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Thermodynamic Properties of Solid Rhodium–Nickel Alloys

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The thermodynamic properties of the solid solutions formed by rhodium and nickel were investigated between 1100 and 1400K, using oxygen concentration cells with a ZrO_2–CaO solid electrolyte. The activities of nickel show positive deviations from Raoult's law in the rhodium-rich alloys and small negative deviations in the nickel-rich alloys. The integral enthalpy of mixing and the excess integral entropy of mixing are positive. The thermodynamic data indicate that a miscibility gap may be expected at low temperatures.

Die thermodynamischen Eigenschaften der festen Rhodium–Nickel Legierungen wurden mit Hilfe von Sauerstoffkonzentrations-zellen mit einem festen ZrO_2–CaO Elektrolyt zwischen 1100 und 1400K untersucht. Die Aktivitäten des Nickels im Bereich der rhodiumreichen Legierungen zeigen positive Abweichungen vom Raoult'schen Gesetz. Im Bereich der nickelreichen Legierungen liegen dagegen negative Abweichungen vom Raoult'schen Gesetz vor. Die integrale Mischungsenthalpie und die integrale Exzeßentropie erweisen sich als positiv. Die thermodynamischen Daten deuten darauf hin, daß bei niedrigeren Temperaturen eine Mischungslücke vorliegen könnte.

Introduction

In the binary alloys which are formed by nickel with the noble metals (gold–nickel (*1, 2*), platinum–nickel (*3*), copper–nickel (*4, 5*)) there exist complete ranges of solid solutions at high temperatures which have the face-centered cubic structure.

But in some ranges of composition there are low-temperature transformations of the order–disorder type, e.g., platinum–nickel (*6*) and a miscibility gap in the system gold–nickel (*7*). The thermodynamic properties of these alloy systems have been investigated (*1–5*) and the information one can get from them corresponds excellently with the investigated low-temperature transformations.

There has not been, however, a thermodynamic investigation of the system rhodium–nickel so far.

The rhodium–nickel system has a particularly simple phase diagram with complete solid solubility (*8*).

There have also been investigations (*9, 10*) which presume the existence of an order–disorder transformation of the Cu_3Au type. Therefore it seemed worthwhile to determine the thermodynamic properties of the rhodium–nickel alloys. With this information it should be possible to decide whether there is a preference for order–disorder transformations or for a miscibility gap.

In this investigation, a galvanic solid-state cell using a solid (0.85 ZrO_2 + 0.15

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CaO) electrolyte was used for the determination of the thermodynamic activities of components in solid alloys at high temperatures. It was our aim to measure the activities to temperatures as low as possible.

The Cell

The method of the galvanic solid-state cell is based on a technique introduced by Kiukkola and Wagner (*11, 12*). In order to determine the activity of nickel in rhodium–nickel alloys, the following cell was used:

$$\text{I Pt/Ni,NiO/}(0.85\ \mathrm{ZrO_2} + 0.15\ \mathrm{CaO})/\mathrm{Ni}_x\mathrm{Rh}_{1-x}\mathrm{,NiO/Ni/Pt.}$$

The nickel foil on the right side of the cell reduced the possibility of change in alloy composition by preferential diffusion of either compound into the platinum contact. The nickel foil played no part in the cell reaction. The cell reaction Ni → Ni (solid solution) gives a direct measurement of the activity of nickel in the alloys as

$$\ln a_{\mathrm{Ni}} = -\frac{2 \cdot F \cdot E}{R \cdot T}, \qquad (1)$$

where a_{Ni} is the actvity of nickel in the alloy, F is Faraday's constant, E is the measured electromotive force, R is the gas constant, and T the absolute temperature.

Experimental Methods

The electrolyte tablets ($0.85\ \mathrm{ZrO_2} + 0.15\ \mathrm{CaO}$) were delivered from Corning Glass Inc.

For the alloy preparation rhodium powder (99.9%) and nickel powder (99.99%) from Goodfellow Metals were used. Weighed amounts of each were mixed in an agate mortar and pressed to tablets. The alloys were vacuum melted in a high-temperature furnace at temperatures higher than 1900K. In every case the loss in weight was negligible, so that the final composition was taken to be the same as that initially weighed out.

