Původní práce

COORDINATION OF Al^{III} ATOMS IN MELTS OF THE SYSTEM CaO−Al_2O_3−SiO_2

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Calculation was carried out of a part of the phase diagram of the system
CaO—Al_2O_3—SiO_2 in the region of primary crystallization of wollastonite,
anorthite, gehlenite and dicalcium silicate ($xCaO/xAl_2O_3 \geq 1$)/. A satis-
factory agreement with the experimentally determined phase diagram was
obtained on the assumption that only one half of the Al^{III} atoms present is
tetrahedrally coordinated and the remaining half shows a higher coordination,
behaves as a modifier of the tetrahedral network, and thus does not contribute
to the cross-linking of the polyanions. The behaviour of Al^{III} atoms in silicate
melts is similar to that of Fe^{III} atoms.

INTRODUCTION

The coordination of Al^{III} atoms in aluminositicate melts is one of the significant directions of research of the structure of melts containing alumina, pursued during the last two decades. The interest is associated with extensive utilization of the-melts in a number of branches of the silicate industry, such as glass, cement, porcelain manufacture, etc.

The first comprehensive findings on the coordination of aluminium atoms in silicate melts, particularly in the system $Na_2O−Al_2O_3−SiO_2$, were provided by the studies by Riebling [1, 2]. Of the other authors who paid attention to the subject, mention can be made e.g. of Brückner et al. [3—5] and Urbain et al. [6—8]. All the-se works presented conclusions on the coordination of Al^{III} atoms based on inter-pretation of the physical properties of aluminosilicate melts, such as density and viscosity, in terms of composition, particularly the ratio $x(MeO)/x(Al_2O_3)$. The basic idea of the studies and thus an assumption in the interpretation of the property vs- composition relationship was the concept that in melts with the ratio $x(MeO)/x(Al_2O_3) \geq 1$, all the Al^{III} atoms were tetrahedrally coordinated and that the octahedral coordination of the Al^{III} atoms only occurs at the ratio $x(MeO)/x(Al_2O_3) < 1$, i.e. at an excess of alumina with respect to MeO.

In the previous work [9], the proportion of tetrahedrally coordinated Fe^{III} atoms in melts of the system $CaO−Fe_2O_3−SiO_2$ was determined by comparing the ex-perimentally established $CaSiO_3$ liquidus surface with that computed by means of a thermodynamic model of silicate melts [10] which allows the structural aspects to be taken into account in the calculation of the activity of a component in solution. In study [9] it was found that in the metasilicate composition region (i.e. $x(CaO)/x(Fe_2O_3) \cong 1$), roughly half of the Fe^{III} atoms are coordinated tetrahedrally, whereas the other half has higher coordination, so that it behaves as a modifier of the tetra-

hedral network of the polyanions. This finding was additionally confirmed by the interpretation of some physical properties of melts in the system $CaO-FeO-Fe_2O_3-SiO_2$ [11—14].

The present study was concerned with calculating a part of the phase diagram of the system $CaO-Al_2O_3-SiO_2$ in the region of primary crystallization of wollastonite, anorthite, gehlenite and dicalcium silicate while taking into account the structural aspects of the coordination of Al^{III} atoms. The calculation was carried out by means of Haase's approach for activity computation of components in solution [15].

THEORETICAL

Let us have a moles of CaO, b moles of Al_2O_3 and c moles of SiO_2 in solution. The amount of substance of oxygen atoms in such a solution is equal to $a + 3b + 2c$. On the assumption that all the Al^{III} atoms present are tetrahedrally coordinated, the amount of substance of the $Si(Al)-O$ bonds in the SiO_4 or AlO_4 tetrahedra is equal to $8b + 4c$. Then the amount of substance of the bridging oxygen atoms, i.e. that link two SiO_4 or AlO_4 tetrahedra, is equal to $8b + 4c - (a + 3b + 2c) = 5b + 2c - a$ and the amount of substance of the non-bridging oxygen atoms is $2a - 2b$. The total amount of substance of all atoms in the given mixture is $2a + 5b + 3c$.

On the assumption that only one half of the Al^{III} atoms present are coordinated tetrahedrally, the amount of substance of the $Si(Al) - O$ bonds in the SiO_4 and AlO_4 tetrahedra is equal to $4b + 4c$. Then the amount of substance of the bridging oxygen atoms is equal to $b + 2c - a$ and the amount of substance of the non-bridging oxygen atoms will be $2a + 2b$. In a similar way one can determine the amounts of substances and thus also concentrations of bridging and non-bridging oxygen atoms in an arbitrary mixture of the system $CaO-Al_2O_3-SiO_2$ for an arbitrary fraction of tetrahedrally coordinated aluminium atoms in the melt.

