Determinant of oxygen and sulfur thermodynamic activity in molten metals

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Abstract. The paper describes computer analysis of concentration dependence of oxygen activity coefficients \( f_\text{O} \) in binary liquid titanium-base alloys containing ions of copper, nickel, molybdenum, vanadium, zirconium and aluminum. The study covers calculations of oxygen activity coefficient \( f_\text{O} \) and sulphur activity coefficient \( f_\text{S} \) in binary melts of the systems Cu – Fe, Cu – Ni, Cu – Co, Ni – Co, Fe – Ni, Fe – Co as a function of the concentration of metal components.

The two main equations suggested in [1] and [2] are chosen for calculations. The first one comprises a selectable energy parameter \( h \) which is proportional to the enthalpy change in case of interstitial metalloid atom \( X \) in tetra– and octahedral vacancies formed by metal atoms:

\[
\ln f_{X[A+B]} = \frac{1}{2} \ln \left[ f_{X[A]} f_{X[B]} \right] - \ln \left\{ \Sigma (\nu) \left[ (1-N_B) / \Phi^{(1/2)} \right] (z\nu) \times \right. \\
\left. \left[ N_B \Phi^{(1/2)} \right] ^{(1/2)} \exp \left( (z^2- i) i h_i h_2) / (2RT) \right) \right\}. 
\]

The second equation involves two parameters \( h_1 \) and \( h_2 \); \( h_1 \) is proportional to the enthalpy change when dissolving atom \( X \) in pure solvent \( A \), \( h_2 \) is proportional to the difference of enthalpies of \( X \) dissolution reactions in pure liquid metal components \( A \) and \( B \) of the alloy:

\[
\ln f_{X[A+B]} = \frac{1}{2} \ln \left[ f_{X[A]} f_{X[B]} \right] - \ln \left\{ \Sigma (\nu) \left[ (1-N_B) / \Phi^{(1/2)} \right] (z\nu) \times \right. \\
\left. \left[ N_B \Phi^{(1/2)} \right] ^{(1/2)} \exp \left( (z^2- i) i h_1 h_2) / (2RT) \right) + ((z^2- i) i h_2 / (6RT)) \right\}. 
\]

In these equations, \( f_{X[A]} \), \( f_{X[B]} \), \( f_{X[A+B]} \) are the activity coefficients of metalloid \( X \) in pure liquid metals \( A \), \( B \) and their binary mixture, respectively; \( N_B \) is the mole fraction of component \( B \); \( z \) is the coordinate number; \( i \) is the number of metal atoms \( A \) and \( B \) surrounding interstitial atom of metalloid \( X \) which varies within 0 to \( z \). Coefficient \( \Phi = f_{X[A]} / f_{X[B]} \); parameter \( h \) varies within \( h/2RT < 1/5\ln\Phi \) [1].

The values \( f_\text{O} \) in pure molten metals required for calculations are taken from [3-5]; the values \( f_\text{S} \) in the same liquid metals are taken from [6-10].

When evaluating \( h \), the respective partial molar enthalpies presented in [11,12] are used for calculations of changes in enthalpies between successive steps of reaction of metalloid atom dissolution in molten metals.

The calculation results are given in Table 1 and Table 2.
It is determined that as the concentration of the second metal component in the melt Ti – Me is increasing, the oxygen activity coefficient is decreasing, at that \( f_o \) is mostly reduced in the systems titanium – zirconium, titanium – vanadium, titanium – aluminum. This can be caused by a significant difference between energies of interparticle interactions \( E_{ij} \) in melts. The oxygen activity coefficients in binary titanium-base melts can be arranged in a row \( f_o^{Al} < f_o^{V} < f_o^{Zr} \); \( f_o^{Mo} < f_o^{Ni} < f_o^{Cu} \). This sequence qualitatively correlates with the values characterizing the change in standard Gibbs energies \( \Delta G^\circ \) of oxides formation of the respective elements \[12\].

### Table 1. Coefficients of Oxygen Activity in Titanium-Base Melts at 2000 K

| System | \(-\ln f_o\) | Eq 1 | Eq 2
|--------|---------------|------|------
| Ti - Cu | 0.3 | 0.2 | 0.3 | 0.2 | 0.2 | 2.6 | 2.9 |
|        | 0.6 | 0.4 | 0.6 | 1.4 | 0.6 | 4.6 | 4.8 |
|        | 0.4 | 0.6 | 2.0 | 2.7 | 0.4 | 6.5 | 6.6 |
|        | 0.2 | 0.8 | 3.5 | 4.0 | 0.2 | 7.6 | 7.7 |
| Ti - Ni | 0.3 | 0.2 | 0.4 | 0.3 | 0.8 | 0.2 | 3.0 | 3.2 |
|        | 0.6 | 0.4 | 0.1 | 1.0 | 0.6 | 0.4 | 5.5 | 5.5 |
|        | 0.4 | 0.6 | 1.0 | 1.9 | 0.4 | 6.9 | 7.5 |
|        | 0.2 | 0.8 | 3.2 | 3.6 | 0.2 | 8.5 | 8.7 |
| Ti - Mo | 0.3 | 0.2 | 0.5 | 0.9 | 0.8 | 0.2 | 7.3 | 7.5 |
|        | 0.6 | 0.4 | 1.0 | 1.8 | 0.6 | 0.4 | 10.5 | 11.0 |
|        | 0.4 | 0.6 | 2.2 | 3.2 | 0.4 | 13.0 | 13.2 |
|        | 0.2 | 0.8 | 3.8 | 4.9 | 0.2 | 14.0 | 14.3 |