After cold working, the ingots were sealed in evacuated fused quartz capsules, homogenized for more than 2 weeks at a temperature of 1400K, and rapidly quenched. Nickel oxide was prepared from $\mathrm{Ni(NO_3)_2 \cdot 6H_2O}$ by thermal decomposition at a temperature of 1450K.

The resulting powder was heated in air for 2 days and ground several times. The alloy powders were made with a dental drill. The tablets for the cell were pressed from mixtures of nickel or alloy powder and NiO powder in the ratio 2:1.

Before use, the nickel oxide was annealed in purified helium at about 1200K for 1 day to remove excess oxygen which would be able to change the alloy composition by the oxidation of nickel in the alloy. The alloy–NiO tablets were equilibrated in evacuated fused quartz capsules at a temperature of 1400K for 1 day before they were used in the galvanic cell.

There are references (e.g., *13*) to the need for "closed cell design" involving two hermetically sealed half-cell compartments to prevent oxygen transfer, via the gas phase, between the electrode compartments. But cell I for the investigation of the rhodium–nickel alloys could be realized by the simple cell construction of Kiukkola and Wagner (*11, 12*), as shown by Sellars and Maak (*1*) and by Rapp and Maak (*4*).

The electromotive forces were measured with a quartz apparatus similar to that reported by Schmalzried (*14*).

The three 0.6-cm-diameter and 0.2-cm-thick tablets of the cell were pressed together between two platinum disks connected with platinum leads. This quartz apparatus was placed into a quartz tube long enough to displace the furnace. This enabled the attainment of a steady temperature within some minutes after the start.

The quartz tube was evacuated before

each run. Purified helium, which had been freed of water and oxygen (Oxisorb/Messer Griesheim and a liquid nitrogen trap) was used as a flowing inert gas atmosphere.

The temperature of the cell was measured with a calibrated Pt/Pt–10% Rh thermocouple. The electromotive force of the cell was measured with a Keithley 172 digital voltmeter. Before the measurements with the rhodium–nickel alloy + nickel-oxide tablets were begun, the experimental apparatus and the pure ionic conduction of the electrolyte were tested using the mixed oxide cell II.

II Pt/Ni,NiO/(0.85 ZrO_2 + 0.15 CaO)/Co,CoO/Pt.

The measured electromotive force for this calibration cell II was 82.75 mV at a temperature of 1150K, in agreement with the value of 83.59 mV from the data of Torkar and Schneider (*15*). The influence of the cell atmosphere as a function of gas flow rate was checked by making measurements with cell I and cell II. There was, however, no influence detectable. Usually a time of less than 5 hr was needed for the electromotive force to reach steady values. After the measurement at 1400K, the temperature of the furnace was lowered stepwise to 900K. On subsequent changes of temperature the new equilibrium electromotive force was attained after times identical with those required for temperature equilibrium.

The achievement of thermodynamic equilibrium was demonstrated by passing a small current (microamperes) for some minutes through the cell and then, when a steady emf value was regained, to repeat the passage of current in the reverse direction. X-Ray diffraction measurements were made using a Philips proportional counter diffractometer with nickel-filtered Cu$K\alpha$ radiation. All samples were investigated before and after the emf experiment and showed no difference. Precise lattice constants were determined for all rhodium–nickel alloys and are shown in Table I.

TABLE I

LATTICE CONSTANTS OF THE RHODIUM–NICKEL ALLOYS

x_{Ni}	a (pm)
0.000	380.31
0.163	376.71
0.305	373.66
0.404	371.08
0.506	368.45
0.600	365.72
0.754	361.10
0.901	356.29
1.000	352.38

The lattice constants of the rhodium–nickel alloys show large positive deviations from Vegard's law.

The lattice constants of this investigation agree perfectly with the data of Raub and Röschel (*8*) and with that of Luo and Duwez (*10*) (Fig. 1).