As indicated in the previous studies [9, 10], the chemical potential of an arbitrary liquid component in a melt can be expressed as a sum of chemical potentials of all the atoms constituting the given component, i.e. e.g. with the system $CaO-Al_2O_3-SiO_2$ and the $Ca_2Al_2SiO_7$ component, as a sum of the chemical potentials of calcium, aluminium, silicon atoms and of the bridging and non-bridging oxygen atoms. The activity of a given component can then be calculated according to the equation [15]

$$a_i = \prod_{j=1}^{k} \left(\frac{y_j}{y_j^0} \right)^n, \tag{1}$$

where n is the amount of substances of j-th particles in one mole of a given component and y_j and y_j^0 are molar fractions of j-th particles in mixture and in the pure component respectively. For example, the following expression can be derived for the activity of $Ca_2Al_2SiO_7$ on the assumption that half of the Al^{III} atoms are coordinated tetrahedrally:

$$a(C_2AS) = \left(\frac{a}{0.167s} \right)^2 \left(\frac{2b}{0.167s} \right)^2 \left(\frac{c}{0.083s} \right) \left(\frac{b + 2c - a}{0.083s} \right) \left(\frac{2a + 2b}{0.5s} \right)^6 \tag{2}$$

where $s = 2a + 5b + 3c$, as according to the above method for determining the bridging and non-bridging oxygen atoms, one mole of $Ca_2Al_2SiO_7$ will contain two moles of calcium atoms, two moles of aluminium atoms, one mole of silicon atoms, one mole of bridging oxygen atoms and six moles of non-bridging oxygen atoms.

The values of activity obtained in this way can be substituted into the simplified LeChatelier-Shreder equation so that the primary crystallization temperature of the given component in solution ($\Delta H_i^f = $ const.) is obtained,

$$T_{i,\text{liq.}} = \frac{\Delta H_i^f T_i^f}{\Delta H_i^f - R T_i^f \ln a_i} \tag{3}$$

where ΔH_i^f and T_i^f are the enthalpy and temperature of melting of component i respectively. The values for the components of the system $CaO - Al_2O_3 - SiO_2$ were taken over from the literature [16] and are listed in Table I.

Table I

Enthalpy of melting and temperature of melting of pure components according to the data by Bottinga and Richet [16]

Component	$\dfrac{T_i^f}{K}$	$\dfrac{\Delta H_i^f}{kJ\ mole^{-1}}$
CaSiO₃	1813	56.0
CaAl₂Si₂O₇	1826	166.8
Ca₂Al₂SiO₇	1866	155.9
Ca₂SiO₄	2403	55.4

RESULTS AND DISCUSSION

Fig. 1 shows a part of the phase diagram of the system $CaO - Al_2O_3 - SiO_2$ in the region of primary crystallization of wollastonite, anorthite, gehlenite and dicalcium silicate, calculated on the basis of the assumption that one half of the aluminium
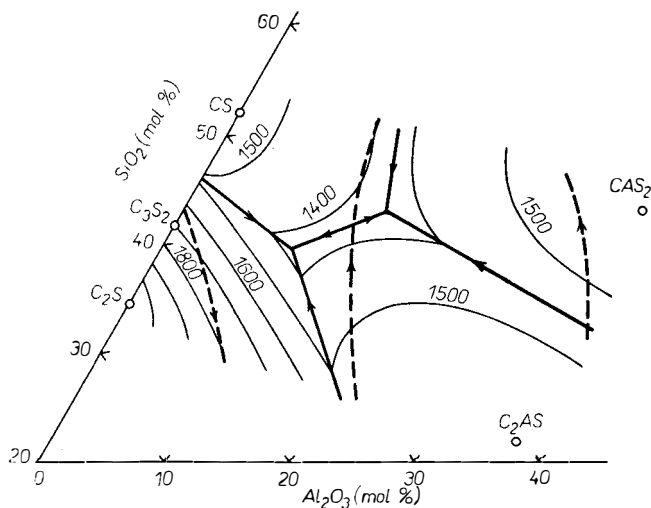

