperature and in the decrease of the molar volume of the melts with the increasing temperature. The system $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$ is nonideal. From the dependences of the partial molar volumes of Fe_2O_3 and SiO_2 on the composition it can be assumed that a part of the Fe(III) atoms is coordinated tetrahedrally, *i.e.* it behaves as a network former. The formal negative charge on the iron in the FeO_4 tetrahedron can be compensated with the Ca^{2+} or Fe^{2+} or Fe^{3+} cations, respectively. The entrance of Fe^{3+} into the polyanionic network is accompanied by the volume contraction.

Определена плотность расплавов системы $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$ в атмосфере воздуха в интервале температур 1540 К—1910 К. Плотность расплавов изучаемой системы возрастает с увеличением содержания окислов железа. Изменение степени окисления Fe в расплаве в зависимости от температуры проявляется в виде нелинейной температурной зависимости плотности и в уменьшении мольного объема расплава при увеличении температуры. С точки зрения объемных свойств, система $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$ неидеальна. Исходя из зависимости парциального мольного объема Fe_2O_3 и SiO_2 от концентрации можно сделать вывод, что по крайней мере часть катионов Fe(III) образует тетраэдры FeO_4 и принимает участие в образовании полианионов. Формальный отрицательный заряд центрального атома железа в тетраэдре FeO_4 компенсируется катионом Ca^{2+} или Fe^{2+} или Fe^{3+} . Включение Fe^{3+} в полианионную сеть сопровождается объемным сжатием.

Because of considerable difficulties at high-temperature measurements of the properties of metallurgical slags at the defined partial pressures of the oxygen, the measurements are most frequently carried out in an inert atmosphere. In the case

of the systems with the iron(II) oxide, the melts are held at equilibrium with the metallic iron, and only iron(II) is present in the melt. Densities of melts in the system FeO—SiO_2 at the given conditions were measured in [1—3] and densities in the system CaO—FeO—SiO_2 were studied in [4—9].

The air is one of the atmospheres with defined oxygen partial pressure. If the iron oxides are present in the melt, an equilibrium between two- and threevalent iron, dependent on the temperature and on the composition, is achieved in the melt. Densities of melts in the system $\text{CaO—Fe}_x\text{O}_y\text{—SiO}_2$ have not been measured at such conditions. The dependences of the equilibrium composition of melts in the system $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$ on the temperature, the oxygen partial pressure and on the total composition were determined in [10, 11] where the portions of two- and threevalent iron were analyzed in the quenched samples.

In the present work the densities of melts in the system $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$ in the air were measured in the temperature range 1540—1910 K. Molar volumes of the investigated melts and partial molar volumes of the components were calculated using the known equilibrium compositions of the melts [10, 11].

Experimental

Densities of the melts $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$ were measured by the Archimedean method by apparatus of our own construction [12]. A PtIr10 sphere with a diameter of 15 mm attached to one side of an analytical balance of the type A3/200 by a PtRh40 wire 0.4 mm in diameter was used. Densities were measured in ca. 20 K intervals. Volume of the measuring body at the given experimental temperature was calculated using the data on the temperature expansion of a PtIr10 alloy. The influence of surface tension of the melt upon the suspension wire was taken into account in the calculations of densities.

The sample (ca. 100 g) was placed in a PtRh20 crucible in the electrical resistance furnace. The temperature was measured with an accuracy ± 5 K with a PtRh6—PtRh30 thermocouple which was immersed into the melt.

The samples were made from calcined CaCO_3 , SiO_2 , and Fe_2O_3 (all of anal. grade) by melting in a PtRh20 crucible. The composition of samples was selected to follow, as possible, the change in the 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 [13]. The compositions of the investigated samples are also represented in Fig. 1. The points correspond to two sections with constant mole ratio $k_1 = x(\text{CaO})/x(\text{SiO}_2) = 1$ and $k_2 = x(\text{CaO})/x(\text{Fe}_2\text{O}_3) = 4$. The equilibrium compositions of melts at the given experimental temperature were calculated according to

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

where $r = x(\text{Fe}_2\text{O}_3)/[x(\text{FeO}) + x(\text{Fe}_2\text{O}_3)]$, $k = x(\text{CaO})/x(\text{SiO}_2)$, T is the temperature (K) and $x'(\text{Fe}_2\text{O}_3)$ is the mole fraction of Fe_2O_3 in the weighed mixture. Eqn (1) was derived in

