Solubility and Activity of Oxygen in Liquid Manganese

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The oxygen concentration of liquid manganese in equilibrium with MnAl_{2+2}O_{4+3} and \( \alpha\)-Al\(_2\)O\(_3\) has been determined in the temperature range 1520 to 1875 K. The oxygen content of quenched samples, wrapped in oxygen-free nickel foil, was determined by an inert gas fusion technique. The results are combined with accurate data now available on the Gibbs energies of formation of MnO and Al\(_2\)O\(_3\)-saturated MnAl\(_{2+2}O_{4+3}\) to derive the oxygen content of liquid manganese in equilibrium with MnO and the Gibbs energy of solution of diatomic oxygen gas in liquid manganese. The enthalpy and entropy of solution of oxygen in manganese are compared with similar data on other metal-oxygen systems.

THE activity coefficient of oxygen dissolved in binary or higher order alloys can be estimated with useful accuracy from thermodynamic data for oxygen in pure metals and activity coefficients of metallic components in binary alloy systems, using methods suggested by Jacob and Alcock, Chang and Hu. The solubility of oxygen or deoxidation equilibria in complex alloys can be readily calculated from the activity coefficients and the Gibbs energy of formation of the oxide phase. Manganese is usually present in many high temperature alloys based on iron, cobalt or nickel. This study is motivated by the lack of accurate information on the activity coefficient of oxygen in liquid manganese.

The high vapor pressure of manganese and electronic conduction at the low oxygen potentials associated with dilute solutions of oxygen in manganese preclude the use of solid electrolytes based on ZrO\(_2\) and ThO\(_2\). The reaction between the metal and silica prevents the use of conventional sampling techniques. The saturation solubility of oxygen can be measured by chemical analysis of quenched samples, provided a closed system can be designed. Since it is difficult to prepare a container system made of MnO, commercially available high purity alumina crucibles and lids are used to contain manganese. Previous studies have shown that dissolved oxygen will react with manganese and alumina to form an adherent layer of MnAl\(_{2+2}O_{4+3}\) on the crucible. The Gibbs energy of formation of Al\(_2\)O\(_3\)-saturated MnAl\(_{2+2}O_{4+3}\) has also been accurately determined. Hence the activity coefficient of oxygen in liquid manganese can be derived from a measurement of the oxygen content of manganese in equilibrium with MnAl\(_{2+2}O_{4+3}\) and Al\(_2\)O\(_3\).

EXPERIMENTAL

Materials
Manganese flakes of 99.99 pct purity were obtained from Apache Chemicals Inc. The monoxide of manganese was prepared by first decomposing Analar MnSO\(_4\) at 1300 K in air to a mixture of MnO and Mn\(_2\)O\(_3\). Then the oxides were heated in a Pt-lined alumina boat in a H\(_2\) stream at 1300 K for 3 h to obtain bright green MnO. The alumina tubes and crucibles were supplied by Morgan Refractories Ltd. High purity argon was dried by passing through magnesium perchlorate and then deoxidized by passage through copper turnings at 900 K and titanium pellets at 1200 K. Residual oxygen in high purity hydrogen was removed by passage through a Matheson hydrogen purifier, which converts oxygen to water vapor. The water vapor is removed by molecular sieves.

Approximately 30 g of manganese and 1.5 g of manganese monoxide were placed in a lidded alumina crucible. The small gap between the lid and the crucible was covered with alumina cement. A schematic diagram of the assembly is shown in Fig. 1. The crucible was supported inside a vertical alumina reaction tube by an alumina thermocouple sheath. The reaction tube was suspended coaxially inside a molybdenum resistance furnace. The space between the reaction and furnace tubes was purged with argon gas.

Prepurified argon gas was passed through the reaction tube at a flow rate of 400 ml/min\(^{-1}\). Titanium internal getters were placed in the reaction tube in the path of incoming argon stream such that their temperature was between 1000 and 1200 K. These internal getters remove residual oxygen from the argon gas and oxygen bearing gas molecules that desorb from ceramic tubes. The temperature of the melt was measured by a Pt-13 pct Rh/Pt-20 pct Rh thermocouple.

