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# Prediction of the Minimum Solubility During Either Deoxidation or Desulfurization Process in Liquid Alloys**

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Deoxidation and desulfurization processes in liquid metallic alloys can be described by four different types of chemical reactions:

$$xM + y\mathrm{O} \rightarrow M_x\mathrm{O}_y$$

$$A + 2M + 4\mathrm{O} \rightarrow AM_2\mathrm{O}_4$$

$$\mathrm{S} + M\mathrm{O} \rightarrow \mathrm{O} + M\mathrm{S}$$

$$R_2\mathrm{O}_3 + \mathrm{S} \rightarrow R_2\mathrm{O}_2\mathrm{S} + \mathrm{O}$$

A state of equilibrium between metallic phase and the reaction products was assumed. A computer procedure, which enables the prediction of the solubility curve and the respective minimum solubility composition, has been developed. The presented approach was tested on Fe—Cr—O, Cu—Mn—O and Fe—O—S dilute solutions. It was found that the value of the interaction parameter $\varepsilon_{\mathrm{O}}^{\mathrm{Mn}}$ in liquid copper reported in the literature is too high. Own experiments suggest a value of $\varepsilon_{\mathrm{O}}^{\mathrm{Mn}} = -220$ at 1 373 K.

*(Keywords: Deoxidation; Desulfurization; Liquid metallic alloys; Solubility)*

### *Die Vorhersage der Löslichkeitsgrenze bei Desoxidierungs- und Entschwefelungs-Prozessen in flüssigen Legierungen*

Desoxidierungs- und Entschwefelungsprozesse in flüssigen metallischen Legierungen können durch vier verschiedene Reaktionen beschrieben werden

$$xM + y\mathrm{O} \rightarrow M_x\mathrm{O}_y$$

$$A + 2M + 4\mathrm{O} \rightarrow AM_2\mathrm{O}_4$$

$$\mathrm{S} + M\mathrm{O} \rightarrow \mathrm{O} + M\mathrm{S}$$

$$R_2\mathrm{O}_3 + \mathrm{S} \rightarrow R_2\mathrm{O}_2\mathrm{S} + \mathrm{O}$$

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** Dedicated to Prof. Dr. *Kurt L. Komarek* on the occasion of his 60th birthday.

Die Einstellung des Gleichgewichts zwischen der metallischen Phase und den Reaktionsprodukten wurde vorausgesetzt. Es wird ein Computerprogramm vorgeschlagen, mit dessen Hilfe man die Löslichkeitsgrenze und die Zusammensetzung minimaler Löslichkeit vorausberechnen kann. Dieses Programm wurde auf die verdünnten Lösungen der Systeme Cu—Mn—O und Fe—S—O angewendet. Ferner wurde festgestellt, daß der in der Literatur zitierte Wert des Wechselwirkungsparameters $\varepsilon_O^{Mn}$ in flüssigem Kupfer zu groß ist. Eigene Untersuchungen ergaben, daß diese Größe bei 1 373 K einen Wert von —220 hat.

## Introduction

During the process of refining, deoxidation as well as desulfurization of metals and alloys decide about the property of metallurgical products. Although the kinetics of these processes may influence significantly final results, their limits however are set by the equilibrium thermodynamics. That is why simple models for predicting optimal conditions can be derived from considerations concerned with respective chemical reactions describing two-phase equilibria. So far experimental information about this subject was available mainly for iron and copper alloys. The technology of deoxidation of steel has been pursued for years, and the determination of oxygen in steel has been the subject of many research efforts [1]. Similarly, selective oxidation of impurities during fire refining of copper was a subject of theoretical considerations as well as reconciliation with effects observed in practice [2]. However, for other alloys experimental information is limited, and usually broad theoretical analysis of the aforementioned processes is difficult.

Recently, the rapid development of electronic industry put forward new demands. The problem of controlling the oxygen level in the liquid phase during the growth of semiconducting single crystals became of great importance. It was observed for example, that GaAs crystals may convert from n- to p-type conductors depending on oxygen activity in the melt. For these reasons it is worth trying to develop a general approach, which can facilitate the process of modelling either deoxidation or desulfurization reactions in a chosen system. Therefore, an attempt has been made to work out a computer program which can generate different situations demonstrated in the present paper.

