

Calculation of liquidus surfaces of CaSiO_3 in the CaO—FeO—SiO_2 and $\text{CaO—Fe}_2\text{O}_3\text{—SiO}_2$ systems

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Activity of CaSiO_3 in the CaO—FeO—SiO_2 and $\text{CaO—Fe}_2\text{O}_3\text{—SiO}_2$ melts was calculated using the approach similar to that used by Haase in the calculation of chemical potential of a component in an ionic solution. From the activity values liquidus surfaces of CaSiO_3 were obtained by the LeChatelier—Shreder equation. A structural analogy of the crystalline phase and the melt was assumed in the calculation. Good agreement of the calculated phase diagrams with the experimental ones was achieved provided that a half of the trivalent iron, present in the melt, was tetrahedrally coordinated (and it behaved as a network former), while the other half behaved as a network modifier. Tetrahedral coordination of a little part of the bivalent iron in the CaO—FeO—SiO_2 system cannot be excluded.

Проведен расчет активности CaSiO_3 в расплавах систем CaO—FeO—SiO_2 и $\text{CaO—Fe}_2\text{O}_3\text{—SiO}_2$, причем был использован метод, подобный методу Хааса расчета химического потенциала компонента в растворе. Области ликвидуса CaSiO_3 были найдены исходя из величин активности с помощью уравнения ЛеШателье—Шредера. При расчете подразумевалась аналогия структур кристаллической фазы и расплава. Было обнаружено хорошее совпадение рассчитанной и экспериментально измеренной фазовой диаграммы при предположении, что половина трехвалентного железа, находящегося в расплаве, располагается в тетраэдрической координации и способствует сшиванию полианионной сетки, в то время как остальная часть находится в виде катионов и компенсирует зарядный дефицит тетраэдрически координированных атомов железа. Однако, нельзя полностью исключить также и тетраэдрическую координацию малой части ионов Fe^{2+} в системе CaO—FeO—SiO_2 .

In the research of structure and properties of the oxide melts a great attention is paid to the coordination and behaviour of some trivalent cations, *e.g.* B^{3+} , Al^{3+} , Fe^{3+} . Of the melts containing Fe^{2+} and Fe^{3+} , which are the basis of metallurgical slags, some are of great technological importance. In the melts of the $\text{CaO—Fe}_x\text{O}_y\text{—SiO}_2$ system iron is present in two oxidation states, the amount

of Fe^{2+} being dependent on temperature, partial pressure of the oxygen and on the melt composition. Phase equilibria in the four-component system CaO — FeO — Fe_2O_3 — SiO_2 are described in [1]. Two phase diagrams corresponding to two partial pressures of the oxygen are generally known [2]. They are the CaO —"FeO"— SiO_2 system in equilibrium with metallic iron, and the CaO —"Fe₂O₃"— SiO_2 system in equilibrium with air (partial pressure of the oxygen being 21 kPa). Quotation marks at the iron oxides emphasize the fact that at the given conditions the above systems are not really the three-component ones. The diagrams in question are projections of the real liquidus surfaces in the four-component system CaO — FeO — Fe_2O_3 — SiO_2 into boundary surfaces along the oxygen reaction lines.

Larson and Chipman [3] established the content of trivalent iron in the CaO — Fe_xO_y — SiO_2 melts at 1550 °C and at different partial pressures of the oxygen. They started from the phase equilibria in the iron—oxygen system at different partial pressures of the oxygen which had been studied by Darken and Gurry [4], and from other works [5, 6] dealing with the real composition of the CaO — Fe_xO_y — SiO_2 melts. The strong increase in the Fe^{3+} content with the increasing concentration of CaO was found [3], while the total concentration of the iron oxides did not have a significant effect. The content of Fe^{3+} depends on the x_c/x_s modulus. The temperature effect on the Fe^{3+} content in the CaO — FeO — Fe_2O_3 — SiO_2 melts was studied by Timucin and Morris [1]. These results are in agreement with [4]. Of all the works cited it can be assumed that in the region of relatively low concentrations of the iron oxides, the content of Fe^{2+} in the CaO —"Fe₂O₃"— SiO_2 system can be neglected with good approximation. For example, in the whole region of primary crystallization of pseudowollastonite, the content of FeO is less than 3 mole %.