### Table 2. Concentration Dependence of Oxygen and Sulphur Activity Coefficients in Metal Copper-, Iron- and Nickel-Base Melts at 1873 K.

| System | \(-\ln f_O\) | Eq 1 | Eq 2 | Eq 3 | \(-\ln f_S\) | Eq 1 | Eq 2 | Eq 3
|--------|---------------|------|------|------|---------------|------|------|------|
| Cu - Fe | 0.8 | 0.2 | 3.82 | 3.25 | 3.61 | 2.11 | 3.27 | 3.55 |
|        | 0.6 | 0.4 | 4.60 | 4.25 | 4.00 | 4.25 | 4.03 | 3.84 |
|        | 0.4 | 0.6 | 4.88 | 4.52 | 4.45 | 4.63 | 4.15 | 3.96 |
|        | 0.2 | 0.8 | 4.95 | 4.55 | 4.54 | 4.78 | 4.27 | 4.18 |
| Cu - Ni | 0.8 | 0.2 | 1.36 | 1.24 | 0.95 | 0.92 | 1.09 | 0.77 |
|        | 0.6 | 0.4 | 1.60 | 1.51 | 1.35 | 1.02 | 1.16 | 0.94 |
|        | 0.4 | 0.6 | 1.98 | 1.84 | 1.46 | 1.23 | 1.32 | 1.16 |
|        | 0.2 | 0.8 | 2.55 | 2.32 | 1.89 | 1.55 | 1.72 | 1.72 |
| Cu - Co | 0.8 | 0.2 | 2.10 | 1.85 | 1.39 | 1.74 | 1.60 | 1.09 |
|        | 0.6 | 0.4 | 2.51 | 2.44 | 2.07 | 2.12 | 2.00 | 1.55 |
|        | 0.4 | 0.6 | 2.40 | 2.36 | 2.08 | 2.10 | 2.00 | 1.55 |
|        | 0.2 | 0.8 | 2.27 | 2.20 | 1.83 | 2.00 | 2.00 | 1.55 |
| Ni - Cu | 0.8 | 0.2 | 1.20 | 1.24 | 1.28 | 1.00 | 1.05 | 1.68 |
|        | 0.6 | 0.4 | 1.43 | 1.44 | 1.40 | 1.15 | 1.15 | 1.15 |
|        | 0.4 | 0.6 | 1.59 | 1.63 | 1.66 | 1.23 | 1.26 | 1.35 |
|        | 0.2 | 0.8 | 1.72 | 1.68 | 1.78 | 1.45 | 1.48 | 1.50 |
| Fe - Ni | 0.8 | 0.2 | 4.49 | 4.18 | 4.52 | 4.04 | 4.16 | 4.05 |
|        | 0.6 | 0.4 | 4.14 | 3.80 | 4.17 | 3.85 | 3.85 | 3.85 |
|        | 0.4 | 0.6 | 3.92 | 3.31 | 3.61 | 3.00 | 3.01 | 3.01 |
|        | 0.2 | 0.8 | 3.90 | 3.20 | 3.90 | 3.30 | 3.29 | 3.29 |
| Fe - Co | 0.8 | 0.2 | 4.25 | 4.21 | 4.26 | 3.95 | 4.00 | 3.75 |
|        | 0.6 | 0.4 | 3.84 | 3.75 | 3.95 | 3.44 | 3.56 | 3.56 |
|        | 0.4 | 0.6 | 3.28 | 3.19 | 3.40 | 2.98 | 2.98 | 2.98 |
|        | 0.2 | 0.8 | 2.56 | 2.45 | 2.67 | 2.20 | 2.22 | 2.22 |

Analysis of \( f_o \) given in Table 1 and Table 2 shows that both the models produce the correlating results in the range of low, or to the contrary, rather high concentrations \( N_B \) of the second component in the metal compound. Under these conditions, the system is no longer a ternary system, therefore
consideration of the second energy parameter becomes insignificant. At mean concentrations, the values $f_X$ calculated according to equation (2) are a little more for all the systems except for the nickel-cobalt system melts. The values $f_X$ (Table 2) are more than $f_c$ which is not in conflict with the assumptions of oxygen behavior in the melt as an element having higher electronegativity and less sizes compared to those of sulphur ions $S^{2-}$.

