

# Distribution of Nickel between Copper-Nickel and Alumina Saturated Iron Silicate Slags

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The solubility of nickel in slag was determined by equilibrating copper-nickel alloys with alumina-saturated iron silicate slags in an alumina crucible at 1573 K. The experiments were carried out under controlled oxygen partial pressures in the range of  $10^{-10}$  to  $10^{-8}$  atm by use of suitable CO-CO<sub>2</sub> gas mixtures, and at Fe/SiO<sub>2</sub> ratio 1.34. The results showed that nickel dissolves in slag both as Ni<sup>2+</sup> (nickel oxide) and Ni<sup>0</sup> (nickel metal), and the relation obtained was:

$$(\text{Wt pct Ni in slag}) = 2.083 \times 10^5 P_{\text{O}_2}^{1/2} a_{\text{Ni}(l)} + 2.334 a_{\text{Ni}(l)}$$

The activity coefficient of nickel oxide ( $\gamma_{\text{NiO}}^0$ ) and distribution coefficient of nickel ( $A_{\text{Ni}}$ ) is calculated to be 0.375 and 233.3, respectively.  $\gamma_{\text{NiO}}^0$  and  $A_{\text{Ni}}$  are found to be independent of oxygen partial pressures. The presence of alumina increases the solubility of nickel in slags.

## I. INTRODUCTION

THE most important factors contributing to nickel solubility in slags are: temperature, oxygen potential of the slag, and slag composition. The solubility of nickel in silica saturated fayalite slags in equilibrium with copper-nickel alloys was investigated by Wang *et al.*<sup>1</sup> under controlled oxygen partial pressures ( $10^{-6}$  to  $10^{-10}$  atm) over the temperature range 1523 to 1623 K. Their results showed that at a constant temperature and constant oxygen pressure, the nickel solubility increases with nickel activity in the alloy. Das and Healy<sup>2</sup> equilibrated copper-nickel alloys with a ternary Cu<sub>2</sub>O-NiO-SiO<sub>2</sub> saturated slags at 1498 K. Their results were correlated using ion-fractions, and the authors suggested that Temkin's method correlates slightly better than the other. A tentative phase diagram of the Cu<sub>2</sub>O-NiO-SiO<sub>2</sub> system at 1498 K was constructed. Taylor and Jeffes<sup>3</sup> measured the distribution of nickel and copper between NiO-CuO<sub>0.5</sub>-FeO-FeO<sub>1.5</sub>-SiO<sub>2</sub> slags in Ni-Cu-Fe alloys. The melts were suspended in an atmosphere of controlled oxygen partial pressure by the levitation technique. They concluded that solubility of nickel in slag depends on slag composition (Fe/SiO<sub>2</sub> ratio).

The solubility of nickel in alumina saturated fayalite slags is discussed here, with results from a study of the distribution of nickel between liquid Cu-Ni alloys and slag. The activity coefficient of nickel oxide in the slag phase over a range of oxygen pressures (at a fixed temperature) is also discussed.

## II. EXPERIMENTAL

Three gram samples of high-purity copper, alloyed with high-purity nickel, were equilibrated with three grams of pre-melted fayalite slag (Fe/SiO<sub>2</sub> = 1.34) in alumina crucibles at a specific partial pressure of oxygen and at 1573 K for 24 hours. The oxygen pressure over the sample was maintained constant by using a mixture of CO and CO<sub>2</sub>

gases, at ratios controlled by capillary flow meters. The gas phase flow rate passing over the sample was 600 cm<sup>3</sup> per minute.

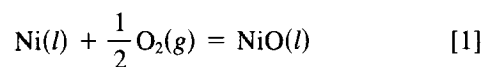
The experimental system had four degrees of freedom. Thus, the system is not unique unless four independent parameters of the slag are specified. These were accommodated by fixing the temperature 1573 K, the Fe/SiO<sub>2</sub> ratio at 1.34, the oxygen partial pressure at  $10^{-8}$ ,  $10^{-9}$ , or  $10^{-10}$  atm, and the activity of nickel in the Cu-Ni alloy.