Preliminary results indicated that the three phase equilibrium between liquid manganese aluminate and alumina was attained after 3 h at 1875 K and 6 h at 1520 K. This was indicated by a constant value for oxygen concentration at each temperature, independent of time for up to 15 h. If the oxygen content of the metal was higher than the equilibrium value, there would have been a driving force for the formation of the spinel. The excess oxygen would have been consumed by the formation of manganese aluminate at a rate governed by ionic diffusion through the spinel.
Table I. Oxygen Content of Liquid Manganese in Equilibrium with MnAl$_{2+2x}$O$_{4+3x}$ and $\alpha$-Al$_2$O$_3$

<table>
<thead>
<tr>
<th>$T$, K</th>
<th>At. Pct O</th>
</tr>
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<tbody>
<tr>
<td>1523</td>
<td>0.00223</td>
</tr>
<tr>
<td>1533</td>
<td>0.00252</td>
</tr>
<tr>
<td>1573</td>
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</tr>
<tr>
<td>1673</td>
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<tr>
<td>1733</td>
<td>0.01733</td>
</tr>
<tr>
<td>1773</td>
<td>0.0253</td>
</tr>
<tr>
<td>1818</td>
<td>0.0381</td>
</tr>
<tr>
<td>1842</td>
<td>0.0420</td>
</tr>
<tr>
<td>1873</td>
<td>0.0545</td>
</tr>
</tbody>
</table>

Layer. When emf sensors were used to monitor oxygen activity in the metal phase during studies of similar three phase equilibria in the Co and Ni systems, it was found that addition of fresh alumina powder to molten metal after the attainment of equilibrium did not affect the emf. At the end of the equilibration period, the crucible was quenched by lowering the assembly onto a water-cooled brass head. An examination of vertical sections of the crucible clearly indicated the formation of a thin layer of MnAl$_{2+2x}$O$_{4+3x}$ spinel on the inner surface of the crucible in contact with the melt. The spinel phase was identified by X-ray diffraction. Samples of manganese, about 1 g in weight, were prepared from the quenched ingot for oxygen analysis. Random metallographic examination of these samples indicated the absence of oxide inclusions, which were mainly confined to the metal-crucible interface.

The manganese samples for oxygen analysis were wrapped in oxygen-free nickel foil. The foil was deoxidized by reacting with dry hydrogen at 1575 K for 5 h. The weight ratio of nickel foil to manganese was about 2:1. The wrapped samples were placed in a carbon crucible and analyzed by an inert gas fusion technique (Leco RO-16). The complete extraction of oxygen from the sample during analysis was verified by using weighed amounts of MnO wrapped in nickel foil, instead of the quenched samples.

**Results**

The oxygen content of liquid manganese in equilibrium with MnAl$_{2+2x}$O$_{4+3x}$ and $\alpha$-Al$_2$O$_3$ determined in this study is summarized in Table I and plotted as a function of temperature in Fig. 2. Since the oxygen concentration is small, the activity of manganese can be taken as unity. The logarithm of oxygen concentration is plotted against the reciprocal of absolute temperature in Fig. 3. The experimental results can be represented by a linear relation. The least-mean squares analysis gives:

$$\log (\text{at. pct O}) = -\frac{11.040}{T} + 4.63 (\pm 0.01)$$

The equilibrium oxygen concentration is determined by the interaction between three condensed phases, which can be written as:

$$\text{Mn (l)} + O + (1 + x) \alpha\text{-Al}_2\text{O}_3 \rightarrow \text{MnAl}_{2+2x}\text{O}_{4+3x} \text{(sp)}$$

If the standard state for dissolved oxygen is chosen as an infinitely dilute solution in which activity equals at. pct, the equilibrium constant for the above reaction is given by;

$$K_2 = 1/(\text{at. pct O}) \cdot f_O$$

where $f_O$ is the Henrian activity coefficient for oxygen. Negative deviations from Henry's (or

![Fig. 1—Schematic diagram of the closed systems for equilibrating liquid Mn with MnAl$_{2+2x}$O$_{4+3x}$ and $\alpha$-Al$_2$O$_3$.](image)

![Fig. 2—Temperature dependence of oxygen concentration in liquid Mn in equilibrium with MnAl$_{2+2x}$O$_{4+3x}$ and $\alpha$-Al$_2$O$_3$.](image)
Sievert's law have been found in Fe-O and Ni-O systems. The values for the self interaction parameter, $e^0_\text{Fe} = (\partial \ln f_\text{Fe}/\partial X_\text{O})_{X_\text{O}=0}$, are similar; $e^0_\text{Fe} = -12.5$ for the Fe-O system and $e^0_\text{Ni} = -11.7$ for the Ni-O system at 1873 K. Assuming that deviations from Sievert's law in the Mn-O system is of the same order of magnitude as for Fe-O and Ni-O melts, the lowest value of $f_\text{O}$, corresponding to the highest measured oxygen content, is 0.99. Therefore, the error introduced by neglecting the activity coefficient is negligible. The Gibbs energy change for reaction [2] can therefore be calculated:

$$\Delta G^0 = -RT \ln K = RT \ln (at. \text{ pct } O)$$

[4]

$$\Delta G^0 = -211,360 + 88.63 T (\pm 400) \text{J mol}^{-1}$$

[5]

