



# THERMODYNAMIC PROPERTIES OF MELTS OF $\text{CaO}_2\text{-SiO}_2$ SYSTEM

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Given is the analysis of literature data on the phase equilibriums of constitutional diagrams and thermodynamic properties of alloys of calcium oxide–silicon oxide system. It was found that data on activities of components of these melts are characterized by high scattering. The activity of calcium oxide and silicon oxide in eutectic melt were calculated from coordinates of liquidus line of constitutional diagram of calcium oxide–silicon oxide system. It was established that the calcium activity at silicon concentration of more than 0.2 shows the negative deviations from perfect solutions and correlates with experimentally established data. Activity of silicon oxide at silicon concentration of less than 0.5 in eutectic melt shows the large negative deviations from perfect solutions and correlates with experimentally established ones. At concentration of silicon oxides of 0.34 the activity of silicon oxide is 0.03, i.e. it is by one order lower than its concentration in solution that is explained by the formation of thermodynamically stable two-calcium silicate. At 725 °C  $\alpha$ - $\gamma$  transformation occurs in this compound, accompanied by change in volume. Therefore, it is recommended to keep such ratio of calcium and silicon oxides in the composition of fluxes for electros slag remelting of hollow ingots and welding, at which two-calcium silicate will be formed in the melt. These fluxes will have a poor interaction with molten metal and provide the excellent removal of solidified slag from the surface of ingot and weld metal. 17 Ref., 1 Table, 3 Figures.

**Keywords:** calcium oxide, silicon oxide, constitutional diagram, activity of melt components, fluxes for welding and electros slag remelting

In mechanized electric arc welding, surfacing, as well as in electros slag remelting (ESR) of steels the slags of  $\text{CaO-Al}_2\text{O}_3\text{-CaF}_2$  are widely used. These slags provide usually requirements specified for them as to metallurgical properties, however in this case their technological properties are not rather high. Adding of  $\text{SiO}_2$  into  $\text{CaO-Al}_2\text{O}_3\text{-CaF}_2$  system improves their forming properties, but they increase their chemical activity as applied to melts on iron base. The result of interaction of  $\text{SiO}_2$ , with molten metal is the silicon reduction process, which leads to enrichment of weld metal with non-metallic silicate inclusions. The intensity of the mentioned reactions is proportional to thermodynamic activity of  $\text{SiO}_2$  in the slag melt. Therefore, the evaluation of the latter is quite important in selection of compositions of fluxes for ESR and welding.

Taking into account the high aggressiveness and refractoriness of oxide-fluoride melts, the experimental methods of their investigations are rather complex. During recent years the theoretical methods of prediction of thermodynamic properties of these melts are developed by using similar data for solid compounds and phase equi-

libriums. To predict the thermodynamic properties of  $\text{CaO-Al}_2\text{O}_3\text{-CaF}_2\text{-SiO}_2$  slag system and ternary systems, included into it, it is necessary to carry out the prediction of corresponding binary systems. Earlier we investigated  $\text{CaO-Al}_2\text{O}_3$  system [1]. The subject of this work is the thermodynamic properties of  $\text{CaO-SiO}_2$  system.

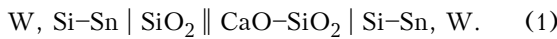
Alloys of  $\text{CaO-SiO}_2$  system represent a great interest for welding and special metallurgy, as they are a base for a number of welding fluxes and refining slags. As the melts of this system have also importance for production of ferrous metals and steels, they serve as an object of many experimental and theoretical investigations [2–14].

To judge about the reactions of interaction of the slag with metallic melts in welding and during metallurgical processes, the information is necessary about their thermodynamic properties, among which the activity of alloy components, heat of formation of compounds and melts are very important. For example, in works [2–10] the activities of silicon dioxide were determined, while in works [3–5, 8–10] the activities of calcium oxide in the range of 1500–1930 °C temperatures were determined. Here the methods of electromotive forces (EMF), high-temperature calorimetry, heterogeneous equilibriums between slags and gas, as well as sulfide capacity



of slags and Knudsen effusion mass-spectrometry were used. The thermodynamic modeling was used also for melts of this system by using the quasi-chemical theory [11], modified quasi-chemical theory [12] and method CALPHAD. As these reactions of interaction between slag and steel in fusion welding proceed at 1800–2300 K, in work [2] the determination of SiO<sub>2</sub> activity in melts of CaO–SiO<sub>2</sub> system was made at higher temperatures than it was done earlier. The activity of SiO<sub>2</sub> was measured by EMF method at temperature 2200 K, and at 1960 K the heat (enthalpy) of formation of CaO–SiO<sub>2</sub> melts was studied.