For a typical run, the experimental set-up (shown in Figure 1) permitted the introduction of the crucible containing the charge into the constant temperature zone of the vertical tube furnace, after the reaction tube had been flushed with purified argon gas. The mixture CO and CO<sub>2</sub> was then switched into the furnace. Following the equilibration, the slag and alloy phases were separated and cleaned for analysis. The slag was analyzed for Ni, Cu, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>. The alloy was analyzed for Ni, Cu, and Fe by conventional methods. Iron could not be detected in the alloy phase. The reproducibility of the analyses was  $\pm 1.0$  pct for the analysis of Cu and Ni, and  $\pm 2.0$  pct for Fe, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>. The slag analyses totaled 100 pct assuming NiO, CuO<sub>0.5</sub>, FeO, FeO<sub>1.5</sub>, AlO<sub>1.5</sub>, and SiO<sub>2</sub> to be molecular species that were present.

## III. RESULTS AND DISCUSSION

The experimental results of this study are summarized in Table I. The solubility of nickel in the slag phase as a function of the nickel in its alloy phase after equilibration for various oxygen potentials over the liquid slag is presented in Figure 2. The solubility of nickel increased with concentration of nickel in alloy for a given partial pressure of oxygen, and also increased with increase in partial pressure of oxygen at a fixed concentration of nickel in alloy. For example, at 0.8 wt pct Ni in alloy, nickel solubility in slag increased from 0.12 to 0.65 wt pct as the oxygen partial pressure increased from  $10^{-10}$  to  $10^{-8}$  atm, respectively.

Both alloy and slag are liquid at the experimental conditions considered, *i.e.*, the oxidation of nickel to form nickel oxide reaction is written as



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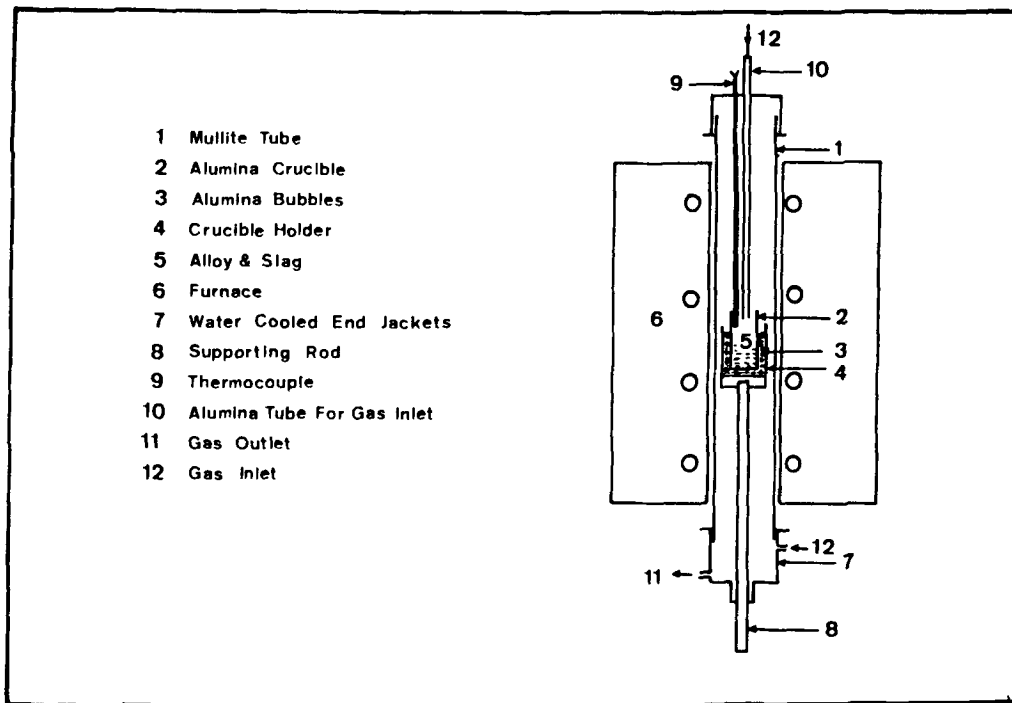


Fig. 1—Experimental set-up (not to scale).