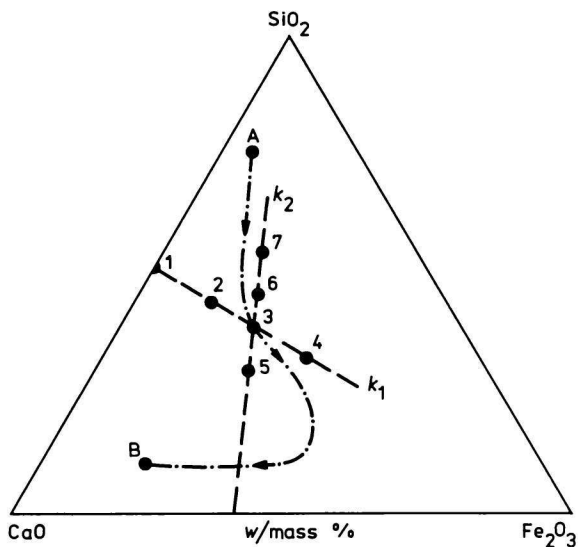


Fig. 1. The chosen sections in the system CaO—Fe₂O₃—SiO₂ (for k_1 , k_2 see the text). 1—7: The weighed compositions of the investigated samples; A—B: the path of the slag composition in the model system CaO—Fe₂O₃—SiO₂ during the steelmaking process [13].

the present work using the data taken from [10, 11] and is valid in the intervals T (1673 K; 1823 K), k (0.5; 1.5) and x' (Fe₂O₃) (0; 0.25). The contents of two- and threevalent iron were also determined experimentally in the quenched samples after measurements. The analyses were carried out by titration and also by the atomic absorption spectroscopy and were in good agreement with compositions calculated according to eqn (1).

Results and discussion

The temperature dependences of densities of the investigated melts were described in the form

$$\rho = a + bT + cT^2 \quad (2)$$

where T is the temperature (K). The parameters of eqn (2) are given in Table 1. The quadratic term in eqn (2) is a consequence of the change of the iron oxidation state with temperature, which also results in the decrease of the molar volumes of the melts with the increasing temperature. Densities of melts in the system CaO—FeO—Fe₂O₃—SiO₂ increase with the increasing contents of calcium oxide and of iron oxides in particular. Molar masses and molar volumes of the investigated melts at 1723 K were calculated using the equilibrium compositions.

Table 1

Temperature dependence of density of the investigated melts in the system CaO—FeO—Fe₂O₃—SiO₂
 $\rho = a + bT + cT^2$ (T —thermodynamic temperature)

Sample	$\frac{a}{\text{g cm}^{-3}}$	$\frac{b \cdot 10^3}{\text{g cm}^{-3} \text{K}^{-1}}$	$\frac{c \cdot 10^7}{\text{g cm}^{-3} \text{K}^{-2}}$	$\frac{\sigma \cdot 10^3}{\text{g cm}^{-3}}$	T/K	$\frac{\rho_{1723 \text{ K}}}{\text{g cm}^{-3}}$
1*	2.990	-0.195	—	4.5	1830—1910	(2.665)
2	4.232	-1.448	3.520	1.1	1740—1900	(2.781)
3	4.189	-1.294	3.123	0.8	1620—1860	2.887
4	4.016	-0.906	1.993	1.5	1540—1830	3.046
5	2.122	1.082	-3.425	1.1	1660—1880	2.960
6	3.497	-0.605	1.198	0.7	1560—1860	2.809
7	2.838	-0.014	-0.382	1.8	1670—1860	2.700

* According to Ref. [14]; the data in brackets are extrapolated.

Table 2

Equilibrium composition, molar mass and molar volume of the investigated melts at 1723 K

Sample	$x(\text{CaO})$	$x(\text{FeO})$	$x(\text{Fe}_2\text{O}_3)$	$x(\text{SiO}_2)$	$\frac{M}{\text{g mol}^{-1}}$	$\frac{V}{\text{cm}^3 \text{mol}^{-1}}$
1*	0.500	—	—	0.500	58.07	21.790
2	0.472	0.010	0.046	0.472	62.88	22.611
3	0.444	0.019	0.092	0.444	67.62	23.422
4	0.412	0.030	0.146	0.412	73.32	24.071
5	0.517	0.009	0.120	0.353	70.00	23.649
6	0.383	0.022	0.074	0.521	66.17	23.556
7	0.312	0.023	0.055	0.610	64.57	23.915

* According to Ref. [14].

