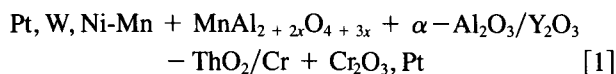


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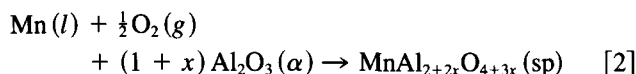
Activity of Manganese in Liquid Ni-Mn Alloys

K. T. JACOB

Manganese is usually present as a minor component in alloys designed for high temperature oxidation resistance, and promotes the formation of protective spinel layers. Although thermodynamic data on liquid Fe-Mn alloys are well established,¹ there is a lack of corresponding experimental information regarding Ni-Mn alloys. Available data on solid Ni-Mn alloys have been evaluated by Hultgren *et al.*¹ A solid state emf cell, with yttria doped thoria as the electrolyte and a mixture of Cr + Cr₂O₃ as the reference electrode, is employed in this study for measurement of the activity of manganese in the Ni-Mn system at 1683 K, for $0.4 > X_{\text{Mn}} > 0.05$. The liquid alloy is contained in an alumina crucible and saturated with MnAl_{2+2x}O_{4+3x}. The cell can be represented as:



The oxygen potential at the alloy electrode is established by equilibrium between three condensed phases:



Three phase equilibria of this type have not been utilized previously in the study of alloy thermodynamics using the emf method. The normal practice is to saturate the alloy with the oxide of reactive metal. The difficulty in finding a container material resistant to MnO and the availability of accurate thermodynamic data on manganese aluminate^{2,3} are the main reasons for the choice of three phase equilibria in this study.

A schematic diagram of the apparatus is shown in Figure 1. The alumina crucible containing the alloy is supported on an alumina sheath inside a vertical reaction tube. Synthetic MnAl₂O₄ is added to the melt and the crucible is covered with an alumina lid to minimize the loss of manganese by vaporization. Two holes in the lid permit the insertion of the solid electrolyte tube and a tungsten lead. The junction between the tungsten lead and the platinum wire is maintained in the constant temperature zone of a molybdenum furnace, thus eliminating thermoelectric force between the two leads. The solid electrolyte tube and the conducting lead are usually suspended above the melt.

A mixture of Cr and Cr₂O₃ is placed inside the solid electrolyte tube, with a platinum lead embedded in the mixture. The molar ratio of Cr to Cr₂O₃ in the reference electrode was 1:2 for alloy compositions producing positive emfs ($X_{\text{Mn}} > 0.18$), and 2:1 for compositions giving negative emfs. In each case, by taking an excess of the component that is consumed by the flux of oxygen through the

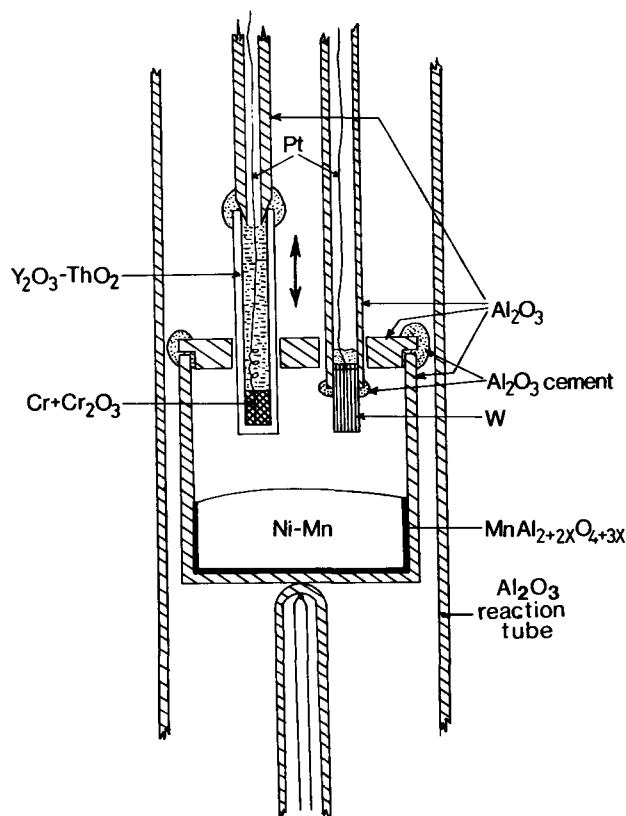


Fig. 1—Schematic diagram of the apparatus.

