

Phase relations and activities in the Co-Ni-O system at 1373 K

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Abstract. The tie-lines delineating equilibria between CoO-NiO and Co-Ni solid solutions in the ternary Co-Ni-O system at 1373 K have been determined by electron microprobe and EDAX point count analysis of the oxide phase equilibrated with the alloy. The oxygen potentials corresponding to the tie-line compositions have been measured using a solid oxide galvanic cell with calcia-stabilized zirconia electrolyte and Ni + NiO reference electrode. Activities in the metallic and oxide solid solution have been derived using a new Gibbs-Duhem integration technique. Both phases exhibit small positive deviations from ideality; the values of G^E/X_1X_2 are 2640 J mol^{-1} for the metallic phase and 2870 J mol^{-1} for the oxide solid solution.

Keywords. Free energy of mixing; cobalt-nickel alloys; cobalt oxide-nickel oxide solid solution; oxygen potential; solid state cell; thermodynamic properties; phase diagram; electromotive force.

1. Introduction

Cobalt and nickel-based alloys are extensively used in high temperature applications. A knowledge of the oxygen potential and temperature for the oxidation of the alloy and the composition of the oxide phase is important for the design of oxidation-resistant alloys. Complex phase relations for commercial alloys can be projected with useful accuracy from a knowledge of the constituent binary and ternary systems. Phase relations in the ternary Co-Ni-O system have not been reported in the literature. Early literature on the Co-Ni binary system has been compiled by Hultgren *et al* (1973). More recently activities in the Co-Ni solid alloys have been measured by Vrestal and Kucera (1971) by the effusion method using isotopes of Co and Ni in the temperature range 1420 to 1600 K, and by Tomiska *et al* (1979) using Knudsen effusion mass spectrometry in the temperature range 1480 to 1875 K. Their investigations show negative deviations from Raoult's law.

Although a number of measurements have been reported in the literature for liquid Co-Ni alloys (Tomiska *et al* 1979; Maruyama and Ban-ya 1978; Tozaki *et al* 1973; Predel and Mohs 1970; Iguchi *et al* 1977; Tsemakhman *et al* 1971) the results are contradictory. Maruyama and Ban-ya (1978), Tozaki *et al* (1973), Predel and Mohs (1970), Iguchi *et al* (1977) report small positive deviations from Raoult's law, while Tomiska *et al* (1979) and Tsemakhman *et al* (1971) suggest mild negative deviations.

Activities in the system NiO-CoO have been evaluated by Torkar and Schneider (1976) for $0.34 < X_{\text{CoO}} < 0.87$ with a solid state electrochemical cell at 1000 and 1300 K using an approximate thermodynamic analysis. Their study indicates small positive deviation from Raoult's law.

In the present study, compositions of coexisting alloy and oxide phases in the Co-Ni-O system, and the equilibrium oxygen potentials corresponding to the tie-lines have been measured at 1373 K. A thermodynamic analysis of (M_1 - M_2 -O) ternary system is

developed which permits the derivation of activities of components in the alloy phase from tie-line compositions and oxygen potentials.

2. Experimental technique

2.1 Materials

Powders of Ni, Co, NiO and CoO of 99.99 + purity and particle size of the order of 100 μm were used. The oxide and metallic solid solutions were prepared by heating compacted pellets at 1573 K for 600 ks. The pellets, contained in alumina crucibles, were held under prepurified argon.

2.2 Apparatus and procedure

2.2a Tie-line determination: Powders of the oxide and metallic solid solution were intimately mixed in equimolar ratios and pelletized. The Co/Ni ratio of the starting solid solutions in each pellet was approximately equal. The pellets were placed in alumina crucibles, sealed under vacuum in silica capsules and heated at 1373 K for 600 ks. After equilibration the capsules were quenched in water. The material was ground, pelletized and heated for another 600 ks under identical conditions. The quenched pellets were then mounted for metallographic examination. The composition of the phases was determined by electron microprobe and energy dispersive x-ray analysis. Pure Co, Ni, NiO and CoO were used as standards. In all cases, atomic absorption and fluorescence effects were eliminated using computer-compensated adjustments. The composition profiles across the grains were found to be uniform and agreement between the two methods of compositional analysis was better than 1%.

