The expert evaluation of literature data was carried out and methods of calculation of thermodynamic properties of melts of the CaO—Al₂O₃ system in the whole concentration range were offered. Thermodynamic activities of aluminium oxide at $0.74 < x_{Al_2O_3} < 1$ were calculated from the coordinates of the liquidus line of constitution diagram of the system CaO—Al₂O₃, determined by different authors. Using calculation and experimental data on thermodynamic activity of Al₂O₃, the evaluation of thermodynamic activities of calcium oxide was carried out by integration of Gibbs–Duhem equation. It was established that they reveal great negative deviations from thermodynamic properties of perfect solutions. Basing on the established values of thermodynamic activity of calcium oxide, the liquidus line of constitution diagram of the system CaO—Al₂O₃ was plotted on the side of calcium oxide. The obtained values of activity of components and liquidus temperature of the system CaO—Al₂O₃ allow evaluating the thermodynamic properties of corresponding three- and four-component systems, predicting processes of interaction in the metal—slag—gaz system and creating new consumables for welding and electroslag remelting. 28 Ref., 2 Tables, 4 Figures.

Keywords: welding, electroslag remelting, slag melts, thermodynamic activity of components, constitution diagram

Slag melts of the system CaO—SiO₂—Al₂O₃—CaF₂ find wide application in metallurgical and welding processes. Basing on this slag system the fluxes for welding of high-alloyed steels and electroslag remelting of structural steels were created. The system CaO—SiO₂—Al₂O₃—CaF₂ is the base of slag-forming mixtures for machines of continuous casting of billets. The scientifically grounded modification of known fluxes, development of new grades, methods of their melting and application are not possible without knowledge of physical and chemical properties, the basic of which are thermodynamic ones.

It is known that oxide-fluoride melts do not behave like perfect solutions. Thermodynamic activities of their components have deviations from the Raoult law. Therefore, the capability of components of melt to enter the chemical reactions is determined as a mole fraction of $x$ components in the melt, as well as their thermodynamic activity $a$ (hereinafter activity). To predict the metallurgical properties of slag melts the data on activity of their components are necessary.

Experimental investigations of physical and chemical properties of multi-component oxide-fluoride melts are complicated due to their refractoriness and high aggressiveness. Therefore, in the last years the methods of their calculation and modeling are developed and constantly modified.

One of the prospective directions is calculations of thermodynamic properties of melts of three- and four-component systems with application of similar data for two-component ones (for the latter they are experimentally determined by different methods). In this connection, it is necessary to determine valid data from all the totality of experimental data and use them for calculation.

The aim of this work is review of existing experimental data, their expert evaluation and establishing of valid values of activities of components of oxide melts of the binary system CaO—Al₂O₃ in the entire concentration range.

In the nearest time the similar investigations of the system CaO—SiO₂, Al₂O₃—SiO₂, Al₂O₃—CaF₂, SiO₂—CaF₂ and CaO—CaF₂ will be prepared. The groups of authors have already performed thermodynamic modeling for most of them. In spite of the fact that the known experimental data were taken as the basis, the obtained results are distinctly differed. Thus, valid thermodynamic properties of mentioned binary melts were tried to be determined using the own methods [1, 2].

The constitution diagram of the system CaO—Al₂O₃ was at the first time plotted already in
In works [4–9] the description of the further investigations of phase equilibriums of the system CaO–Al2O3 is given. However until the recent time the coordinates of liquidus line $T_L$ of alloys of the system CaO–Al2O3 at $0.75 < x_{CaO} < 1$ are not determined. It is predetermined by very high temperatures of melting of these objects. Only thermochemical properties of intermediate phases of this system were experimentally investigated [10–16].

The activities of components of liquid melts of the system CaO–Al2O3 were formerly investigated by different methods in the temperature range of 1773–2060 K (Figure 1). In the most works [17–21] the activities of calcium oxide $a_{CaO}$ were determined, and activities of aluminium oxide $a_{Al_2O_3}$ – only in [17, 18, 22]. It should be noted that activities of components obtained using method of electromotive forces [22] reveal the highest positive deviations from the perfect solutions. It is probably predetermined by the fact that membranes in the concentration element have no the pure ion conductance. Therefore, authors did not take these data into account. As is seen from Figure 1, the activities of components are determined in the limited range of concentrations, which is predetermined by the refractoriness of Al2O3 and, especially, CaO.

For the correct description of thermodynamic properties of liquid melts of the system CaO–Al2O3, $T_L$ of the constitution diagram in the range of concentrations 35–100 wt.% Al2O3 were used. According to the developed methods [1, 2] the $a_{Al_2O_3}$ at 84–100 wt.% Al2O3 were calculated. The results of calculation are given in Table 1. The liquidus temperature line changed in this system from 2140 to 2313 K.

Combining these calculation results with $a_{Al_2O_3}$ values in melts of the system CaO–Al2O3 [17], determined by a very precise method of Knudsen applying mass-spectrometer at 2060 K, $a_{CaO}$ was evaluated using integration of Gibbs–Duhem equation. The obtained results are given in Figure 2.

It is seen that activities reveal negative deviations from the Raoult law and satisfactorily correlate with the data on $a_{Al_2O_3}$ in the melts of the system CaO–Al2O3 [17]. It is more distinctly shown in Figure 1.

Liquidus curve of melts of the system CaO–Al2O3 on the side of CaO (up to 35 wt.% Al2O3) $a_{CaO}$ mole fr.