## Method

### *Deoxidation Equilibria*

During the process of deoxidation the main aim is to find out the minimum oxygen solubility and the corresponding alloy content for a given deoxidizer. Deoxidation equilibria in a liquid A—M—O alloy can be represented by the following reaction:

$$xM + y\text{O} \rightarrow M_x\text{O}_y \tag{1}$$

where $x$ and $y$ are stoichiometric coefficients, $M$ and O are, respectively, the metallic deoxidizer and oxygen in solution, and $M_x\text{O}_y$ is the deoxidation product remaining in equilibrium with the melt.

The equilibrium constant of the reaction (1) is:

$$K_{(1)} = \left\{ \frac{a_{M_x\text{O}_y}}{a_M^x \, a_\text{O}^y} \right\} \tag{2}$$

which upon rearrangements and putting in logarithmic form yields:

$$x \ln \gamma_M + x \ln N_M + y \ln \gamma_\text{O} + y \ln (\text{atom pct. O}) = \ln a_{M_x\text{O}_y} + \Delta G_f^\circ / RT \tag{3}$$

Expressing according to *Wagner* [3] $\ln \gamma_M$ and $\ln \gamma_\text{O}$ in the linear form:

$$\ln \gamma_M = \ln \gamma_M^\circ + \varepsilon_M^M N_M + \varepsilon_M^\text{O} N_\text{O} \tag{4}$$

and

$$\ln \gamma_\text{O} = \ln \gamma_\text{O}^\circ + e_\text{O}^\text{O} (\text{atom pct. O}) + \varepsilon_\text{O}^M N_M \tag{5}$$

where $\gamma$ is the activity coefficient of solute (either $M$ or O) in $A$—$M$—O solution; $\gamma^\circ$ is the activity coefficient of solute at infinite dilution in solvent $A$; $\varepsilon$ is the first-order interaction coefficient defined as

$$\varepsilon_i^i = \lim_{N_A \to 1} \left( \frac{\partial \ln \gamma_i}{\partial N_i} \right)$$

and

$$\varepsilon_i^j = \lim_{N_A \to 1} \left( \frac{\partial \ln \gamma_i}{\partial N_j} \right)$$

and

$$e_\text{O}^\text{O} = \varepsilon_\text{O}^\text{O} / 100$$

Substituting $\ln \gamma_M^\circ = \Delta \bar{G}_M^{E\infty} / RT$, and $\ln \gamma_\text{O}^\circ = \Delta G_{\text{O}(A)}^\circ / RT$, one can obtain from Eq. (3):

$$\begin{aligned} & y \ln (\text{atom pct. O}) + y e_\text{O}^\text{O} (\text{atom pct. O}) + x (\varepsilon_M^\text{O}/100) (\text{atom pct. O}) \\ & = - x \ln N_M - x \varepsilon_M^M N_M - y \varepsilon_\text{O}^M N_M + \ln a_{M_x\text{O}_y} - x \Delta \bar{G}_M^{E\infty} / RT \\ & \quad - y \Delta G_{\text{O}(A)}^\circ / RT + \Delta G_f^\circ / RT \end{aligned} \tag{6}$$

Next, after splitting the *Gibbs* free energy into enthalpy and entropy terms in the general from:

$$\Delta \bar{G}_M^{E\infty} = A + BT \tag{7}$$

$$\Delta G^{\circ}_{\mathrm{O}(A)} = C + DT \tag{8}$$

$$\Delta \mathrm{G}_{f=}\ E + FT \tag{9}$$

Eq. (6) can be rewritten in the final form:

$$y \ln(\text{atom pct. O}) + y e_{\mathrm{O}}^{\mathrm{O}}(\text{atom pct. O}) + x(\varepsilon_M^{\mathrm{O}}/100)(\text{atom pct. O}) = -x \ln N_M - x\varepsilon_M^M N_M - y\varepsilon_{\mathrm{O}}^M N_M + \ln a_{M_x\mathrm{O}_y} + (E - xA - yC)/RT + (F - xB - yD)/R \tag{10}$$

Accordingly, the saturation solubility curve i.e. (atom pct. O) vs. $N_M$ can be obtained from Eq. (10).

Depending on the oxygen potential in the solution, reaction of a spinel formation is possible:

$$A + 2M + 4\mathrm{O} \rightarrow AM_2\mathrm{O}_4 \tag{11}$$

where $A$ denotes metallic solvent.