2.2b Oxygen potential measurements: The equilibrium oxygen potential over each alloy/oxide pellet at 1373 K was measured using a solid-state electrochemical cell

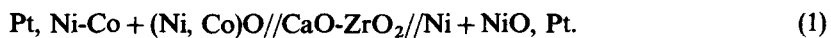


Table 1. Equilibrium compositions, EMF, partial pressures and activities at 1373 K for Co-Ni-O System

X_{Co}	X_{CoO}	EMF (mV)	$P_{\text{O}_2} \times 10^{-9}$ (atm)	a_{Co}	a_{Ni}	a_{CoO}	a_{NiO}
0.07	0.313	16.5	0.644	0.084	0.931	0.352	0.704
0.139	0.511	29.9	0.410	0.163	0.865	0.543	0.522
0.181	0.595	36.8	0.324	0.209	0.825	0.620	0.443
0.246	0.688	46.0	0.238	0.278	0.764	0.705	0.351
0.317	0.759	54.4	0.178	0.350	0.698	0.771	0.278
0.401	0.819	62.9	0.134	0.433	0.620	0.826	0.214
0.610	0.910	79.2	0.0773	0.630	0.423	0.912	0.111
0.738	0.946	87.1	0.0590	0.749	0.295	0.947	0.067
0.829	0.967	92.2	0.0496	0.834	0.198	0.967	0.041
0.892	0.980	95.6	0.0443	0.894	0.128	0.980	0.025
1.00	1.00	101.1	0.00396	1.0	0.0	1.0	0.0

The reference electrode consisted of an equimolar mixture of Ni and NiO. The working electrode consisting of metallic solid solution in equilibrium with the oxide solid solution was taken from the set of pellets prepared for tie-line determination. The details of the experimental set-up have been discussed earlier (Petric and Jacob 1982). Prepurified inert gas was passed over each electrode.

The emf of the cell was measured with a digital voltmeter with an internal impedance greater than $10^{12} \Omega$. The reversibility of the cell was checked by passing small currents in either direction through the cell. In each case the emf was found to return to the original value. The emf was found to be independent of the flow rate of argon over the electrodes. The time required to reach equilibrium was ≈ 4 ks at 1373 K. No attempt was made to measure the emf as a function of temperature since compositions are temperature dependent and compositional changes are diffusion controlled. Hence very long periods are required to obtain a stable emf at other temperatures.

3. Results

3.1 Tie-line study

The equilibrium composition of Co-Ni alloy and (Co Ni)O solid solution at 1373 K is given in table 1. Tie-lines representing the exchange reaction;



are shown in figure 1.