The standard state of the nickel and nickel oxide are taken to be pure supercooled liquid nickel and liquid nickel oxide, respectively. The free energy change  $\Delta G^\circ$  for reaction [1] has been calculated using the thermodynamic values recommended by Nagamori and Mackey<sup>4</sup> and Wang *et al.*<sup>5</sup> The resulting free energy change for reaction [1] is

$$\Delta G^\circ = -208.66 + 0.0763 T \text{ kJ/g-mole} \quad [2]$$

From Eq. [1]  $a_{\text{NiO}(l)}$  can be written as

$$a_{\text{NiO}(l)} = K_1 a_{\text{Ni}(l)} P_{\text{O}_2}^{1/2} \quad [3]$$

where, from Eq. [2]

**Table I. Analyses of Equilibrated Alloys and Slags, and Data Related to Calculation of Activity Coefficient of Nickel Oxide ( $\gamma_{\text{NiO}}$ ) and Distribution Coefficient ( $A_{\text{Ni}}$ ) at 1573 K and Fe/SiO<sub>2</sub> Ratio 1.34**

Expt. No.	Pct Alloy		$a_{\text{Ni}(l)}$	Wt Pct Ni in Slag	Wt Pct Ni in Slag $a_{\text{Ni}(l)}$	Wt Pct Ni <sup>o</sup> in Slag	Wt Pct Ni <sup>2+</sup> in Slag	$X_{\text{NiO}}$	$a_{\text{NiO}(l)}$	$\gamma_{\text{NiO}}$	$A_{\text{Ni}} = \text{Wt Pct Ni}^{2+} \text{ in Slag}$
	Wt Pct Ni Initial	Wt Pct Ni Equil.									
Partial Pressure of Oxygen $1.0 \times 10^{-10}$ atm											
1	0.2	0.241	0.009	0.04	4.22	0.021	0.019	$2.1156 \times 10^{-4}$	$7.847 \times 10^{-5}$	0.370	242.12
2	0.5	0.420	0.0156	0.08	5.12	0.0364	0.0436	$4.874 \times 10^{-4}$	$1.3602 \times 10^{-4}$	0.279	320.4
3	1.0	0.475	0.0177	0.100	5.65	0.0413	0.0587	$6.584 \times 10^{-4}$	$1.5433 \times 10^{-4}$	0.234	380.28
4	3.0	1.067	0.0389	0.195	5.01	0.0907	0.1043	$1.191 \times 10^{-3}$	$3.3918 \times 10^{-4}$	0.284	306.5
5	5.0	1.302	0.0471	0.240	5.09	0.1099	0.1300	$1.489 \times 10^{-3}$	$4.1067 \times 10^{-4}$	0.275	316.5
6	8.0	1.560	0.0564	0.265	4.69	0.1316	0.1334	$1.544 \times 10^{-3}$	$4.9176 \times 10^{-4}$	0.318	271.06
Partial Pressure of Oxygen $1.877 \times 10^{-9}$ atm											
7	0.2	0.160	0.0058	0.054	9.27	0.0135	0.0405	$4.558 \times 10^{-4}$	$2.1973 \times 10^{-4}$	0.482	183.86
8	0.5	0.280	0.01046	0.103	9.84	0.0242	0.0787	$9.023 \times 10^{-4}$	$3.9491 \times 10^{-4}$	0.437	199.28
9	1.0	0.420	0.0156	0.180	11.53	0.0364	0.1436	$1.668 \times 10^{-3}$	$5.8897 \times 10^{-4}$	0.353	243.9
10	3.0	0.870	0.0320	0.320	10.00	0.0746	0.2453	$2.901 \times 10^{-3}$	$1.2081 \times 10^{-3}$	0.416	203.04
11	5.0	1.107	0.0405	0.401	9.90	0.0945	0.3064	$3.639 \times 10^{-3}$	$1.529 \times 10^{-3}$	0.420	200.39
12	8.0	1.333	0.0484	0.600	12.39	0.1129	0.4870	$5.805 \times 10^{-3}$	$1.827 \times 10^{-3}$	0.314	266.51
Partial Pressure of Oxygen $1.0 \times 10^{-8}$ atm											
13	0.2	0.125	0.0047	0.121	25.58	0.0109	0.1100	$1.225 \times 10^{-3}$	$4.0893 \times 10^{-4}$	0.333	269.01
14	0.5	0.227	0.0085	0.210	24.60	0.0198	0.1901	$2.117 \times 10^{-3}$	$7.4261 \times 10^{-4}$	0.350	256.06
15	1.0	0.390	0.0145	0.354	24.41	0.0338	0.3201	$3.579 \times 10^{-3}$	$1.264 \times 10^{-3}$	0.353	253.2
16	3.0	0.756	0.0279	0.64	22.93	0.0651	0.5748	$6.464 \times 10^{-3}$	$2.4326 \times 10^{-3}$	0.376	236.2
17	5.0	0.952	0.0350	0.742	21.20	0.0816	0.6603	$7.554 \times 10^{-3}$	$3.0517 \times 10^{-3}$	0.404	216.3
18	8.0	1.200	0.0438	0.972	22.19	0.1022	0.8697	$1.048 \times 10^{-2}$	$3.819 \times 10^{-3}$	0.364	227.7