Fig. 1. Calculated part of the phase diagram of the system CaO—Al₂O₃—SiO₂; *full lines — one half of* Al[III] *atoms in tetrahedral coordination, dashed lines — all of the* Al[III] *atoms in tetrahedral coordination.*

atoms present are tetrahedrally coordinated over the entire concentration range in question, and that the other half of the Al^{III} atoms has a higher coordination, obviously an octahedral one, and do not participate in the formation of the poly-anionic network. As follows from a comparison with the experimentally determined phase diagram [17], the agreement is very satisfactory, which indicates that the assumption was acceptable (Fig. 2). The existing idea of tetrahedral coordination
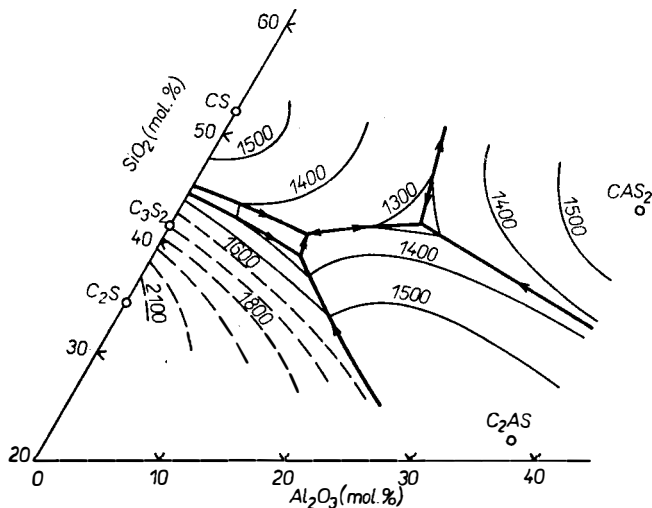

Fig. 2. *Experimentally determined part of the phase diagram of the system* CaO—Al$_2$O$_3$—SiO$_2$ *according to the data by Muan and Osborn [17].*

of all the Al^{III} atoms in the given concentration range $(x(\text{CaO})/x(\text{Al}_2\text{O}_3) \geqq 1)$ is therefore obviously incorrect, as also follows from the boundary lines of the liquidus surfaces for the individual components calculated for this case and designated by dashed lines in Fig. 1. The finding on the partial tetrahedral coordination of Al^{III} atoms in the composition range where the ratio $x(\text{CaO})/x(\text{Al}_2\text{O}_3) \geqq 1$, is relatively surprising in view of the available information on the behaviour of Al^{III} atoms in silicate melts. However, it is in agreement with the similar behaviour of Fe^{III} atoms in the melts of the system CaO—Fe$_2$O$_3$—SiO$_2$ [9].

The results of the calculation of the part of the phase diagram of the system CaO—Al$_2$O$_3$—SiO$_2$, regardless of the good agreement with the experimentally determined phase diagram, can only be considered as qualitative ones in view of the certain simplifications employed in the calculation. The conversion of wollastonite to pseudowollastonite was neglected, as was the narrow region of primary crystallization of rankinite at the dicalcium silicate side. The succes of the calculation procedure suggested is further restricted by the realiability of the thermodynamic data on the melting enthalpy of the components in question. From this point of view, it was decided to use the data specified in the review study by Bottinga and Richet [16]. Precise calorimetric measurements in this system are anyway indispensable.

It can be concluded that the activity calculation method employed is well applicable for various other types of glass-forming oxidic melts, and that it allows the

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structural aspects of the systems being studied to be taken into account by expressing semiquantitatively the various coordinations of some of the atoms present as an adjustable parameter. In this way the method can serve as a calculation method in the study of the structure of oxidic melts.

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KOORDINÁCIA Al[III] ATÓMOV V TAVENINÁCH SÚSTAVY CaO—Al₂O₃—SiO₂

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Uskutočnil sa výpočet časti fázového diagramu sústavy CaO—Al₂O₃—SiO₂ v oblasti primárnej kryštalizácie wollastonitu, anortitu, gehlenitu a dikalciumsilikátu ($x(CaO)/x(Al_2O_3)$) ≥ 1). Ako vyplýva z obrázkov 1 a 2, dobrá zhoda s experimentálne stanoveným fázovým diagramom sa získala za predpokladu, že len polovica prítomných Al[III] atómov je tetraédricky koordinovaná a podieľa sa na tvorbe polyaniónovej siete tetraédrov Si(Al)O₄. Zvýšná polovica Al[III] atómov je vyššie koordinovaná, pravdepodobne oktaédricky, správa sa ako modifikátor tetraédrickej siete a neprispieva teda k zosieťovaniu polyaniónov. Je zrejmé, že doterajšie predstavy o tetraédrickej koordinácii všetkých atómov Al[III] v uvedenej koncentračnej oblasti nezodpovedá skutočnosti. Správanie sa Al[III] atómov v kremičitanových taveninách je podobné ako správanie sa Fe[III] atómov v týchto taveninách.