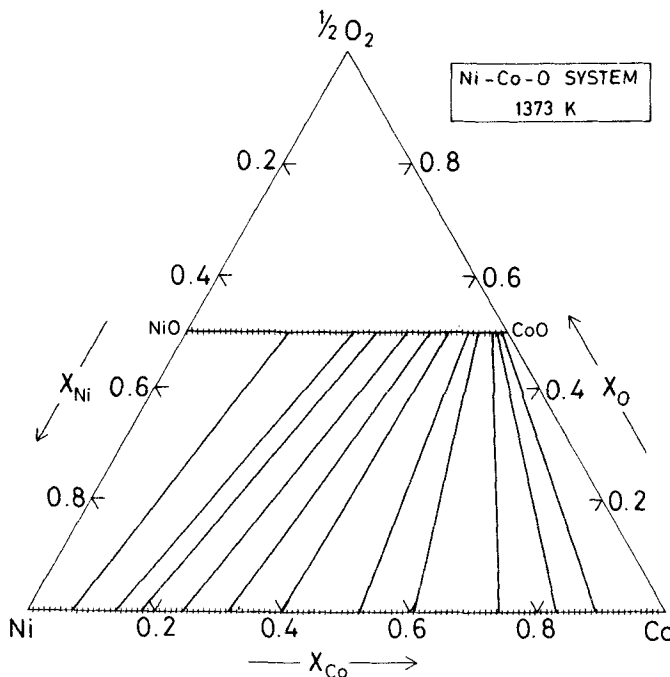


Figure 1. Phase diagram of the Co-Ni-O system showing the tie-lines between the metallic and rocksalt phases at 1373 K.

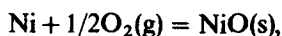
3.2 Emf study

The emf of cell 1 is related to the oxygen potential corresponding to the tie-lines. The emf values are summarized in table 1 and plotted in figure 2 as a function of composition of both the oxide and metallic solid solution phases.

The open circuit potential is expressed as

$$E = (RT/2F) \ln [p_{O_2(i)}^{1/2}/p_{O_2(ii)}^{1/2}], \quad (3)$$

where $p_{O_2(i)}$ and $p_{O_2(ii)}$ are the oxygen potentials at the right and left hand electrodes respectively, T the absolute temperature, F the Faraday constant and R the gas constant. The oxygen potential of the reference electrode is defined by (Steele 1968);



$$\Delta G^\circ = 1/2\Delta\mu_{O_2} = -234,160 + 84.89 T \text{ J mol}^{-1}. \quad (4)$$

The oxygen potential over the two phase alloy is deduced from the measured emf values using equation (3). The partial pressures are given in table 1 as a function of composition. The corresponding oxygen potential diagram at 1373 K is shown in figure 2. Topological rules that apply to the more common T - X phase diagrams are also valid for this chemical potential-composition ($\Delta\mu$ - X) diagram. The oxygen potentials for the oxidation of any Co-Ni alloy and the composition of the oxide phase can be readily obtained from this diagram. Similar diagrams at other temperatures can be easily constructed from the thermodynamic information obtained in this study.

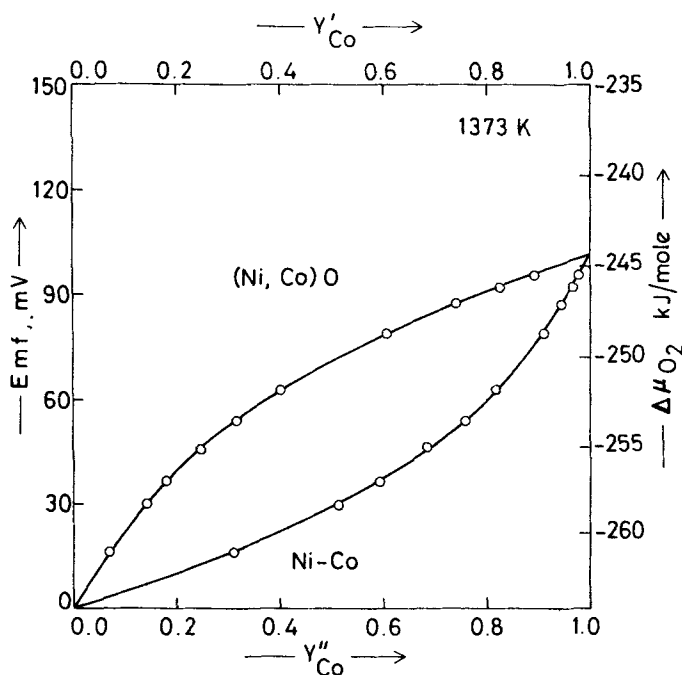


Figure 2. Emf and oxygen potential—composition diagram for the Co-Ni-O system at 1373 K

3.3 Thermodynamic analysis

In thermodynamic analysis of ternary systems involving a nonmetallic component, it is convenient to introduce composition variables, Y_i defined as:

$$Y_{\text{Co}} = n_{\text{Co}}/n_{\text{Ni}} + n_{\text{Co}}; Y_{\text{Ni}} = n_{\text{Ni}}/n_{\text{Ni}} + n_{\text{Co}}; Y_{\text{O}} = n_{\text{O}}/n_{\text{Ni}} + n_{\text{Co}},$$

where n_i is the number of moles of component i . It follows from the above that $Y_{\text{Ni}} = 1 - Y_{\text{Co}}$. The parameter Y_{O} represents the ratio of nonmetallic (anionic) to the metallic (cationic) component in a given phase.