To determine SiO<sub>2</sub> activity in above-said melts by EMF method, a concentration element with ion transfer was manufactured in work [2] in the form



SiO<sub>2</sub> activity was calculated from the obtained EMF values. Results of calculation are given in the Table and Figure 1.

In Figure 1 the obtained values of SiO<sub>2</sub> activities [2] were compared with data given in other sources [3–9]. These data are only qualitatively correlated between themselves showing alternate deviations from perfect melts that is correlated with their behavior in a solid state. Data [2] correlate with the main number of literature data, but have less deviation from perfect melts. It is probably caused by the higher temperature of making measurements, at the increase of which, as is known, the inter-particle interaction is decreased.

The comparison of available data on activities of components of melts of CaO–SiO<sub>2</sub> system allowed establishing that only in works [8, 10] they were determined at close temperatures (1903 and 1933 K) and have a quite good correlation between themselves (Figure 2).

To determine validity of these data and to describe mostly correctly the thermodynamic properties of molten alloys of CaO–SiO<sub>2</sub> system, the coordinates of liquidus of constitutional diagram of this system were used and using the procedure developed by us [15], the  $a_{CaO}$  was calculated in eutectic melt with  $x_{CaO} = 0.295$ . This value is correlated with those experimentally found in works [8, 10] (see Figure 2).

As is seen from Figure 2, the activities of silica in melts of CaO–SiO<sub>2</sub> system reveal the alternate deviations from Raoult's law. In melts of this system with  $x_{SiO_2} < 0.65$  the SiO<sub>2</sub> activity is characterized by negative, and at  $x_{SiO_2} > 0.65$  by more positive deviations from perfect solutions.

Activity of silicon dioxide in melts of CaO–SiO<sub>2</sub> system [2]

Molar fraction of SiO <sub>2</sub> in melt CaO–SiO <sub>2</sub>	EMF, mV	$a_{SiO_2}$ , molar fraction
0.675	11	0.786 ± 0.002
0.604	16	0.712 ± 0.002
0.503	53	0.325 ± 0.001
0.393	85	0.166 ± 0.001

This is correlated with behavior of melts in solid state. In silicate-silica alloys enriched with SiO<sub>2</sub> there is a large region of delamination. And vice-versa, in alloys with  $x_{SiO_2} < 0.65$  in solid state two compounds are formed, one of which (Ca<sub>2</sub>SiO<sub>4</sub>) is very refractory and melted congruently. It is seen from Figure 2 that in melts at  $x_{SiO_2} > 0.4$  the activity of SiO<sub>2</sub> is by one order lower than its molar fraction in perfect solution and, consequently, they will poorly interact with weld pool metal. This is explained with the formation of congruently melted compound Ca<sub>2</sub>SiO<sub>4</sub>, in which compound 2CaO·SiO<sub>2</sub> is formed, that stipulates the significant reduction of activities of both components. According to the constitutional diagram of CaO–SiO<sub>2</sub> system this compound is melted at very high temperature (2130 °C). Thus, in fluxes on base of CaO–SiO<sub>2</sub> system the content of silica should be less than 0.4 molar fractions. This can decrease the harmful effect of silica in melts of CaO–SiO<sub>2</sub> system and