Trivalent cations, e.g. Al^{3+} , Fe^{3+} can enter into polyanion network being in the fourfold coordination (network former), or similarly to bivalent cations, be in higher coordination and behave as the network modifier [7, 8]. From the conductance measurements in the CaO — FeO — Fe_2O_3 — SiO_2 melts [9] it follows that at least a part of the present Fe^{3+} ions is tetrahedrally coordinated. However, quantitative conclusions cannot be drawn from the conductance measurements only. Partially tetrahedral coordination of Fe^{3+} ions is also indicated by the X-ray diffraction in the FeO — Fe_2O_3 — SiO_2 melts [10]. The dependence of interatomic distance Fe — O on the composition is similar to that of Si — Si , which corresponds to the transition of Fe^{3+} ions from the octahedral sites to the tetrahedral ones.

Relatively unambiguous situation is in the CaO —"FeO"— SiO_2 system, where Fe^{2+} ions are placed in the interstitial sites with the higher than fourfold coordination. However, according to the results of density measurements [11], these melts tend to microsegregation into regions richer in calcium oxide, and regions richer in iron oxide.

Comparison of liquidus curves or surfaces calculated using a suitable thermodynamic model with the experimental ones is one of the indirect methods of melt structure study. In the previous papers [12, 13] the thermodynamic model of silicate melts has been suggested, based on an analogy in the structure of the crystalline phase and of the melt. The model was used for the calculation of liquidus curves in the CaO—MgO—SiO_2 [12] and $\text{M}_2\text{O—B}_2\text{O}_3$ ($\text{M} = \text{Li, Na, K}$) [13] systems. In the present work the calculation of liquidus surfaces of CaSiO_3 in the CaO—FeO—SiO_2 and $\text{CaO—Fe}_2\text{O}_3\text{—SiO}_2$ systems was carried out.

Calculations

Let us consider the three-component system CaO—FeO—SiO_2 consisting of a moles of CaO , b moles of FeO , and c moles of SiO_2 . The total amount of substance of the oxygen in an arbitrary mixture is then $a + b + 2c$; the amount of substance of the Si—O bonds in the SiO_4 tetrahedrons is $4c$. The amount of substance of bridging oxygen is then equal to $4c - (a + b + 2c) = 2c - a - b$, and the amount of substance of nonbridging oxygen is $2a + 2b$. According to Haase approach [14], activity of the i -th component in solution is given by

$$a_i = \prod_{j=1}^k \left(\frac{y_j}{y_{i,j}^0} \right)^{n_{i,j}} \quad (1)$$

where $y_{i,j}^0$ and y_j are the mole fractions of the j -th particles (Ca^{2+} , Fe^{2+} , Si^{4+} , bridging and nonbridging oxygen) in the pure i -th component and in the mixture defined by the relations

$$y_{i,j}^0 = \frac{n_{i,j}}{\sum_j n_{i,j}}, \quad y_j = \frac{\sum_i (n_{i,j} \cdot x_i)}{\sum_i (x_i \sum_j n_{i,j})} \quad (2)$$

$x_i = a, b, c$, i.e. the mole fraction of the fundamental component (CaO , FeO , SiO_2) and $n_{i,j}$ is the number of the j -th particles in the fundamental component. Activity of CaSiO_3 (CS) is then given by the equation

$$a_{\text{CS}} = \left(\frac{a}{0.2s_j} \right) \left(\frac{c}{0.2s_j} \right) \left(\frac{2c - a - b}{0.2s_j} \right) \left(\frac{2a + 2b}{0.4s_j} \right)^2 \quad (3)$$

where $s_j = 2a + 2b + 3c$.