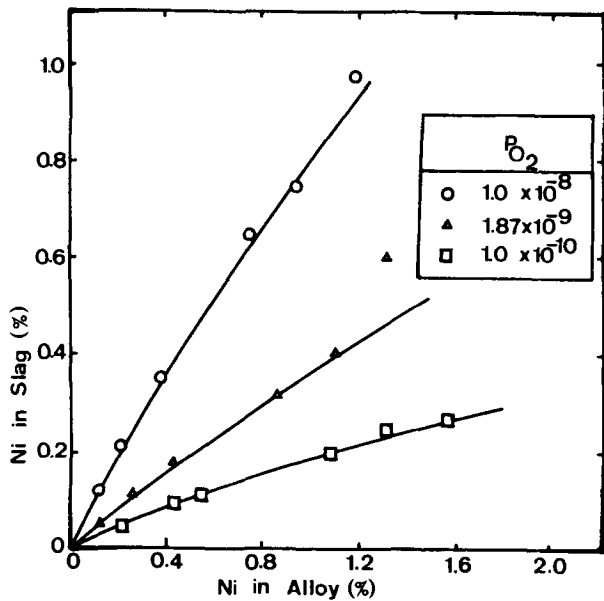


Fig. 2—Solubility of nickel in slag as a function of the equilibrium nickel in the alloy at 1573 K and Fe/SiO<sub>2</sub> = 1.34.

$$K_1(\text{at } 1573 \text{ K}) = 874.58 \quad [4]$$

where  $a_{\text{Ni}(l)}$  and  $a_{\text{NiO}(l)}$  are the activities of liquid nickel in alloy and liquid nickel oxide in slag, respectively, and  $K_1$  is the equilibrium constant for reaction [1].

The activities of Cu and Ni in Cu-Ni alloy for each experiment were determined from the data of Rapp and Maak<sup>6</sup> and Schultz *et al.*<sup>7</sup> Using the calculated values of  $a_{\text{Ni}}$  and  $K_1$ , the activities of NiO in the slags were calculated. The activity coefficient ( $\gamma_{\text{NiO}}$ ) was calculated using the standard relationship  $\gamma_{\text{NiO}} = a_{\text{NiO}}/X_{\text{NiO}}$ , where  $X_{\text{NiO}}$  is the mole fraction of NiO in slag.

Since the nickel content of slag, expressed as wt pct Ni in slag, is proportional to  $X_{\text{NiO}}$ , and on the assumption that Henry's law is obeyed over the entire NiO range studied, *i.e.*,  $\gamma_{\text{NiO}}$  is constant, Eq. [3] can be rewritten as

$$(\text{Wt pct Ni in slag})/a_{\text{Ni}(l)} = K_1 P_{\text{O}_2}^{1/2} \quad [5]$$

If all the nickel in the slag is present as nickel oxide, its solubility should only be a function of the partial pressure of oxygen ( $P_{\text{O}_2}^{1/2}$ ), and will be zero when  $P_{\text{O}_2}^{1/2} = 0$ . In Figure 3 (wt pct Ni in slag)/ $a_{\text{Ni}(l)}$  is plotted as a function of  $P_{\text{O}_2}^{1/2}$  at 1573 K, and should pass through the origin. A positive intercept on the ordinate, in fact, shows a metallic nickel solubility in the slag. A linear regression equation was obtained for all the data points and is given by

$$(\text{Wt pct Ni in slag})/a_{\text{Ni}(l)} = 2.083 \times 10^5 P_{\text{O}_2}^{1/2} + 2.334 \quad [6]$$