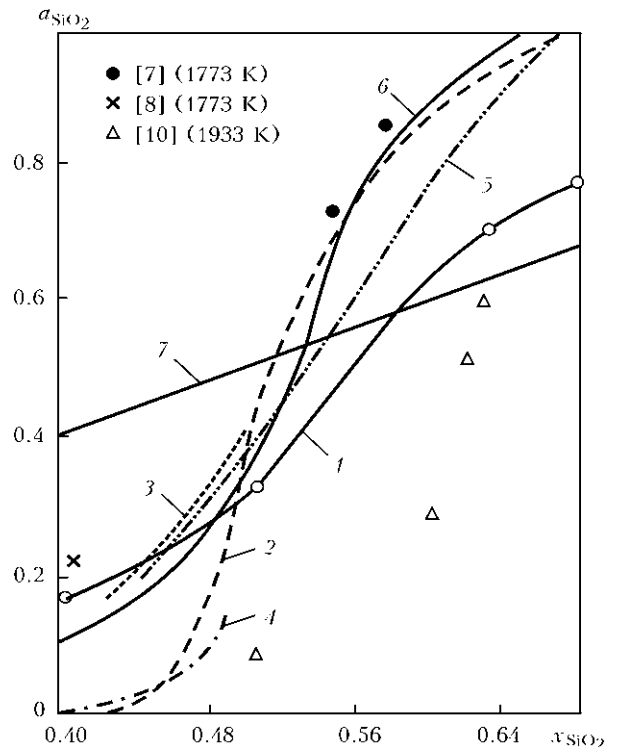
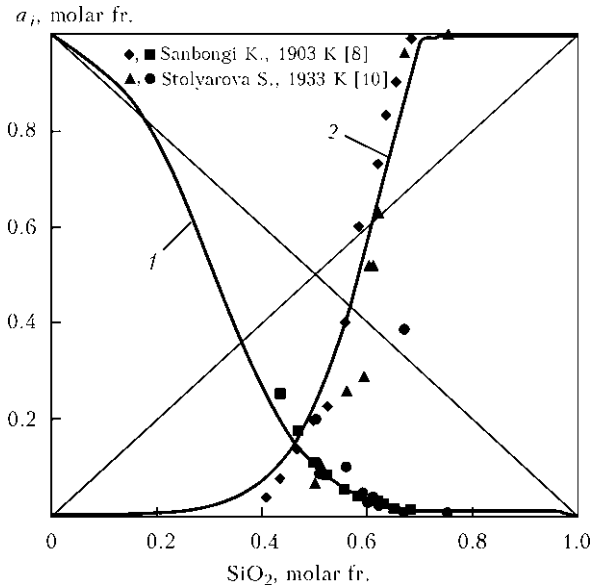


Figure 1. Activity of silicon dioxide in melts of CaO–SiO<sub>2</sub> system: 1 – data of work [2] (2200 K); 2–5 – [3–6] (1873 K); 6 – [9] (1773 K); 7 – perfect solution



**Figure 2.** Activity of components in melts of CaO–SiO<sub>2</sub> system: 1 – activity of CaO, calculation by constitutional diagram, 2000 K; 2 – the same, activity of SiO<sub>2</sub>

in multicomponent slags on metallurgical and technological properties of fluxes.

By the present time the heat of formation of melts of CaO–SiO<sub>2</sub> system was not almost studied. In work [2] the heat (enthalpy) of formation of these melts was investigated by the method of calorimetry to have a complete idea about their nature. The calorimetric cell, mixer and housing of thermocouple were manufactured of molybdenum, which did not interact with the melts being studied. The investigation was made at temperature 1960 ± 15 K. Calibration of calorimeter was made by specimens, manufactured of molybde-

num, tungsten or tin (all these metals do not interact with melts of CaO–SiO<sub>2</sub> system). During experiments the alloy of required composition was placed into calorimetric pool, and then the samples of SiO<sub>2</sub> and CaO in solid state were added to it from drum-type proportioning device. The powder-like calcium oxide was placed preliminary into ampoules, manufactured of tin or copper foils. The obtained data on partial and integral molar enthalpies of components with calculated confidence intervals are given in Figure 3.

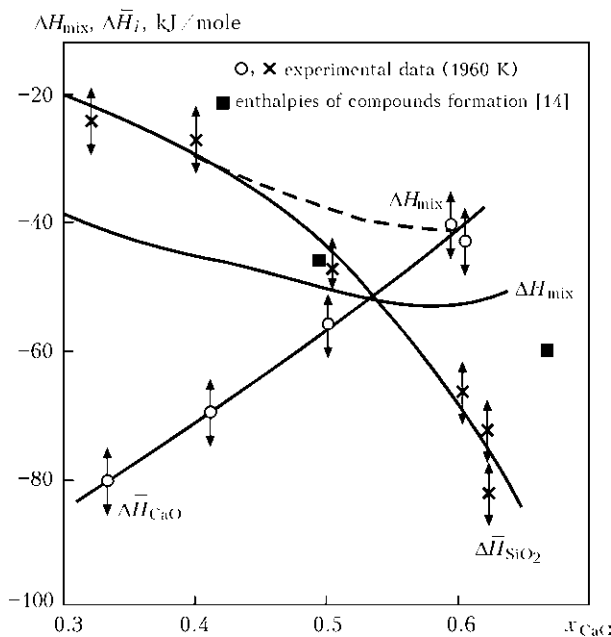
The Figure gives also the values of  $\Delta H_{\text{mix}}$ , calculated by the modified variant of quasi-chemical theory [14]. It is seen that between data of works [2, 11] there is a qualitative correlation. Comparison of definite thermodynamic properties of melts of CaO–SiO<sub>2</sub> system with constitutional diagram showed that they have a good correlation.