In the three-component system $\text{CaO—Fe}_2\text{O}_3\text{—SiO}_2$ consisting of a moles of CaO , b moles of Fe_2O_3 , and c moles of SiO_2 the total amount of substance of the oxygen in an arbitrary mixture is equal to $a + 3b + 2c$. Provided that all present Fe^{3+} ions are tetrahedrally coordinated, the amount of substance of the M—O

bonds in tetrahedrons MO_4 ($\text{M} = \text{Si}, \text{Fe}$) is equal to $8b + 4c$. The amount of substance of bridging oxygen is then $2c - a + 5b$ and of nonbridging oxygen $2a - 2b$. For the activity of CaSiO_3 it holds

$$a_{\text{CS}} = \left(\frac{a}{0.2s_j} \right) \left(\frac{c}{0.2s_j} \right) \left(\frac{2c - a + 5b}{0.2s_j} \right) \left(\frac{2a - 2b}{0.4s_j} \right)^2 \quad (4)$$

where $s_j = 2a + 5b + 3c$. It is evident that similar relation can be derived for the case, when the whole iron will be present as the Fe^{3+} ions with higher coordination number and will behave as the network modifier.

Liquidus surfaces of CaSiO_3 in the CaO —“ FeO ”— SiO_2 and CaO —“ Fe_2O_3 ”— SiO_2 systems were calculated for chosen values of a , b , c according to the modified and simplified LeChatelier—Shreder equation ($\Delta H_f = \text{const}$)

$$T_{\text{liq}} = \frac{\Delta H_f \cdot T_f}{\Delta H_f - R \cdot T_f \cdot \ln a_{\text{CS}}} \quad (5)$$

where ΔH_f and T_f are the enthalpy and temperature of fusion of CaSiO_3 , respectively and a_{CS} is the activity of CaSiO_3 . Boundary curves of liquidus surface of CaSiO_3 were obtained by a similar calculation of liquidus surfaces of Ca_2SiO_4 , and Fe_2SiO_4 and Fe_2O_3 , respectively. Boundary curve with liquidus surface of tridymite could not be determined because of large immiscibility gap in the region of high concentrations of SiO_2 ; the thermodynamic model used does not imply such cases. The required thermodynamic data for the calculation of liquidus temperatures according to eqn (5) were adopted from [15, 16]. The calculated parts of

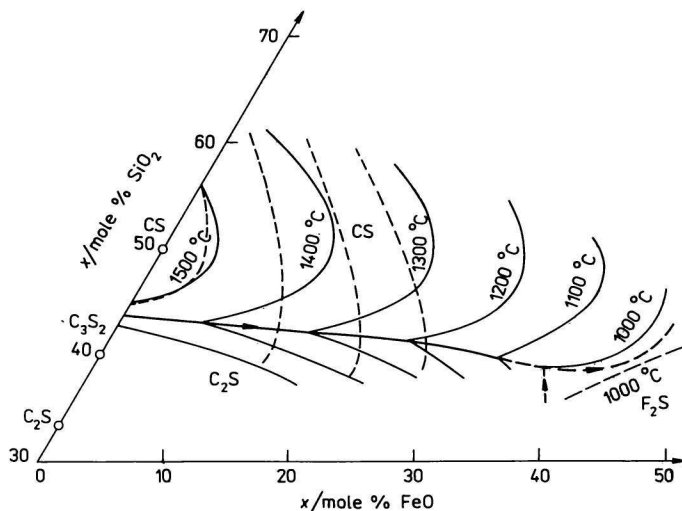


Fig. 1. The calculated part of phase diagram of the CaO —“ FeO ”— SiO_2 system.