The amount of nickel dissolved in the slag as Ni<sup>0</sup>, when the theoretical activity of nickel is one, is given by 2.334. The Eq. [6] may be written as

$$(\text{Wt pct Ni in slag}) = 2.083 \times 10^5 P_{\text{O}_2}^{1/2} a_{\text{Ni}(l)} + 2.334 a_{\text{Ni}(l)} \quad [7]$$

the metallic nickel solubility in slag at equilibrium with any given nickel activity is presented as

$$(\text{Wt pct Ni}^0 \text{ in slag}) = 2.334 a_{\text{Ni}(l)} \quad [8]$$

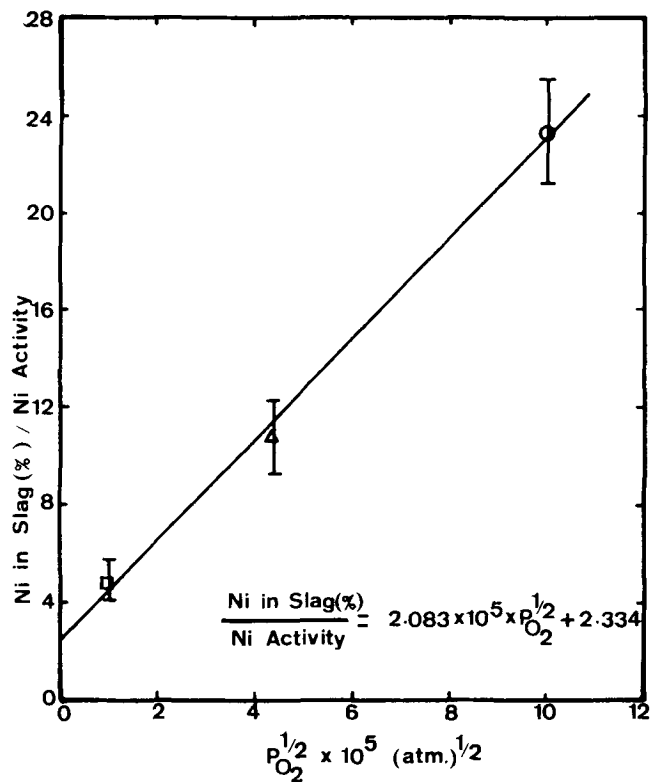


Fig. 3—Effect of oxygen partial pressure on nickel content of slag in equilibrium with the theoretical nickel activity of one (relative to pure super-cooled liquid Ni). Symbols are defined in Fig. 2.

and the nickel solubility dissolving as Ni<sup>2+</sup> is given by

$$(\text{Wt pct Ni}^{2+} \text{ in slag}) = 2.083 \times 10^5 P_{\text{O}_2}^{1/2} a_{\text{Ni}(l)} \quad [9]$$

The metallic nickel (Ni<sup>0</sup>) solubility in slag was calculated using Eq. [8], and from the relationship (wt pct Ni in slag) = (wt pct Ni<sup>0</sup> in slag) + (wt pct Ni<sup>2+</sup> in slag) the corrected wt pct Ni<sup>2+</sup> in the slag was calculated and is listed in Table I; Figure 4 shows the comparison of the experimental data with the predicted solubilities from Eq. [9], where wt pct Ni<sup>2+</sup> in slag is plotted as a function of  $a_{\text{Ni}(l)}$  for various oxygen partial pressures studied. As can be seen, an excellent agreement between predicted and experimental data is obtained. Figure 4 also includes data from other investigators.<sup>1,3</sup> The linear regression line obtained from their experimental data is not passing through the origin, indicating that the assumption of all the nickel solubility dissolved in the slag as Ni<sup>2+</sup> form is questionable. Dissolution of copper metal in lime-silica-alumina slag at 1798 K<sup>8</sup> and nickel metal in silica saturated and lime containing fayalite slags at 1573 K<sup>10</sup> has been reported earlier.