For melts containing more than 0.3 molar fractions of CaO, the enthalpies of mixing are the negative values. Minimum on the curve of dependence  $\Delta H_{\text{mix}}$  on composition is 52 kJ/mole and corresponds to the melt close to the congruently melted compound CaSiO<sub>3</sub>.

We compared the integral enthalpies of formation of melts and compounds of CaO–SiO<sub>2</sub> system determined in work [14] in the calorimeter of dissolution. It is seen that they have a good correlation.

So, for binary system CaO–SiO<sub>2</sub> the positive deviations from perfectness (with region of delamination of given temperatures), are typical for alloys with  $x_{\text{SiO}_2} > 0.5$ . At the lower content of SiO<sub>2</sub> these deviations become negative (that correlates with formation of stable solid compounds). The highest negative values are reached in the fields of solidification of such complex compound as 2CaO·SiO<sub>2</sub>. It is thermodynamically stable, i.e. it will have a poor interaction with metal in welding and ESR. This is confirmed by results of our calculations of SiO<sub>2</sub> activity.

Thus, it is possible to select the zone of slag melt compositions, where SiO<sub>2</sub> activity will be minimal and proceeding of processes of interaction with metal will be limited. This analysis was made. It was found that from the point of view of providing the best forming properties of the flux the formation of 2CaO·SiO<sub>2</sub> in the melt will be most priority. Two-calcium silicate has the melting temperature 2130 °C, i.e. at this temperature the solid phase 2CaO·SiO<sub>2</sub> in molten slag melt will form. The presence of the solid phase in the liquid solution will lead to the change of properties, in particular, to the increase in effective toughness that is the positive factor from the point of view of weld formation in weld-



**Figure 3.** Partial and integral enthalpies of mixing of melts of CaO–SiO<sub>2</sub> system: solid curves – approximating curves for  $\Delta H_i$  and  $\Delta H_{\text{mix}}$  [2]; dashed curves – calculation [11]



ing at forced conditions and in ESR in a movable mould. The investigation of melts of CaO–SiO<sub>2</sub>–MgO–Al<sub>2</sub>O<sub>3</sub>–CaF<sub>2</sub> system carried out by Park [16] showed that adding of CaF<sub>2</sub> into composition of oxide melt allows decreasing the solidus temperature of the melt, decreasing the size of solid-phase constituent in the molten slag melt. Thus, there are potentialities for control of constitution and properties of the slag melt.

In addition, the formation of 2CaO·SiO<sub>2</sub> in the melt is positive from the point of view of providing the better slag removal from the metal surface. It is known [17] that at 725 °C the α–γ transformation takes place in this compound, which is accompanied by the change in volume. As a result the significant local stresses occur in the slags, which become the cause of self-disintegration of slags. This effect is very important first of all for the technology of ESR of hollow ingots, where the problem of slags removal from ingot inner surface is very acute.

### Conclusions

1. The carried out critical analysis of literature data on phase equilibriums and thermodynamic properties of alloys of CaO–SiO<sub>2</sub> system made it possible to establish that the constitutional diagram is correct and activity of components of these melts are characterized by large scattering.

2. It is shown that integral enthalpies of formation of melts and compounds of CaO–SiO<sub>2</sub> systems, determined experimentally in isoperibolic calorimeter and calorimeter of dissolution, correlate between themselves.

3. From the coordinates of liquidus line of constitutional diagram of CaO–SiO<sub>2</sub> system determined by different authors were  $a_{\text{CaO}}$  calculated in eutectic melt with  $x_{\text{CaO}} = 0.295$ . It was found that it has large negative deviations from perfect solutions and correlates with experimentally established ones.

4. From the coordinates of liquidus line of constitutional diagram of CaO–SiO<sub>2</sub> system, determined by different authors,  $a_{\text{SiO}_2}$  were calculated. It was found that at  $x_{\text{SiO}_2} < 0.5$  and in eutectic melt it shows the large negative deviations from perfect solutions and correlates with earlier experimentally established ones. At  $x_{\text{SiO}_2} = 0.34a_{\text{SiO}_2}$  it amounts to 0.03, i.e. the activity of SiO<sub>2</sub> is by one order lower of its concentration in solution. This is explained by the formation of thermodynamically stable compound 2CaO·SiO<sub>2</sub>. Taking into account that at 725 °C the α–γ transformation occurs in this compound, accompanied by changing volume, the

namely such ratio of calcium oxides and silicon can be recommended in the composition of fluxes for ESR of hollow ingots and welding. These fluxes will poorly interact with molten metal and provide an excellent removal of solidified slag from the surface of ingot and weld metal.

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