The equilibrium constant of the reaction (11) is:

$$K_{11} = \left\{\frac{a_{AM_2\mathrm{O}_4}}{a_A\, a_M^2\, a_{\mathrm{O}}^4}\right\} \tag{12}$$

Assuming $a_A = N_A$, and taking into account that $N_A + N_M \approx 1$ ($N_{\mathrm{O}} \ll N_M$), one can obtain:

$$\ln(\text{atom pct. O}) + e_{\mathrm{O}}^{\mathrm{O}}(\text{atom pct. O}) + (\varepsilon_M^{\mathrm{O}}/100)(\text{atom pct. O}) = -\ln[(1 - N_M)\sqrt{N_M}] - 1/2\,\varepsilon_M^M N_M - \varepsilon_{\mathrm{O}}^M N_M + 1/4 \ln a_{AM_2\mathrm{O}_4} + (\Delta G^{\circ}_f - 4\Delta G^{\circ}_{\mathrm{O}(A)} - 2\Delta \bar{G}_M^{E\infty})/4RT \tag{13}$$

Expressing *Gibbs* free energy terms in the form:

$$\Delta \bar{G}_M^{E\infty} = A + BT \tag{14}$$

$$\Delta G^{\circ}_{\mathrm{O}(A)} = C + DT \tag{15}$$

$$\Delta G^{\circ}_f = E + FT \tag{16}$$

and upon necessary rearrangements one can obtain:

$$\ln(\text{atom pct. O}) + \varepsilon_{\mathrm{O}}^{\mathrm{O}}(\text{atom pct. O}) + (\varepsilon_M^{\mathrm{O}}/100)(\text{atom pct. O}) = -\ln[(1 - N_M)\sqrt{N_M}] + 1/2\,\varepsilon_M^M N_M - \varepsilon_{\mathrm{O}}^M N_M + 1/4 \ln a_{AM_2\mathrm{O}_4} + (E - 4C - 2A)/4RT + (F - 4D - 2B)/4R \tag{17}$$

Again, the solubility curve (atom pct. O) vs. $N_M$ can be derived from Eq. (17).

### *Desulfurization Equilibria*

Generally, alloying elements should form stable sulfides. Consequently, the best desulfurizing agents are Ca added by alloy injection, and Ce introduced in the form of Mischmetal. Desulfurizing reactions consist in transferring sulfur from metal to slag. The added metal will also react with oxygen in the solution. Due to the high oxides stability, Ca as well as rare earth elements will react completely with oxygen. Thus, the overall reaction will involve the formation of an oxide and a sulfide. In the case of rare earth alloying elements the formation of rare earth oxysulfides plays an important role. In this situation reactions are limited to two possibilities:

$$\mathrm{S} + M\mathrm{O} \rightarrow \mathrm{O} + M\mathrm{S} \tag{18}$$

$$R_2\mathrm{O}_3 + \mathrm{S} \rightarrow R_2\mathrm{O}_2\mathrm{S} + \mathrm{O} \tag{19}$$

It is clear that minimum sulfur solubility cannot be defined in the same sense as for oxygen. There are rather optimal conditions achieved for both sulfur and oxygen for a chosen deoxidizer.

In the first case the equilibrium constant $K_{(18)}$ is:

$$K_{(18)} = \left\{\frac{a_\mathrm{O}\, a_{M\mathrm{S}}}{a_\mathrm{S}\, a_{M\mathrm{O}}}\right\} \tag{20}$$

After rearrangements, and taking the logarithm of $K_{(18)}$, the following dependence can be obtained:

$$\begin{gathered}\ln\gamma_\mathrm{O} + \ln(\text{atom pct. O}) - \ln\gamma_\mathrm{S} - \ln(\text{atom pct. S}) + \ln(a_{M\mathrm{S}}/a_{M\mathrm{O}}) \\ = -\Delta G^\circ_T/RT\end{gathered} \tag{21}$$

where $\Delta G^\circ_T = -RT\ln K_{(18)}$.