By dividing each term in the general Gibbs–Duhem equation,

$$\sum n_i d \ln a_i = 0 \quad (4)$$

by $(n_{\text{Ni}} + n_{\text{Co}})$, one obtains,

$$\sum Y_i d \ln a_i = 0. \quad (5)$$

Since activities are constant along tie-lines, the Gibbs–Duhem relation in the two-phase region of the ternary Co-Ni-O system may be written as,

$$Y'_{\text{Co}} d \ln a_{\text{Co}} + (1 - Y'_{\text{Co}}) d \ln a_{\text{Ni}} + Y'_{\text{O}} d \ln p_{\text{O}_2}^{1/2} = 0, \quad (6)$$

$$Y''_{\text{Co}} d \ln a_{\text{Co}} + (1 - Y''_{\text{Co}}) d \ln a_{\text{Ni}} + Y''_{\text{O}} d \ln p_{\text{O}_2}^{1/2} = 0, \quad (7)$$

where (') denotes the oxide phase and (") represents the alloy. Subtracting (7) from (6),

$$(Y'_{\text{Co}} - Y''_{\text{Co}}) d \ln a_{\text{Co}} + (Y'_{\text{Co}} - Y''_{\text{Co}}) d \ln a_{\text{Ni}} + (Y'_{\text{O}} - Y''_{\text{O}}) d \ln p_{\text{O}_2}^{1/2} = 0, \quad (8)$$

or

$$(Y'_{\text{Co}} - Y''_{\text{Co}}) d \ln (a_{\text{Co}}/a_{\text{Ni}}) + (Y'_{\text{O}} - Y''_{\text{O}}) d \ln p_{\text{O}_2}^{1/2} = 0. \quad (9)$$

Therefore,

$$d \ln (a_{\text{Ni}}/a_{\text{Co}}) = \frac{(Y'_{\text{O}} - Y''_{\text{O}})}{(Y'_{\text{Co}} - Y''_{\text{Co}})} d \ln p_{\text{O}_2}^{1/2}. \quad (10)$$

Because of the negligible solid solubility of oxygen in Co-Ni alloys, Y'_{O} can be considered to be zero, and Y'_{O} is approximately unity for the oxide phase. At an oxygen pressure of 1 atm and 1373 K, the nonstoichiometry parameter y has values of 8×10^{-3} for Co_{1-y}O and 2×10^{-3} for Ni_{1-y}O (Kofstad 1972). Equation (10) then simplifies to,

$$d \ln (a_{\text{Ni}}/a_{\text{Co}}) = \frac{1}{Y'_{\text{Co}} - Y''_{\text{Co}}} d \ln p_{\text{O}_2}^{1/2}. \quad (11)$$

It has been shown earlier (Jacob and Jeffes 1972) that activity of any component in a binary or pseudobinary system can be deduced from the composition dependence of activity ratio. For the Co-Ni binary this relation is

$$\ln a_{\text{Ni}} = \int_1^{Y_{\text{Ni}}} Y''_{\text{Co}} d \ln (a_{\text{Ni}}/a_{\text{Co}}). \quad (12)$$

Combining (11) and (12),

$$\ln a_{\text{Ni}} = \int_{p_{\text{O}_2(\text{Ni} + \text{NiO})}}^{p_{\text{O}_2}} \frac{Y''_{\text{Co}}}{2(Y'_{\text{Co}} - Y''_{\text{Co}})} d \ln p_{\text{O}_2}. \quad (13)$$