The Gibbs energy of formation of alumina-saturated manganese aluminate from component oxides has recently been measured using emf and equilibrium techniques over a large temperature range extending from 973 to 1873 K. For the reaction,

$$\text{MnO (r.s) + (1 + x) } \alpha\text{-Al}_2\text{O}_3 \rightarrow \text{MnAl}_{2+2x}\text{O}_{4+3x} \text{ (sp)}$$

Values for the nonstoichiometric parameter $x$ in the MnAl$_{2+2x}$O$_{4+3x}$, are 0.1 and 0.13 at 1873 and 1923 K, respectively. Combining Eqs. [2] and [6], one obtains

$$\Delta G^0_2 = -37,760 + 6.28 T (\pm 800) \text{J mol}^{-1}$$

[6]

[7]

This equation defines the saturation solubility of oxygen in the Mn-O binary system. Neglecting deviations from Sievert's law, the saturation solubility is,

$$\log(\text{at. pct } O)_{\text{sat}} = -\log K = - \frac{9,070}{T} + 4.30 (\pm 0.03)$$

[10]

The calculated oxygen content of liquid Mn in equilibrium with MnO is plotted as a function of temperature in Fig. 4. The earlier measurements of Schenck et al. using MnO crucibles are also shown for comparison. While there is fair agreement at temperatures close to the melting point of Mn the results of this study suggest a larger solubility at higher temperatures.

The Gibbs energy of formation of MnO is,

$$\text{Mn}(1) + 1/2 \text{O}_2(g) \rightarrow \text{MnO (r.s)}$$

$$\Delta G^0_{11} = -406,700 + 87.99 T (\pm 650) \text{J mol}^{-1}$$

[12]

This value is in good agreement with more recent emf measurements. From Eqs. [8] and [11], the Gibbs energy of solution of diatomic oxygen gas in liquid manganese can be derived:

$$1/2 \text{O}_2(g) \rightarrow \text{O}$$

$$\Delta G^0_{13} = -233,100 + 5.65 T (\pm 110) \text{J mol}^{-1}$$

[14]

At 1873 K, the value suggested by this equation is 12.2 kJ mol$^{-1}$ more negative than the corresponding value derived from the solubility measurements of Schenck et al. On the other hand, the present result (Eq. [14]) is 26.9 kJ mol$^{-1}$ more positive that the value
used by Chang and Hu\textsuperscript{3} to predict the interaction between manganese and oxygen in liquid iron at 1873 K.

Discussion

Fitzner and Jacob\textsuperscript{10} have established a nonlinear correlation between the enthalpy of solution of diatomic oxygen in liquid metals at temperatures above their melting points and the standard enthalpy of formation of corresponding oxides at 298 K. More recent results of Otsuka \textit{et al}\textsuperscript{11} support this correlation. In Fig. 5 the information on Mn obtained in this study is compared with data in the literature for other metal-oxygen systems.\textsuperscript{10} The behavior of Mn is similar to other 3d transition metals, Ni, Co and Fe. The values for enthalpy of solution in these metals is 40 (±10)kJ more positive compared to values for non-transition elements. The data for U is not very accurate.

The difference in behavior of oxygen in transition metals in comparison to normal metals is also evident in the correlation (Fig. 6) between enthalpy and entropy of solution at infinite dilution. As discussed by Alcock and Jacob\textsuperscript{12} and Fitzner \textit{et al},\textsuperscript{13} the decrease in the entropy of solution with enthalpy, or the strength of metal-oxygen bonds, can be attributed to the increasing vibrational frequency of oxygen. For dilute solutions the configurational contribution to the entropy of oxygen would be similar for all the metals considered. Otsuka \textit{et al}\textsuperscript{11} have suggested that, although the correlations between entropy and enthalpy of solution of oxygen exhibit the same trends as in Fig. 6, a separate curve is required to represent data for elements of each group of the periodic table. The substantial differences obtained by Otsuka \textit{et al}\textsuperscript{11} for normal metals from different groups are at least in part based on an inadequate experimental method. The loss of oxygen from metals in the form of volatile oxides during their coulometric titrations, have not been quantitatively treated in their analysis of data.

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REFERENCES