Introducing for consecutive reactions:

$$\Delta G^\circ_{\mathrm{O}(A)} = A + BT \tag{22}$$

$$\Delta G^\circ_{\mathrm{S}(A)} = C + DT \tag{23}$$

$$\Delta G^\circ_T = E + FT \tag{24}$$

and assuming that sulfur and oxygen obey *Henry*'s law over dilute solution range, one can obtain the final formula:

$$\begin{gathered}\ln(\text{atom pct. S}) - (\varepsilon^\mathrm{S}_\mathrm{O}/100)(\text{atom pct. S}) = \ln(\text{atom pct. O}) \\ - (\varepsilon^\mathrm{O}_\mathrm{S}/100)(\text{atom pct. O}) + \ln(a_{M\mathrm{S}}/a_{M\mathrm{O}}) + (A - C + E)/RT \\ + (B - D + F)/R\end{gathered} \tag{25}$$

In the second case, an equilibrium constant $K_{(19)}$ is:

$$K_{(19)} = \left\{\frac{a_{R_2\mathrm{O}_2\mathrm{S}}\, a_\mathrm{O}}{a_{R_2\mathrm{O}_3}\, a_\mathrm{S}}\right\} \tag{26}$$

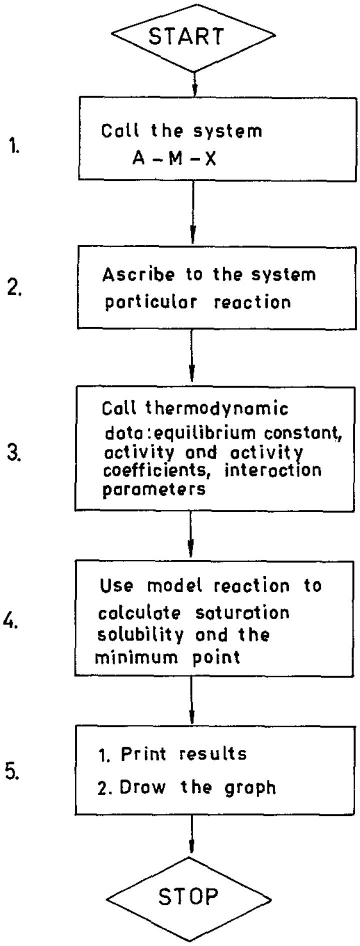

Fig. 1. Scheme of the computing program

A similar procedure as that used above leads to the expression almost identical with Eq. (25), except for the term: ln $(a_{R_2O_2S}/a_{R_2O_3})$. *Henry*'s law is assumed both for sulfur and oxygen in the solution.

## *Computing Procedure*

Having the deoxidation as well as the desulfurization process described by four different types of chemical reactions, one can envisage the general procedure of predicting saturation solubility curves together with their minimum points. The scheme of the computing program is shown in Fig. 1. The crucial information, necessary for successful computation, is comprised in the third step. Let's have a more careful look at it in order to find out if it could be possible to work out a way of predicting all those data, and then recall them on demand from computers memory.

1. The required equilibrium constant of a chosen reaction can be calculated from *Gibbs* free energy change, which in turn can be found in numerous thermochemical tables. As almost all oxides (and a number of sulfides) have their free energy change measured, it is possible in principle to store it in the computer memory using a simple formula $\Delta G_T^\circ = a + b\ T$. Tables given by *Turkdogan* can be a good example of this approach [4].

2. Although *Hultgren*'s evaluation [5] of thermodynamic properties of liquid binary alloys is available for a number of systems, experimental data for numerous solutions are still missing. Moreover, since the controversy of *Doležalek-Van Laar*, a unified approach to the interpretation of thermodynamic properties of solutions has still not been worked out. Among many models, only the regular solution model [6] coupled with *Miedema*'s theory of alloy formation [7] gives a chance of predicting $\ln \gamma_M^\circ$ and $\varepsilon_M^M$, provided the regular solution parameter $b = \Delta H^M / N_1 N_2$ is obtained from the heat of mixing calculated for the binary alloy from *Miedema*'s equations.

Another very promising theory [8, 9] based on pseudopotential concept made a big advance but is still far from being completed.

3. Thermodynamic properties of oxygen and sulfur in liquid metals and alloys can be predicted either from respective correlations [10, 11] or many theoretical models [12–15]. However, a unified approach is still not possible because it is difficult to suggest "*a priori*" a proper shape of $\ln \gamma_{\text{non-metal}}$ vs. $N_M$ dependence. The simplest *Alcock-Richardson* model requires only information concerned with $\gamma_{\text{non-metal}}$ in pure metals, and $\Delta G^E$ of the alloy but produces large discrepancies. The *Jacob-Alcock* model seems to be more reliable but again it needs $\gamma_{\text{non-metal}}$ values, which, if being unavailable from experiments, can be predicted only from empirical correlations. *Chiang* and *Chang* enabled to make use of *Wagner*'s model to the proposed way of *h*-parameter prediction, but this model requires again values of $\gamma_{\text{non-metal}}$ in pure metals to be known.