The same result can also be derived by equating the third term in (7) to zero, and then

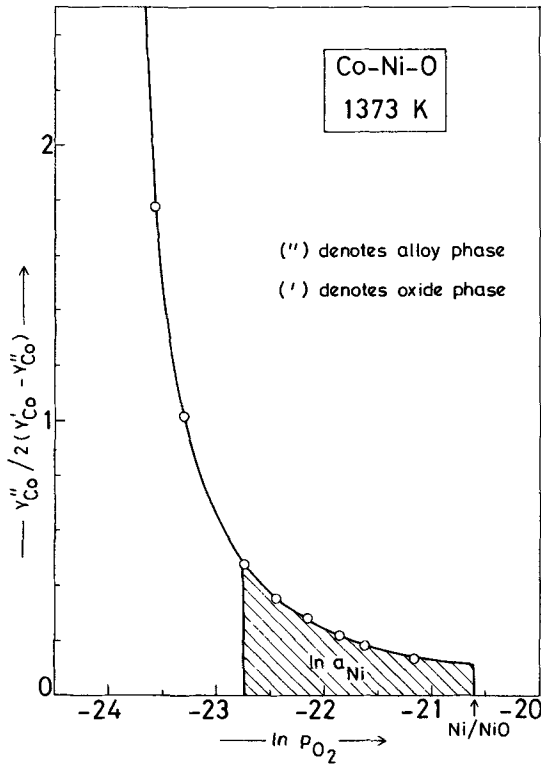


Figure 3. Gibbs-Duhem integration plot for the Co-Ni binary alloy.

combining (6) and (7) with algebraic rearrangement. A similar equation can be written for the activity of cobalt.

$$\ln a_{\text{Co}} = \int_{p_{\text{O}_2(\text{Co} + \text{CoO})}^{p_{\text{O}_2}} \frac{Y''_{\text{Ni}}}{2(Y'_{\text{Ni}} - Y''_{\text{Ni}})} d \ln p_{\text{O}_2}. \quad (14)$$

3.4 Activities in metal and oxide solid solutions

From the partial pressures obtained through emf study, the activity of Ni and Co were deduced using (13) and (14). The integration plot for evaluating the activity of Ni is shown in figure 3. It is important to note that $Y''_{\text{Co}}/2(Y'_{\text{Co}} - Y''_{\text{Co}})$ does not go to zero at $Y_{\text{Ni}} \rightarrow 1$. The corresponding activities of the oxide components were calculated from the activities of Co and Ni, the partial pressure of oxygen and the standard free energies of formation of CoO and NiO available in the literature (Steele 1968; Jacob and Pandit 1985). The activities of the oxide components and the metallic components in the oxide and metallic solid solution phases at the tie-line compositions are listed in table 1.

4. Discussion

The thermodynamic properties of Co-Ni and CoO-NiO solid solutions obtained in this

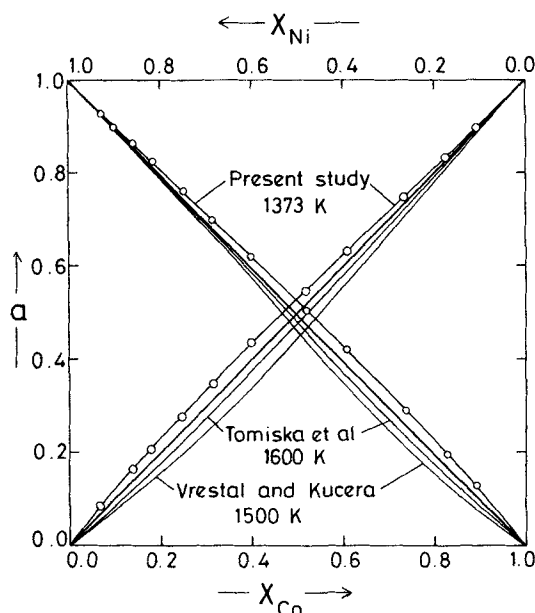


Figure 4. Activity-composition relationship in the Co-Ni binary alloy.