The corrected wt pct Ni<sup>2+</sup> in slag was used to calculate mole fraction of nickel oxide ( $X_{\text{NiO}}$ ). The corrected values are listed in Table I. Activity of NiO is plotted against mole fraction of NiO in slag in Figure 5. The value of  $\gamma_{\text{NiO}}^0$  from the slope of the best fit line to all the experimental data points was calculated to be 0.375. In the experimental range of 0 to 0.9 wt pct Ni in slag, the activity coefficient ( $\gamma_{\text{NiO}}^0$ ) is determined to be constant and independent of partial pressure of oxygen. This behavior is thermodynamically consistent because it indicates that Henry's law is valid for this range of dilute region of the slags.

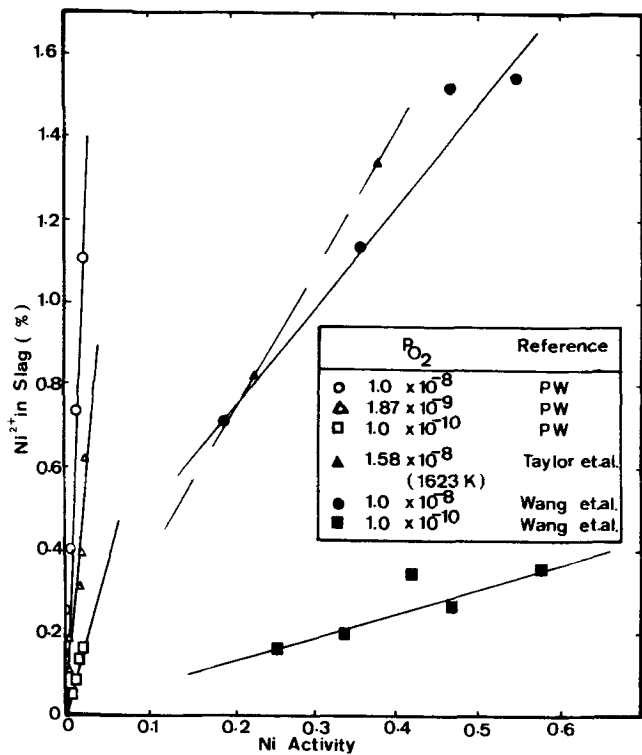


Fig. 4—Activity of nickel (relative to pure super-cooled liquid nickel) as a function of corrected nickel in slag.

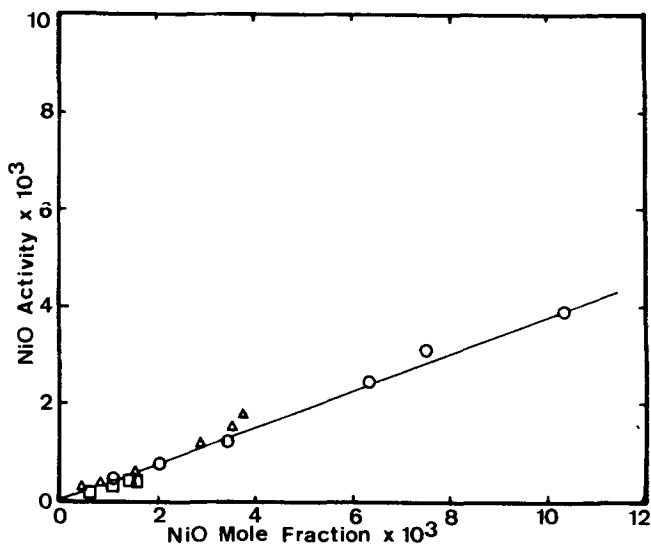


Fig. 5—Activity of nickel oxide (relative to pure super-cooled liquid nickel oxide) as a function of corrected mole fraction of nickel oxide in slag at 1573 K. Symbols are defined in Fig. 2.

As shown above, the NiO forms a dilute solution with the slag, and combining Eqs. [3] and [5] it can be shown that:

$$(\text{Wt pct Ni}^{2+} \text{ in slag}) = A a_{\text{NiO}(l)} \quad [10]$$

where  $A$  is the proportionality constant (*i.e.*, distribution coefficient).