From the picture presented above it is clear that a comprehensive approach cannot be worked out. A complete prediction, in which necessary information required by step 3 is calculated from the theory, is not possible. Thermodynamic data for the liquid phase must be evaluated separately. An improvement in the procedure can be made parallel to the advances in solution theory.

## Results and Discussion

### Fe—Cr—O *System*

As an example, deoxidation of iron with chromium can be given. Calculations were performed at 1 873 K for two respective reaction:

$$2\,Cr + 3\,O \rightarrow Cr_2O_3 \qquad (27)$$

and

$$Fe + 2\,Cr + 4\,O \rightarrow FeCr_2O_4 \qquad (28)$$

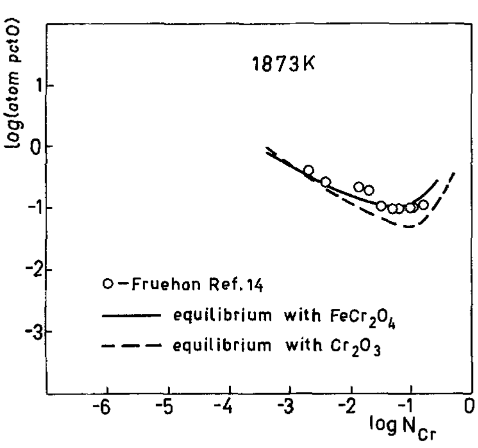

Fig. 2. Saturation solubility curves in Fe—Cr—O alloys at 1 873 K

It was assumed that the solution is in equilibrium with pure, solid reactions products ($a_{Cr_2O_3} = a_{FeCr_2O_4} = 1$), Fe—Cr solution is ideal ($\Delta \bar{G}^{E\infty}_{Cr} = 0$) and oxygen in the solution obeys *Henry*'s law ($e^O_O = 0$). Values of $\Delta G^\circ_{(27)}$ and $\Delta G^\circ_{(28)}$ were taken from [4], $\Delta G^\circ_{O(Fe)}$ from [15], and the interaction parameter $\varepsilon^M_O = \varepsilon^O_M = \varepsilon^{Cr}_O = -8.5$ was taken from *Sigworth* and *Elliott's* evaluation [16].

Results of our prediction are shown and compared with experimental results of *Fruehan* [17] in Fig. 2. The solubility curve predicted under the assumption of equilibrium with an oxide phase $FeCr_2O_4$ corresponds well to the measured values. The calculated minimum point ($N_{Cr} = 0.05$, 0.09 atom pct. O) is compatible with that determined experimentally ($N_{Cr} = 0.075$, 0.09 atom pct. O). In practice, the solution remains in equilibrium with $Cr_2O_3$ for alloy compositions $N_{Cr} > 0.03$. Observed discrepancies can be attributed to the uncertainity of thermochemical data, and the assumption about ideality of Fe—Cr liquid alloys.

### Cu—Mn—O *System*

It seems more interesting to apply our computational procedure to a system where the saturation solubility curve remains unknown. The interaction parameter $\varepsilon_{\mathrm{O}}^{\mathrm{Mn}}$ in liquid copper was measured independently by *Seetharaman* et al. [18], and *Fischer* and *Janke* [19], who used emf method. Extrapolation of the obtained results to 1 373 K yields the value of $\varepsilon_{\mathrm{O}}^{\mathrm{Mn}} = -2\,490$. Thermodynamic properties of liquid Cu—Mn alloys were investigated by *Sato* and *Kleppa* [20], and *Spencer* and *Pratt* [21]. They can be described by the following equations:

$$\ln \gamma_{\mathrm{Cu}} = \left(\frac{-4\,600}{T} - 1.374\right) N_{\mathrm{Mn}}^{2.18} + \left(\frac{6\,290}{T} + 2.488\right) N_{\mathrm{Mn}}^{3.18} \tag{29}$$

$$\ln \gamma_{\mathrm{Mn}} = \left(\frac{6\,290}{T} + 2.488\right) N_{\mathrm{Mn}}^{3.18} + \left(\frac{-13\,775}{T} - 5.01\right) N_{\mathrm{Mn}}^{2.18} + \left(\frac{8\,510}{T} + 2.54\right) N_{\mathrm{Mn}}^{1.18} + \left(\frac{-1\,043}{T} - 0.02\right) \tag{30}$$