electrolyte, polarization at the reference electrode is eliminated. The electrolyte tube is then filled tightly with thoria powder to prevent manganese vapor from reaching the reference electrode. Prepurified argon gas is passed through the reaction tube at a rate of 300 ml min^{-1} . After the cell is assembled, the furnace is heated to 1683 K. Preliminary results indicated that the equilibrium between the alloy, manganese aluminate, and alumina is established in approximately four hours. After this time interval, the solid electrolyte tube and the tungsten lead are lowered into the melt and the emf is monitored as a function of time using a high impedance digital voltmeter ($>10^{12}\Omega$). For alloys containing less than 40 at. pct Mn, the emf remains constant for approximately two minutes, after which it begins to decrease slowly. The signal decay can be arrested and reversed by vibrating the solid electrolyte tube. This indicates that the decrease in emf is caused by concentration polarization at the alloy electrode due to the flux of oxygen through the electrolyte. Steady emfs lasting approximately 15 minutes can be obtained by mechanical vibration of the electrolyte tube. During this period the tungsten rod was only intermittently dipped into the alloy for emf measurements to minimize its dissolution. When the manganese concentration in the alloy exceeds 40 at. pct, vibration of the tube does not completely suppress the drift in emf. This finding is compatible with increasing electronic transport in doped thoria with increasing manganese concentration or decreasing oxygen potential, and consequent electrochemical permeability of oxygen. The steady emf for alloys with less than 40 at. pct manganese is plotted as a function of the composition of the alloy in Figure 2. Eventually there is some penetration of the solid electrolyte tube by manganese and

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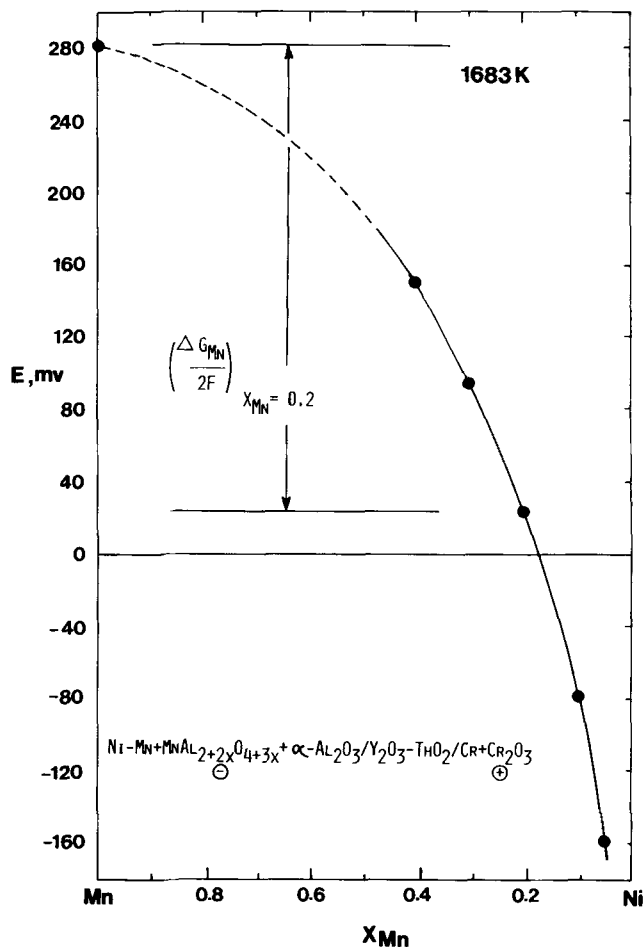
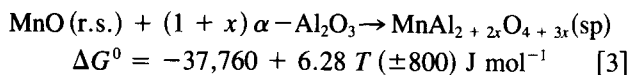


Fig. 2—Composition dependence of the emf at 1683 K.

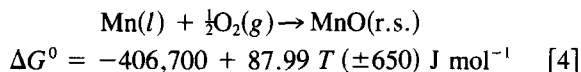
manganese oxide resulting in a drop of emf even for low manganese alloys.

After the cell is cooled to room temperature, the alumina crucible is sectioned to examine the alloy/crucible interface. Both X-ray diffraction and electron microprobe traces indicate the presence of $\text{MnAl}_{2+2x}\text{O}_{4+3x}$ at the interface. The atomic ratio of nickel to manganese in the spinel phase is less than 0.005 for all alloy compositions. Hence, the activity of manganese aluminate can be taken as unity. The alloy composition after the experiment is determined by chemical analysis. For all compositions, there is a loss of manganese from the alloy due to vaporization. The concentration of tungsten in liquid Ni-Mn alloys, determined by chemical analysis after each experiment, is less than 0.3 at. pct, and is not expected to influence the measured activities.