Additions of iron, nickel and cobalt to molten copper result in decreasing of $f_c$. The growth of iron concentration in the melt has the strongest influence on $f_c$. This phenomenon can be caused by local areas of prevailing arrangement of iron atoms around oxygen atoms due to their high chemical affinity. Upon achieving the nickel or cobalt concentration $N_i \geq 0.6$, the increase in $f_c$ in liquid copper can be connected with formation of unmixed areas in the melts of copper-nickel, copper-cobalt systems containing the higher concentrations of the second component. Cobalt addition to molten nickel results in decreased $f_c$. Increase in $f_c$ with the growth of nickel or cobalt concentration in the melts of iron-nickel, iron-cobalt systems is apparently caused by release of a certain portion of oxygen when iron atoms in the melt are replaced with other atoms of less energy of binding with oxygen.

The results show that $f_X$ calculated according to equation (2) closely resemble the literature data [2,3,13]. Equation (1) correctly describes the general behavior of $f_X$ as a function of composition. Considering of two parameters is effective if there is a significant difference between heats $\Delta H_{[i]}$ of metalloid dissolution in pure metals. In case of near values $\Delta H_{[i]}$ the results of calculation according to equations (1), (2) do not differ much.

In spite of diversity of analytical equations, all the existing model have thermodynamic concepts based on the assumptions of random distribution of atoms in liquid metal compounds and do not consider the system entropy change, which always occurs during dissolving. Moreover, activity calculations according to equations (1), (2) are accompanied by some difficulties relating to determination of parameters $h$, $h_1$, $h_2$ which are introduced into the equations for the heuristic purpose.

The study includes the trial to determine the analytical equation which would contain the parameters characterizing nonadditivity of binding energy of different pairs of atoms in the melt and their arrangement ordered to a certain extent at the temperatures which do not too exceed the alloy melting point. These parameters are $\Delta H$ and $\Delta S$, i.e. change in enthalpy and entropy of metal compound when dissolving metalloid atoms in the melt.

The main formulas are derived based on the known equation [14]:

$$\mu_i - \mu_i^{st} = RT \ln a_i,$$

where $\mu_i$ is the chemical potential of the component in the actual solution; $\mu_i^{st}$ is the chemical potential of the component in the standard state.

The difference between chemical potentials of the component in the solution is governed by the change in partial molar quantity of Gibbs energy during dissolving. The latter is the difference between the partial molar quantities characterizing the change in the component dissolution enthalpy and entropy at $T = \text{const}$:

$$\mu_i - \mu_i^{st} = G_i - G_i^{st} = \Delta G_i = \Delta H_i - T \Delta S_i,$$

where $\Delta H_i = H_i - H_i^{0}$, $\Delta S_i = S_i - S_i^{0}$, and $H_i$ and $S_i$ are partial molar enthalpy and entropy in the solution, $H_i^{0}$ and $S_i^{0}$ are the respective values of these parameters for the pure component.

The equation describing the concentration dependence of the metalloid activity coefficients for its dilute solutions in binary liquid metal systems is as follows:

$$\ln f_{X[A-B]} = \ln [f_{X[A]} f_{X[B]}] + \ln [P \exp(\Delta H_{\text{mix}}/(RT)) \exp(-\Delta S_{\text{mix}}/R)].$$

In equation (5) the first term characterizes the interdependent contribution of metal atoms into near ordering in the melt; $P$ is the multiplier that determines the mixing heat portion depending on the contribution of the neighbors’ interaction energy, and is calculated according to [15] using the data on surface tension and change in the component volumes during mixing, the latter are classified in [16,17].

The values $\Delta H_{\text{mix}}$ are calculated according to the equation

$$\Delta H_{\text{mix}} = (\Delta H_{[A]} + \Delta H_{[B]}) - \Delta H_{[A-B]}.$$
where $\Delta H_{\text{O[A]}}$ and $\Delta H_{\text{O[B]}}$ are thermal effects typical of reactions of metalloid dissolution in liquid pure metals A and B; $\Delta H_{\text{[A+B]}}$ is an enthalpy change resulting from formation of binary metal alloy, this value depends on concentration and is taken from [18,19] for the systems under study.

The entropy change of binary metal compound with oxygen as a function of composition is calculated based on the method described in [20] and the data of X-ray structural analysis of liquid metal systems [21]. $\Delta S_{\text{mix}}$ is presented as the difference between additive entropy of component A and component B when dissolving oxygen therein, and excess entropy of metal atom mixing during binary alloy formation:

$$\Delta S_{\text{mix}} = (S_{\text{O[A]}} + S_{\text{O[B]}}) - \Delta S_{\text{[A+B]}}. $$

(7)

The results of calculation for $f_o$ and $f_s$ according to equation (5) and given in Table2 have the same order as $f_o$ and $f_s$ determined according to equations (1), (2) and resemble the experimental data [11,12].

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