Table 1. Calculation of Al2O3 activities according to coordinates $T_L$ of the CaO–Al2O3 system constitution diagram

<table>
<thead>
<tr>
<th>$T_L$, K</th>
<th>$\omega_{Al_2O_3}$, wt.%</th>
<th>$x_{Al_2O_3}$, mole fr.</th>
<th>$a_{Al_2O_3}$, mole fr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2140</td>
<td>84</td>
<td>0.74</td>
<td>0.60</td>
</tr>
<tr>
<td>2210</td>
<td>92</td>
<td>0.86</td>
<td>0.76</td>
</tr>
<tr>
<td>2280</td>
<td>95</td>
<td>0.91</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Figure 1. Activities of components of the CaO–Al2O3 system melts

Figure 2. Activities of components of the CaO–Al2O3 system melts at 2100–2300 K (spots – calculation data on the basis of $T_L$, lines – optimized)
is not determined and was calculated by the authors from $a_{CaO}$ in the following way:

$$\mu_i^l = \mu_i^{s_0} + RT_L \ln a_i = \mu_i^{s_0} + \frac{\Delta H_{melt_i}}{R \ln a_i} = \frac{\Delta H_{melt_i}}{R \ln a_i - \Delta S_{melt_i}}$$

where $\mu_i^{s_0}$ is the chemical potential of $i$-th component in liquid and solid phases, respectively; $T_L$ is the liquidus temperature, at which solid component–solution equilibrium is considered; $a_i$ is the activity of $i$-th component; $\Delta H_{melt_i}$, $\Delta S_{melt_i}$ is the enthalpy and entropy of melting of $i$-th component, respectively.

The obtained results are given in Table 2 and Figure 3.

Comparison of these data with experimental results [4] showed (see Figure 3) that they are well correlated with each other.

The $Al_{2}O_3$ activities according to the results of these works were calculated using the method developed by the authors [1, 2]. In the area of compositions enriched with $Al_{2}O_3$, the $T_L$ was determined in [4, 7–9]. In the area of compositions of melts of the system $CaO–Al_{2}O_3$ at $0.63 < x_{Al_{2}O_3} < 1$, the liquidus temperature varies [4–9]. According to these data the $a_{Al_{2}O_3}$ calculation was carried out. The obtained results were compared with the data of [17], which have the best correlation with those calculated from $T_L$ [4]. In work [11] the preference of $T_L$ was also given established in [4].

The expert evaluation of thermodynamic properties of melts and phase equilibriums of the system $CaO–Al_{2}O_3$ was carried out the most fully in [23–25]. The activities of components of alloys of the system $CaO–Al_{2}O_3$ are calculated in the limited range of the compositions $0.25 < x_{Al_{2}O_3} < 0.7$. For $a_{Al_{2}O_3}$, the results of all these works coincide both with each other as well with experimental data [17]. As for $a_{CaO}$, then they differ a little bit between themselves. This can be explained by the fact that the temperature of melting of calcium oxide in [23–25] was taken as equal to 3172 K (Figure 4) but not as 2900 K, as is accepted in all the known handbooks, for example [26–28]. Consequently, the calculated in [23–25] liquidus curve of mixtures, enriched by $CaO$, is located higher than that determined by us.

The modeling of activities of components of melts of the system $CaO–Al_{2}O_3$ carried out in the whole concentration range, as well as liquidus temperature, will allow further evaluating of thermodynamic properties of corresponding three- or four-component systems, developing new consumables for welding and related processes with predicted metallurgical characteristics.

### Table 2. Calculation of coordinates $T_L$ of constitution diagram of the $CaO–Al_{2}O_3$ system melts by $CaO$ activities

<table>
<thead>
<tr>
<th>$\omega_{Al_{2}O_3}$ wt.%</th>
<th>$x_{Al_{2}O_3}$ mole fr.</th>
<th>$a_{Al_{2}O_3}$ mole fr.</th>
<th>$T_L$, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.05</td>
<td>0.95</td>
<td>2838</td>
</tr>
<tr>
<td>20</td>
<td>0.12</td>
<td>0.80</td>
<td>2630</td>
</tr>
<tr>
<td>32</td>
<td>0.205</td>
<td>0.65</td>
<td>2424</td>
</tr>
<tr>
<td>38</td>
<td>0.25</td>
<td>0.45</td>
<td>2123</td>
</tr>
<tr>
<td>43</td>
<td>0.28</td>
<td>0.40</td>
<td>2040</td>
</tr>
</tbody>
</table>

Figure 3. Constitution diagram of the system $CaO–Al_{2}O_3$: 1 – calculated data; 2 – data of work [4]

Figure 4. Constitution diagram of the system $CaO–Al_{2}O_3$ modeled in work [23]
Conclusions

1. Modeling of thermodynamic properties of the system CaO–Al2O3 in the whole concentration range was carried out. Among the coordinates of liquidus line of the constitution diagram CaO–Al2O3, determined by different authors, a Al2O3 at 0.74 < x Al2O3 < 1 were calculated. It was established that only according to the data of constitution diagram of [4], the Al2O3 activities correlate with the data of [4].

2. From the calculated and valid experimental data on a Al2O3, the aCaO were evaluated by integration of Gibbs–Duhem equation. It was established that they reveal noticeable negative deviations from the perfect solutions.

3. From the established values of aCaO the liquidus line on the side of calcium oxide was plotted. It is shown that in the range of experimental errors it correlates with the data of [4].

4. The obtained data on activity of components and liquidus temperature of melts of the system CaO–Al2O3 allow evaluating the thermodynamic properties of corresponding three- and four-component systems, developing new consumables for welding and electroslag remelting with predicted metallurgical characteristics.

References


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