Results are given in Table 2. Molar volume of melts in the system in question can be described generally

$$V = x(\text{CaO}) \cdot V^\circ(\text{CaO}) + x(\text{FeO}) \cdot V^\circ(\text{FeO}) + x(\text{Fe}_2\text{O}_3) \cdot V^\circ(\text{Fe}_2\text{O}_3) + x(\text{SiO}_2) \cdot V^\circ(\text{SiO}_2) + V^e \quad (3)$$

where $x(i)$ are the equilibrium mole fractions of the oxides and $V^\circ(i)$ are the corresponding molar volumes, V^e is the excess molar volume. The excess molar volume of melts in the multicomponent oxide system can be expressed, according to [14], with a good approximation, by adding together the excess molar volumes of the boundary binary systems

$$V^e = \sum_i \sum_j x_i x_j (A_0 + x_j A_1 + \dots) \quad (4)$$

On the basis of the present experimental results it is not possible to calculate all volumes $V^\circ(i)$ in eqn (3) and coefficients A_i in eqn (4) using a regression analysis. Some simplifications were therefore taken in solution of eqns (3) and (4). Because of generally low contents of FeO in the investigated melts all contributions of the excess molar volumes from binary systems comprising FeO were neglected. Molar volumes of the pure oxides were taken from literature [15]. For 1723 K they were: $V^\circ(\text{CaO}) = 16.5 \text{ cm}^3 \text{ mol}^{-1}$, $V^\circ(\text{FeO}) = 12.8 \text{ cm}^3 \text{ mol}^{-1}$, $V^\circ(\text{Fe}_2\text{O}_3) = 52 \text{ cm}^3 \text{ mol}^{-1}$, $V^\circ(\text{SiO}_2) = 26.8 \text{ cm}^3 \text{ mol}^{-1}$. From the given values the excess molar volumes in the investigated melts were calculated. Using a regression analysis and by minimizing the standard deviation as well as by excluding the statistically nonsignificant terms, eqn (4) was expressed in the form

$$\begin{aligned} \frac{V^e}{\text{cm}^3 \text{ mol}^{-1}} = & x(\text{CaO}) \cdot x(\text{SiO}_2) [8.9002 - 16.872x(\text{SiO}_2)] + \\ & + 35.625x(\text{CaO}) \cdot x(\text{Fe}_2\text{O}_3) - \\ & - x(\text{Fe}_2\text{O}_3) \cdot x(\text{SiO}_2) [148.165 - 189.959x(\text{SiO}_2)] \end{aligned} \quad (5)$$

Standard deviation of V^e was $\sigma = 0.026 \text{ cm}^3 \text{ mol}^{-1}$. This value is lower than the experimental error $\pm 0.005 \text{ g cm}^{-3}$ or $\pm 0.04 \text{ cm}^3 \text{ mol}^{-1}$ [12].

In order to obtain the information about the influence of calcium oxide and iron(III) oxide on the structure of melts in the system $\text{CaO}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ the partial molar volumes of the oxides were calculated. The calculations were carried out along the sections with constant ratios $x(\text{CaO})/x(\text{Fe}_2\text{O}_3) = k_2$ and $x(\text{FeO})/x(\text{Fe}_2\text{O}_3) = k_3$ passing through the SiO_2 peak of the concentration tetrahedron. Partial molar volumes of the oxides were obtained by the differentiation of eqn (3) with respect to $x(\text{SiO}_2)$ and substituting in eqns

$$V(\text{SiO}_2) = V + [1 - x(\text{SiO}_2)] \frac{dV}{dx(\text{SiO}_2)} \quad (6)$$

$$V(\text{M}_x\text{O}_y) = V - x(\text{SiO}_2) \frac{dV}{dx(\text{SiO}_2)} \quad (7)$$

where $V(\text{M}_x\text{O}_y)$ is the partial molar volume of the oxide mixture on the $\text{M}_x\text{O}_y-\text{SiO}_2$ line. The calculations were carried out for the boundary binary systems $\text{CaO}-\text{SiO}_2$ ($k_2 = \infty$, $k_3 = 0$) and $\text{Fe}_2\text{O}_3-\text{SiO}_2$ ($k_2 = k_3 = 0$). Molar volumes and the partial molar volumes of the components in the system $\text{CaO}-\text{SiO}_2$ are represented in Fig. 2. The system is nonideal and the maximum deviation from the additive molar volume is 4.5 %. Volume expansion occurs in the range of high contents of CaO. Comparing with the CaO melt larger structural particles are present in this concentration range. Orthosilicate anions and the anions with short chains predominate in these melts. In the range of high contents of SiO_2 (acidic melts) volume contraction occurs. This may be caused by a destruction of the