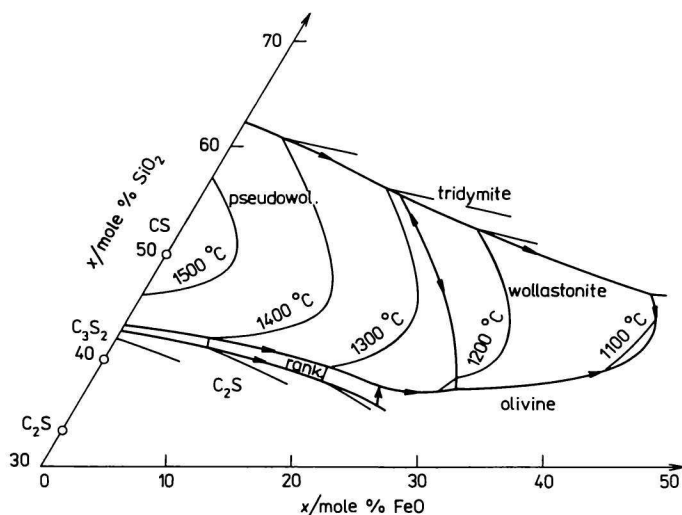


Fig. 2. The part of phase diagram of the CaO—"FeO"—SiO₂ system according to Muan and Osborn [2].

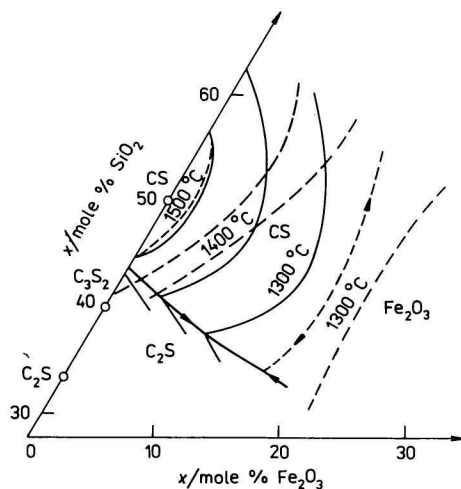


Fig. 3. The calculated part of phase diagram of the CaO—"Fe₂O₃"—SiO₂ system.

phase diagrams are presented in Figs. 1 and 3; for the comparison the experimental ones according to Muan and Osborn [2] are presented in Figs. 2 and 4.

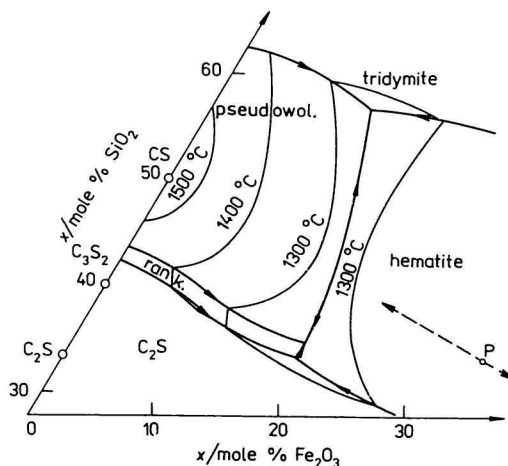


Fig. 4. The part of phase diagram of the CaO — Fe_2O_3 — SiO_2 system according to Muan and Osborn [2].

Discussion

The comparison of the calculated and experimentally determined phase diagrams of the system CaO — FeO — SiO_2 presented in Figs. 1 and 2 shows a relatively good agreement, provided that all present Fe^{2+} cations are in higher coordination and behave as the network modifier. The dotted lines in Fig. 1 represent isotherms in liquidus surface of CaSiO_3 calculated for the case, when all Fe^{2+} ions behave as the network former. It is evident that such assumption is not correct. However, a little part of tetrahedrally coordinated Fe^{2+} ions cannot be excluded. In these calculations the presence of rankinite was neglected, because of narrow region of its primary crystallization. The transition of pseudowollastonite to wollastonite was neglected, too. These simplifications, however, have not essential effect on the conclusions concerning the behaviour of Fe^{2+} cations in the melts.

The calculations of liquidus surfaces in the CaO — Fe_2O_3 — SiO_2 system were carried out for two cases:

- a) The whole trivalent iron is coordinated tetrahedrally and together with the SiO_4 tetrahedrons participates on creating polyanions.
- b) The half of the trivalent iron is coordinated tetrahedrally and the other one behaves as cations with higher coordination.