Obr. 1. Vypočitaná časť fázového diagramu sústavy CaO—Al₂O₃—SiO₂; *plné čiary — polovica* Al[III] *atómov v tetraédrickej koordinácii, čiarkované čiary — všetky* Al[III] *atómy v tetraédrickej koordinácii.*

Obr. 2. Experimentálne stanovená časť fázového diagramu sústavy CaO—Al₂O₃—SiO₂ *podľa údajov Muana a Osborna [17].*

КООРДИНАЦИЯ Al^{III} АТОМОВ В РАСПЛАВАХ СИСТЕМЫ CaO—Al$_2$O$_3$—SiO$_2$

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Проводили расчет части фазовой диаграммы системы CaO—Al$_2$O$_3$—SiO$_2$ в области первичной кристаллизации волластонита, анортита, геленита и дикальциумсиликата (x(CaO)/(Al$_2$O$_3$) ≥ 1). Из рисунков 1 и 2 следует, что хорошее совпадение с установленной экспериментальным путем фазовой диаграммой получается при предположении, что только половина присутствующих Al^{III} атомов тетраэдрически координирована и способствует образованию полианионной сетки тетраэдров Si(Al)O$_4$. Оставшаяся половина Al^{III} атомов координирована выше, правдоподобно октаэдрически, и ведет себя как модификатор тетраэдрической сетки, а следовательно, не способствует структурированию полианионов. Видно, что до сих пор имеющиеся представления относительно тетраэдрической координации всех атомов Al^{III} в приводимой области концентрации не отвечает действительности. Поведение Al^{III} атомов в силикатных расплавах подобно поведению Fe^{III} атомов в данных расплавах.

Рис. 1. Расчитанная часть фазовой диаграммы системы CaO—Al$_2$O$_3$—SiO$_2$; сплошные линии — половина Al^{III} атомов в тетраэдрической координации, штриховые линии — все Al^{III} атомы в тетраэдрической координации.

Рис. 2. Установленная экспериментальным путем часть фазовой диаграммы системы CaO—Al$_2$O$_3$—SiO$_2$ согласно данным Муана и Осборна [17].

C. H. P. LUPIS: CHEMICAL THERMODYNAMICS OF MATERIALS.

(Chemická termodynamika materiálů) 608 str; cena 75 dolarů
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Schopnost aplikovat metody termodynamiky na řešení konkrétních úkolů se dnes pokládá za samozřejmý požadavek na vědeckého pracovníka pracujícího v oblasti vědy o materiálech a materiálového inženýrství. Snahou autora bylo vytvořit učebnici, která by dala potřebný základ pro užití termodynamiky studentům specializace technologie materiálů zejména kovových, a současně by poskytla profesionálním pracovníkům tohoto oboru obraz o současném stavu poznání tj. o nových možnostech použití termodynamiky. Podařilo se účelně vybrat látku a zvolit vhodný způsob zpracování, který je vyvážený jak z hlediska teorie, tak i jejího použití.

Kniha zahrnuje dobře srozumitelně formulovaný výklad základních pojmů i výstavbu celé teorie a ukazuje použití termodynamické metody na řešení problémů fázových a chemických rovnováh, na otázky stability rovnovážných stavů a na otázky chování fázových rozhraní. Účelně je k výkladu užito řešených příkladů, většinou zaměřených na metalurgické problémy a na konci každé kapitoly je uvedena řada zadaných úkolů, na nichž si čtenář může ověřit jak látku pochopil. Správnost způsobu, který použil, si pak může zkontrolovat s řešením uvedeným na konci knihy. Škoda je, že autor nepoužil soustavy SI jednotek. Některé kapitoly např. o standardních stavech a rovnovahách chemických reakcí by se staly pojmově jasnější. Z celé koncepce jsou zřejmé zkušenosti autora s přednášením tohoto oboru (Technische Hochschule Aachen a Carnegie-Mellon University) a také jeho zkušenosti experimentální.

Knihu lze doporučit zejména odborníkům pracujícím ve výzkumu oboru fyzikální metalurgie.

V. Šatava-