However, if the reaction:

$$\mathrm{Mn} + \mathrm{O} \rightarrow \mathrm{MnO} \tag{31}$$

[with $\Delta G^{\circ}_{(31)}$ from [22], $\Delta G^{\circ}_{\mathrm{O(Cu)}}$ from [15], $\Delta \bar{G}^{E\infty}_{\mathrm{Mn}} = -8\,670 - 0.17\,T\,(\mathrm{J})$ and $\varepsilon_{\mathrm{Mn}}^{\mathrm{Mn}} = 4.8$ obtained from Eq. (30)] is considered, Eq. (10) becomes insoluble ($e_{\mathrm{O}}^{\mathrm{O}} = 0$, and $a_{\mathrm{MnO}} = 1$ are assumed). It was found that the value of $\varepsilon_{\mathrm{O}}^{\mathrm{Mn}} = -2\,490$ is responsible for this failure. This problem had to be resolved by direct experiment.

An alloy $\mathrm{Cu_{0.95}Mn_{0.05}}$ (Cu and Mn were obtained from Johnson and Matthey and were spectrographically pure) was prepared by a levitation technique. Then, the sample was placed together with MnO powder in a zirconia crucible, sealed under vacuum in a silica capsule, and equilibrated for 24 h at 1 373 K. After quenching, the sample was analysed for its oxygen content which was equal to 0.0237 atom pct. O. The value of $\ln \gamma_{\mathrm{O}} = -17.69$ was obtained from the equilibrium constant $K_{(31)}$. Interaction parameter $\varepsilon_{\mathrm{O}}^{\mathrm{Mn}}$ estimated from the obtained slope as:

$$\left\{\frac{\ln \gamma_{\mathrm{O\,(CuMn)}} - \ln \gamma_{\mathrm{O(Cu)}}}{(N_{\mathrm{Mn}} = 0.05) - (N_{\mathrm{Mn}} = 0)}\right\} = \left\{\frac{-17.69 - (-6.73)}{0.05}\right\}$$

is equal to $-220$.

With the value Eq. (10) can be solved, and the results of the calculations are shown in Fig. 3. The minimum oxygen solubility $1 \cdot 10^{-5}$ atom pct. O corresponds to the alloy composition $N_{\mathrm{Mn}} = 0.005$.

Using the value of $\varepsilon_{\mathrm{O}}^{\mathrm{Mn}} = -220$, and accepting one $h$-parameter mod-

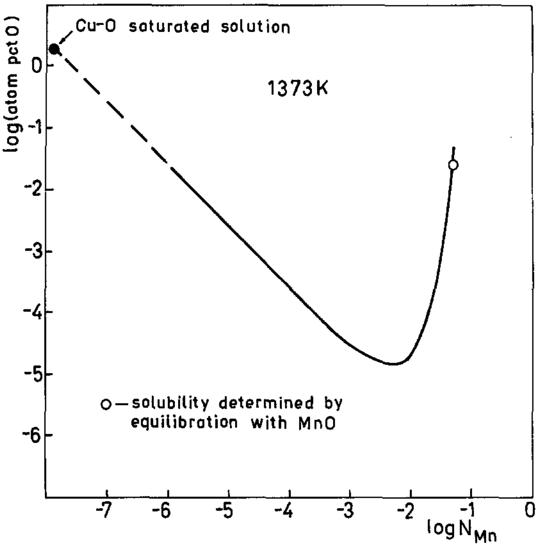

Fig. 3. Saturation solubility curves in Cu—Mn—O alloys at 1 373 K

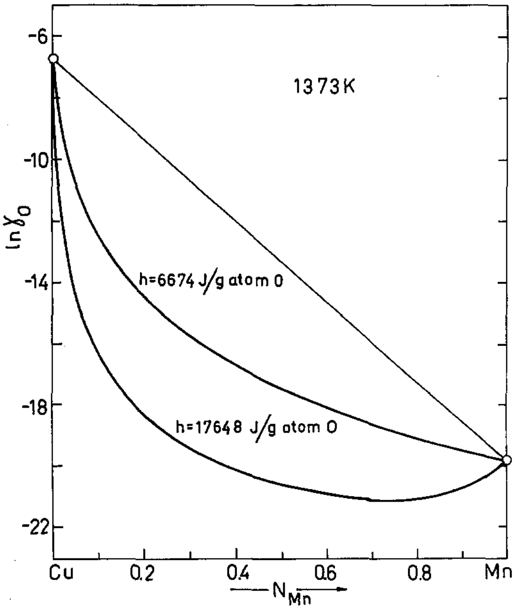

Fig. 4. Activity coefficient of oxygen in dilute liquid Cu—Mn alloys at 1 373 K predicted from *Wagner*'s model