In Figure 6, wt pct Ni<sup>2+</sup> in slag is plotted as a function of the  $a_{\text{NiO}(l)}$  in the slag for all the partial pressures of oxygen at 1573 K. It can be seen from the figure that the distribution coefficient is independent of the oxygen partial pressure. The value of  $A$  from the best fitted line through all the experimental data is calculated to be 233.3.

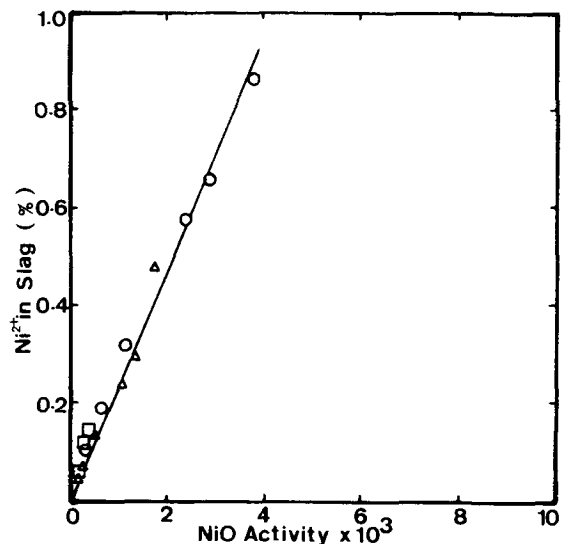


Fig. 6—Activity of nickel oxide (relative to pure super-cooled liquid nickel oxide) as a function of corrected nickel in slag at 1573 K.

Table II. Values of  $\gamma_{\text{NiO}}^0$  and  $A_{\text{Ni}}$  for Estimating Nickel Oxide Solubility in Iron Silicate Slags

Slag System	$\gamma_{\text{NiO}}^0$	$A_{\text{Ni}}$	Reference
<u>Alumina Saturated Slag</u>			
Fe/SiO <sub>2</sub> = 1.34	0.375	233.3	present work
1573 K, $P_{\text{O}_2} = 10^{-10}$ to $10^{-8}$ atm			
<u>Silica-Unsaturated Slag</u>			
Alumina Free			
$P_{\text{O}_2} = 10^{-5}$ to $10^{-10}$ atm	1.166	65.3	3
1673 K to 1723 K			
Fe/SiO <sub>2</sub> = 1.54	1.083	72.0	3
as above Fe/SiO <sub>2</sub> = 5.07			
<u>Silica Saturated Slag</u>			
Alumina Free			
1573 K			
$P_{\text{O}_2}: 10^{-8}$ atm	—	37.6	1
$P_{\text{O}_2}: 10^{-10}$ atm	—	64.3	1

The values of  $\gamma_{\text{NiO}}^0$  and  $A_{\text{Ni}}$  from the present study and along with other investigators<sup>1,3</sup> are presented in Table II. The higher distribution coefficient ( $A_{\text{Ni}}$ ) values and lower values of activity coefficient ( $\gamma_{\text{NiO}}^0$ ) indicate that presence of alumina increases the solubility of nickel in alumina saturated iron silicate slags.

#### IV. CONCLUSIONS

The solubility of up to 1 wt pct of nickel in alumina saturated fayalite slags in the range of oxygen partial pressure  $10^{-8}$  to  $10^{-10}$  atm at 1573 K shows that nickel dissolves in slag both as Ni<sup>2+</sup> (nickel oxide) and Ni<sup>0</sup> (nickel metal), and the relation obtained was

$$(\text{Wt pct Ni in slag}) = 2.083 \times 10^5 P_{\text{O}_2}^{1/2} a_{\text{Ni}(l)} + 2.334 a_{\text{Ni}(l)}$$

where  $a_{\text{Ni}(l)}$  is the activity of nickel relative to pure liquid nickel as standard state. The activity coefficient of nickel oxide in slags remains approximately constant at 0.375, and

is independent of oxygen partial pressure. The distribution coefficient  $A_{Ni} = (\text{wt pct Ni}^{2+} \text{ in slag})/a_{NiO(l)}$  is calculated to be 233.3, and is independent of oxygen partial pressure.

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