study at 1373 K can be expressed by,

$$G_{\text{Ni-Co}}^E = 2460 X_{\text{Ni}} X_{\text{Co}} \text{ J mol}^{-1}, \quad (15)$$

$$G_{\text{NiO-CoO}}^E = 2870 X_{\text{NiO}} X_{\text{CoO}} \text{ J mol}^{-1}. \quad (16)$$

The activities of components obtained in this study are compared with the data reported by Vrestal and Kucera (1971) and Tomiska *et al* (1979) in figure 4. The present results indicate a slight positive deviation from Raoult's law in contrast to the negative deviation suggested by Vrestal and Kucera (1971) and Tomiska *et al* (1979). The measurements of Vrestal and Kucera (1971) are based on the Knudsen effusion technique using molybdenum cells. Phase diagrams for Co-Mo and Ni-Mo systems show stable intermetallic compounds at the experimental temperature. Formation of these intermetallics by reaction between the vapour species and molybdenum could have interfered with the attainment of equilibrium inside the Knudsen cell. Further Vrestal and Kucera (1971) have not demonstrated the absence of surface depletion in their samples by measuring vapour pressure as a function of orifice diameter. Tomiska *et al* (1979) have used a Knudsen effusion mass spectrometric technique for activity measurements and their results can be approximated by $G^E/X_{\text{Ni}}X_{\text{Co}} = -2012 \text{ J mol}^{-1}$ at 1600 K. The authors (Tomiska *et al* 1979) have not discussed possible surface depletion of the volatile component during their measurements.

The activity-composition relationship for the rocksalt solid solution is shown in figure 5 along with the data of Torkar and Schneider (1976) who estimated the composition of this alloy phase by making a number of assumptions including unit activity coefficients for the alloy. They have estimated the values of $G^E/X_{\text{CoO}}X_{\text{NiO}}$ equal to $4500 (\pm 1200) \text{ J mol}^{-1}$ at 1000 K and $2300 (\pm 1600) \text{ J mol}^{-1}$ at 1300 K. When extrapolated to 1373 K, results of Torkar and Schneider (1976) yield $G^E/X_{\text{CoO}}X_{\text{NiO}}$

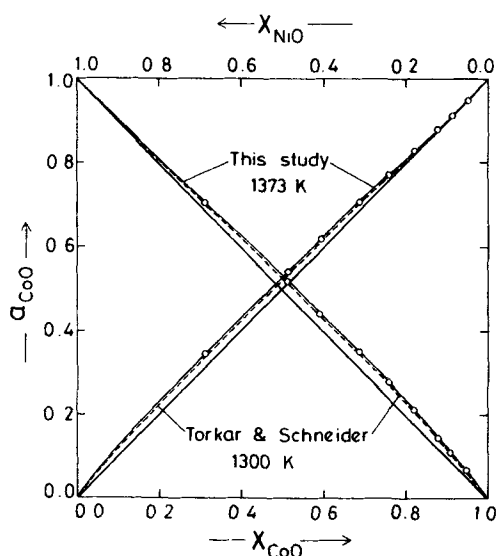


Figure 5. Activities for NiO and CoO in the rocksalt solid solution.

equal to 1770 J mol^{-1} which compares with a value of $2870 (\pm 500) \text{ J mol}^{-1}$ obtained in this study. Since the derivation of thermodynamic data reported in this study is rigorous, and free from simplifying assumptions, the data obtained in this study is considered to be more reliable than that reported earlier. Positive deviations in the oxide solid solution arise from the small size difference between Co^{2+} and Ni^{2+} ions. The ionic radii of Co^{2+} and Ni^{2+} in low spin state are 0.79 and 0.84 Å respectively (Shannon and Prewitt 1969, 1970).

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