el after *Wagner* [14], one can calculate $h = 6\,674$ J/g · atom O provided, the $\ln \gamma_O$ value for oxygen in liquid, supercooled Mn is taken from [23]. The $\ln \gamma_O$ vs. $N_{Mn}$ plot at 1 373 K predicted from *Wagner*'s model is shown in Fig. 4. Also, a similar dependence calculated for the value of $h = 17\,648$ J/g · atom O, which was obtained from $\varepsilon_O^{Mn} = -2\,490$, is shown for comparison in Fig. 4.

### Fe—S—O *System*

As an example, the desulfurization reactions (18) in liquid iron with BaO, SrO and CaO were considered. For a given level of deoxidation a lower residual sulfur content in metal is expected with higher equilibrium ratio (pct. O/pct. S). Results of calculations are shown in Fig. 5. An interaction parameter $\varepsilon_O^S = \varepsilon_S^O = -17$ was accepted according to [16]. It is clear that for a given oxygen level the best desulfurization of iron is expected with barium oxide.

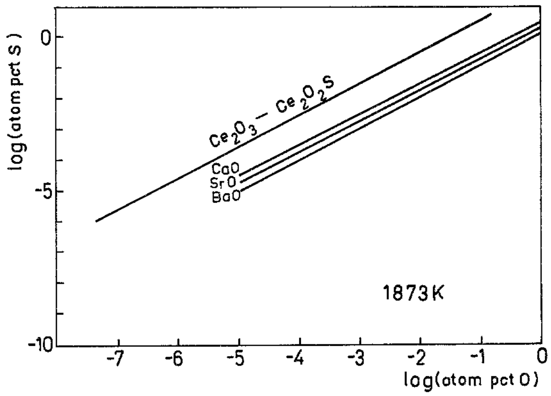

Fig. 5. Sulfur content vs. oxygen content interpendence in dilute Fe—S—O alloys at 1 873 K

For comparison, results of desulfurization with cerium are also shown. The *Gibbs* free energy change of the reaction:

$$Ce_2O_3 + S \rightarrow O + Ce_2O_2S \qquad (32)$$

is: $\Delta G_T^\circ = 43\,040 + 5.15\,T$ (J) [15, 24, 25]. The equilibrium constant $K_{(32)}$ is expressed by the ratio (atom pct. O/atom pct. S). The respective solubility dependence at 1 873 K is shown in Fig. 5. One can conclude that in order to achieve a low level of sulfur, the metal should be first deoxidized with a strong deoxidizer to bring down the corresponding oxygen level in the melt.

## *Conclusions*

Prediction of the solubility minima in oxide-metal equilibria was the subject of a number of studies in the past [26–28]. Recently, *Liang* et al. [29, 30] developed a powerful method of predicting solubility minima, which requires only binary data on the $A$—O, $B$—O and $A$—$B$ system to obtain the ternary system $A$—$B$—O where $B$ is the deoxidizer. However, prediction of a regular solution parameter $b$ from *Miedema*'s theory used in this model may lead to errors if the real heat of mixing changes its sign with concentration in the $A$—$B$ system.

A simple model of deoxidation and desulfurization processes derived in this paper can be easily extended to multicomponent solutions. A first-order interaction parameter formalism is satisfactory to achieve the required solutions. For compositions of alloys higher than $N_M = 0.1$ a function $\gamma_M = f(T, N)$ resulting from a chosen way of interpretation of solutions should be introduced. Calculated equilibrium solubilities exhibit a degree of accuracy which is adequate for practical purposes. In our opinion, the observed discrepancies between calculated and measured values result either from inaccuracy of thermochemical data or rate processes which could influence experimental results. The suggested approach may significantly facilitate prediction of solubility minima in more complex situations e.g. encountered during crystal growth from multicomponent solutions.

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