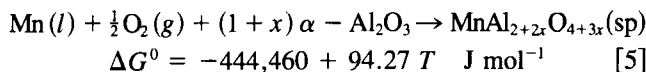
Since steady emfs are not registered at high manganese concentrations, the emf of the cell corresponding to pure liquid manganese is calculated from accurate data now available^{2,3} for the Gibbs energy of formation of alumina-saturated manganese aluminate. For the reaction,



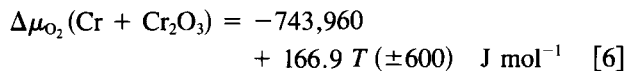
The standard Gibbs energy of formation of MnO, available in thermochemical tables,⁴ and confirmed by more recent electrochemical measurements,⁵ can be represented by the equation:



Combining Eqs. [3] and [4] one obtains:



This data, together with information on the chemical potential of oxygen in the reference electrode,⁶



are used to compute the emf of the cell with pure manganese instead of Ni-Mn alloy (see Figure 2). The activities of manganese in alloys are calculated from the difference between the measured emfs for alloys and the computed emf for pure liquid manganese, which is the standard state.

$$E_{X_{\text{Mn}}} - E_{X_{\text{Mn}}=1} = \frac{RT}{nF} \ln a_{\text{Mn}} \quad [7]$$

The use of this equation for an alloy containing 20 at. pct Mn is illustrated by an arrow in Figure 2. The activity-composition relationship for liquid Ni-Mn alloys is shown in Figure 3. The alpha function for manganese [$\alpha = \log \gamma_{\text{Mn}} / (1 - X_{\text{Mn}})^2$] is plotted as a function of composition in Figure 4. The experimental data in the limited composition range amenable for investigation can be represented by the linear relation:

$$\log \gamma_{\text{Mn}} / (1 - X_{\text{Mn}})^2 = -0.4536 - 1.0802 X_{\text{Ni}} \quad [8]$$

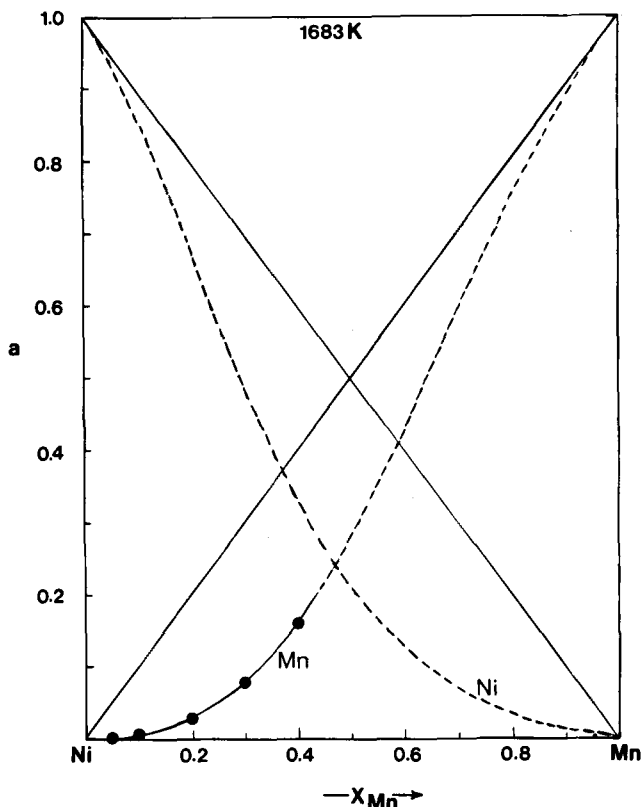


Fig. 3—Activity-composition relation in liquid Ni-Mn alloys at 1683 K, based on emf measurements and Eqs. [10] and [11].