The third possibility, that the whole trivalent iron behaves as the network modifier was, as unlikely, not considered. Dotted lines in Fig. 3 represent isotherms of liquidus surface of CaSiO_3 for the first case. Such assumption is obviously

unsuitable. Very good agreement with the experimental phase diagram (Fig. 4) was achieved in the second case. In Fig. 3 the corresponding isotherms are represented by full lines. Therefore, it may be stated that in the melts of the CaO—"Fe₂O₃"—SiO₂ system with the x_c/x_s modulus in the range 0.6—1.5 roughly the half of the present trivalent iron is coordinated tetrahedrally and behaves as the network former, while the other one contributes to the polyanion destruction and behaves as the network modifier. Such arrangement does not exclude the possibility of formation of ferritic ions of the type Fe₂O₄²⁻ and Fe₂O₅⁴⁻, respectively, as it is given in papers of Mori and Suzuki [17] and Engell and Vygen [9]. In the calculations of the liquidus surface of CaSiO₃ in the CaO—"Fe₂O₃"—SiO₂ system the region of primary crystallization of rankinite was also neglected. Because of the lack of thermodynamic data, the calculation of boundary curve with hematite was carried out using the experimentally determined coordinates of the cross section of compatibility join CaSiO₃—Fe₂O₃ and boundary curve between the regions of primary crystallization of hematite and magnetite (point P in Fig. 4).

It is to be concluded that in spite of simplifications made in the calculations, valuable information on the structure of the oxide melts on the semiquantitative level can be obtained by the method used. The conclusions concerning the coordination of iron atoms in the silicate melts are obviously valid only in the region with the modulus $x_c/x_s \approx 1$.

References

1. Timucin, M. and Morris, A. E., *Met. Trans.* 1, 3193 (1970).
2. Muan, A. and Osborn, E. F., *Phase Equilibria Among Oxides in Steelmaking*. Addison-Wesley Publishing Co., Reading, Mass., 1965.
3. Larson, H. and Chipman, J., *Trans. Met. Soc. AIME* 197, 1089 (1953).
4. Darken, L. S. and Gurry, R. W., *J. Amer. Chem. Soc.* 68, 798 (1946).
5. Fetters, K. L. and Chipman, J., *Trans. Met. Soc. AIME* 145, 95 (1941).
6. Taylor, C. R. and Chipman, J., *Trans. Met. Soc. AIME* 154, 228 (1943).
7. Bates, T., in *Modern Aspects of the Vitreous State*. (Mackenzie, J. D., Editor.) P. 195. London, 1962.
8. Henderson, J., *Trans. Met. Soc. AIME* 230, 501 (1964).
9. Engell, H.-J. and Vygen, P., *Ber. Bunsenges. Phys. Chem.* 72, 5 (1968).
10. Waseda, Y., Shiraishi, Y., and Toguri, J. M., *Trans. Jap. Inst. Met.* 21, 51 (1980).
11. Lee, Y. E. and Gaskell, D. R., *Met. Trans.* 5, 853 (1974).
12. Pánek, Z. and Daněk, V., *Silikáty* 21, 97 (1977).
13. Daněk, V. and Pánek, Z., *Silikáty* 23, 1 (1979).
14. Haase, R., *Thermodynamic Properties of Gases, Liquids and Solids*, in *Physical Chemistry*, Vol. 1, p. 352. (Eyring, H., Henderson, D., and Jost, W., Editors.) Academic Press, New York, 1971.

15. Barin, I. and Knacke, O., *Thermochemical Properties of Inorganic Substances*. Springer Verlag, Berlin—Verlag Stahleisen, Düsseldorf, 1973.
16. Bottinga, Y. and Richet, P., *Earth Planet. Sci. Lett.* 40, 382 (1978).
17. Mori, K. and Suzuki, K., *Trans. Iron Steel Inst. Jap.* 8, 382 (1968).

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