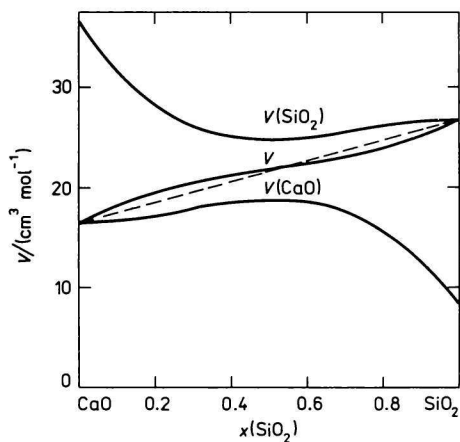


Fig. 2. Volume properties of melts in the system CaO—SiO₂ at 1723 K.

V — molar volume of the melts, $V(\text{CaO})$ — partial molar volume of CaO, $V(\text{SiO}_2)$ — partial molar volume of SiO₂.

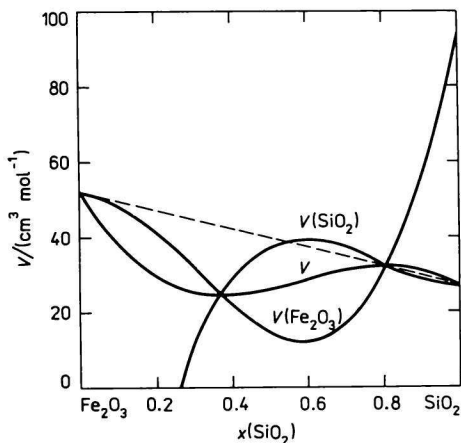


Fig. 3. Volume properties of melts in the system Fe₂O₃—SiO₂ at 1723 K.

V — molar volume of the melts, $V(\text{Fe}_2\text{O}_3)$ — partial molar volume of Fe₂O₃, $V(\text{SiO}_2)$ — partial molar volume of SiO₂.

polyanionic network by the effect of CaO. In this concentration region silicate polyanions are formed, in particular, by globular particles [16] that liberate their inner free volume during the depolymerization. This process leads to the statistically closer arrangement of the SiO₄ tetrahedrons.

As it was mentioned above, the contributions of the excess molar volumes due to FeO were neglected because of its low content in the investigated melts. The application of eqns (6) and (7) would therefore lead to an ideal mixing in the system FeO—SiO₂. However, with respect to the chemical properties of Fe²⁺ cation, interactions between particles in the FeO—SiO₂ system, similar to those in the CaO—SiO₂ system, may be assumed. Similar courses of the volume functions may therefore be expected.

Entirely different behaviour was found in the system Fe₂O₃—SiO₂. The dependences of the molar volume and of the partial molar volumes of the components on the melt composition are represented in Fig. 3. Wide region of the volume contraction is obvious. The partial molar volume of Fe₂O₃ decreases with the increasing SiO₂ content, and it passes through a minimum at ca. 60 mole % SiO₂. This leads to the decrease in the molar volume when Fe₂O₃ is added to a mixture in the concentration range 35—85 mole % SiO₂. The phenomenon may be explained by the entrance of Fe₂O₃ into the polyanionic network in the form of FeO₄ tetrahedrons. Formal negative charge on the iron in FeO₄ tetrahedron may be compensated by another Fe³⁺ cation which is more highly coordinated with unshared oxygen atoms. The double-dealing behaviour of Fe³⁺ cations has to

be imagined in some dynamic equilibrium. In the multicomponent system $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$ the charge compensation may also be done by Ca^{2+} and Fe^{2+} cations, respectively.

In paper [17] it was shown that in the investigated concentration range of the system $\text{CaO—Fe}_2\text{O}_3\text{—SiO}_2$ approximately a half of Fe(III) is coordinated tetrahedrally (it behaves as a network former), while the other half of Fe(III) is coordinated higher, *i.e.* it behaves as a network modifier. It means that each Fe_2O_3 formula unit introduces one oxygen atom into melt which breaks the polyanionic network. The other two oxygen atoms participate in the FeO_4 tetrahedron formation. This results in the decrease of polymerization degree of the melt when Fe_2O_3 is added. Consequently, the smaller anions will statistically be present in the melt, which results, *e.g.*, in the decrease of viscosity of the melt [18].

A narrow region of the unmarked volume dilatation at the high SiO_2 contents may be a consequence of a phase immiscibility in this concentration region.

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