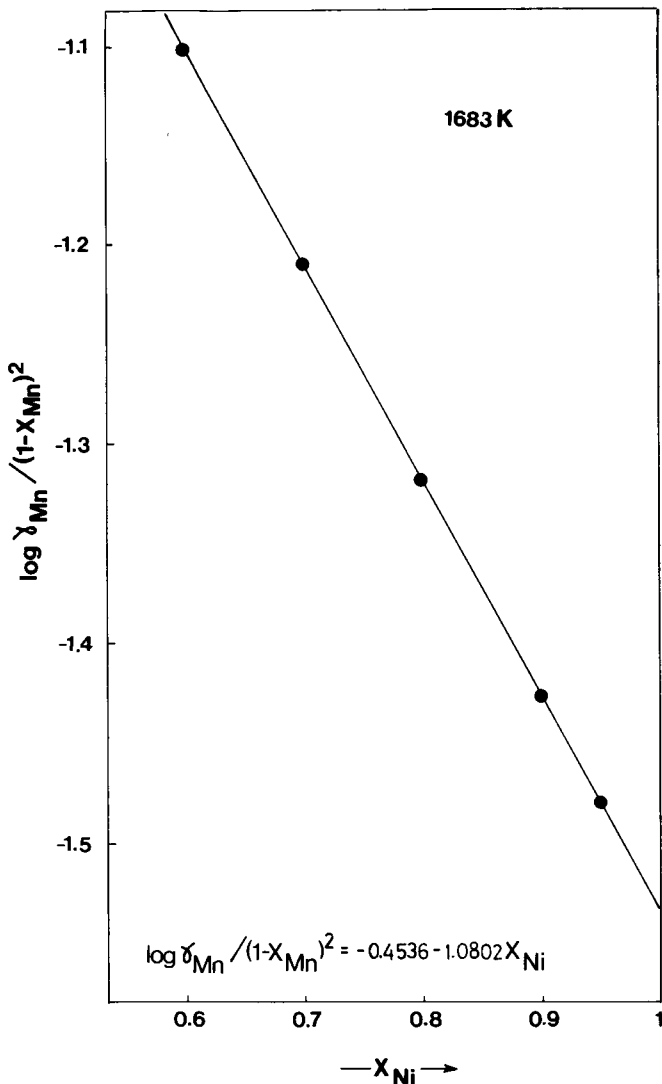


Fig. 4—Variation of $\log \gamma_{Mn} / (1 - X_{Mn})^2$ with alloy composition.

If this relation is assumed to be valid for high manganese alloys, then the excess Gibbs energies of mixing in the liquid Ni-Mn system can be represented by a subregular model:⁷

$$\Delta G^E = X_{Ni}X_{Mn}(-32,010X_{Mn} - 49,410X_{Ni}) \text{ J mol}^{-1} \quad [9]$$

$$\Delta G_{Ni}^E = -66,810X_{Mn}^2 + 34,800X_{Mn}^3 \text{ J mol}^{-1} \quad [10]$$

$$\Delta G_{Mn}^E = -14,610X_{Ni}^2 - 34,800X_{Ni}^3 \text{ J mol}^{-1} \quad [11]$$

These data are useful in calculating deoxidation equilibria and the partitioning of manganese between alloy and slag in pyrometallurgical processes.

The activity coefficient of manganese at infinite dilution at 1683 K, relative to pure liquid manganese as the standard state, is 0.029. This contrasts with a value of unity for the activity coefficient given by Sigworth *et al*⁸ in their tabulation of thermodynamic data on dilute nickel alloys.

ACKNOWLEDGMENT

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Standard Free Energy of Formation of NiAsS

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The arsenic bearing minerals niccolite (NiAs), maucherite (Ni₁₁As₈), rammelsbegite (NiAs₂), and gersdorffite (NiAsS) are found in nickel sulfide ores. The ore, after concentration, is roasted and then smelted in a reverberatory furnace, electric furnace, or flash smelting furnace. The As not liberated as As₄O₆ vapor during roasting, concentrates during smelting in the matte, and depending on the copper content of the matte, arsenic can concentrate in the nickel sulfide phase produced upon solidification. Once As enters the nickel sulfide phase it follows the nickel into the anodes, where 0.5 wt pct is not uncommon.¹ The As is removed during electrolytic refining where it concentrates in the electrolyte. The arsenic must be removed from the electrolyte to prevent its physical entrainment in the cathode.

Arsenic and many of its compounds are volatile, and thus it is feasible to eliminate the As during roasting. Recent investigations with arsenious copper concentrates have helped identify the conditions which lead to retention of arsenic.² If this retention is to be minimized, thermodynamic data for As and its compounds will be necessary to perform the pertinent calculations. This study examines the standard free energy of formation of NiAsS.

Yund examined the Ni-As-S system at 723, 873, and 973 K.³ The NiAsS compound as shown in the phase diagram in Figure 1 exhibits a homogeneity range on the NiAs₂-NiS₂ pseudo binary system. Thus, the simple formula NiAsS is insufficient to designate its composition. In lieu of specifying the composition, the recognized procedure of placing a bar over the top of S in NiAsS is used to indicate that the composition of the compound is at the sulfide rich phase boundary in the binary system.^{4,5} Similarly, NiAsS represents the compound with a composition at the arsenide rich phase boundary.

Yund has experimentally determined the tie lines in many of the two* phase regions in the ternary system shown in

*Only condensed phases are represented in the phase diagram. The two phase region referred to acknowledges only the presence of condensed phases. Vapor is also a stable phase at all compositions.

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