Results and Discussion

The measurements were confined in the

TABLE II

EXPERIMENTAL DATA ON SOLID RHODIUM–NICKEL ALLOYS

x_{Ni}	Temperature range (K)	A (mV K^{-1}) · 10^2	B (mV)
0.163	1100–1530	12.12	−70.27
0.305	970–1530	7.708	−35.38
0.404	900–1530	5.112	−14.44
0.506	870–1530	3.503	−4.552
0.600	900–1530	2.928	−7.630
0.754	870–1530	1.451	−1.571
0.901	870–1530	0.436	0.1574

Note. The least-squares lines were calculated in the form $E = A \cdot T + B$.

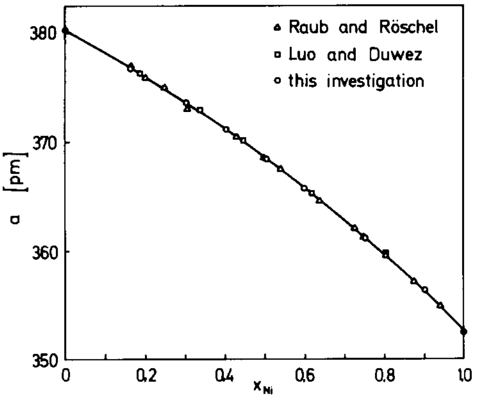

FIG. 1. Lattice constants of the system rhodium–nickel.

range of x_{Ni} from 0.163 to 0.901 and in the temperature range from 870 to 1530K. The electromotive forces show linear dependence on temperature. The least-squares lines for the emf vs temperature relations at each composition are presented in Table II.

The electromotive forces of the rhodium-rich alloys could not be measured at lower temperatures. Although meaningful emf readings could be obtained at these temperatures with the nickel-rich alloys, the values of the rhodium-rich alloys fluctuated with time at constant temperature and did not give the same result during heating and cooling of the galvanic solid-state cell. All those data were discarded.

From the measured electromotive forces of the cell the activities of nickel, a_{Ni}, were calculated according to Eq. (1) and are plotted in Fig. 2.

When the activities of nickel are known, then the activity coefficients for rhodium, f_{Rh}, with pure rhodium as the standard state, may be calculated from a Gibbs–Duhem integration (*16*) according to the expression

$$\ln f_{Rh} = -\frac{x_{Ni}\ln f_{Ni}}{1-x_{Ni}} + \int_0^{x_{Ni}} \frac{\ln f_{Ni}}{(1-x_{Ni})^2}\,dx_{Ni}. \quad (2)$$

The function $\ln f_{Ni}/(1-x_{Ni})^2 = \alpha_{Ni}$ plotted against x_{Ni} (Fig. 3) was used to evaluate graphically the integrals.

The simple phase diagram suggests a simple α function. Therefore the function was extrapolated as shown by the broken lines. Experimentally, the composition range of the nickel-rich alloys is susceptible to systematic errors, which are negligible at lower nickel contents. This resulted in larger scatter of the data at the nickel-rich side of the phase diagram.

The activities of rhodium, a_{Rh}, obtained from integration of these functions are also plotted in Fig. 2.

It can be seen that the activities of nickel change from high positive to small negative deviations from Raoult's law. The activities of rhodium, however, show small positive deviations from Raoult's law.

The temperature dependence is larger on the rhodium-rich side.

Nickel, cobalt, and iron alloys with platinum and palladium (*3, 17, 18*) also show such a change of activities, but in the reverse direction. Comparing the small negative deviation on the nickel-rich side ($x_{Ni} > 0.45$) with that in the system Pd–Ni (*3*), it can be presumed that there is also no order-

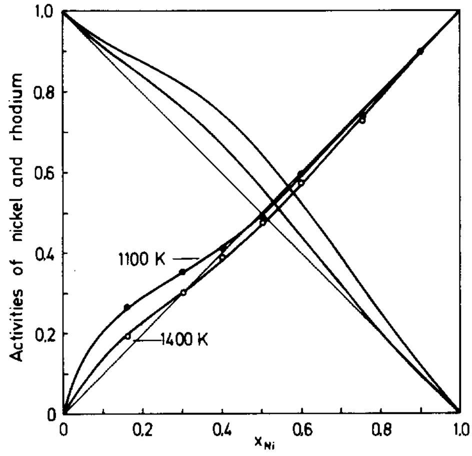

FIG. 2. Activities of nickel and rhodium at 1100 and 1400K.

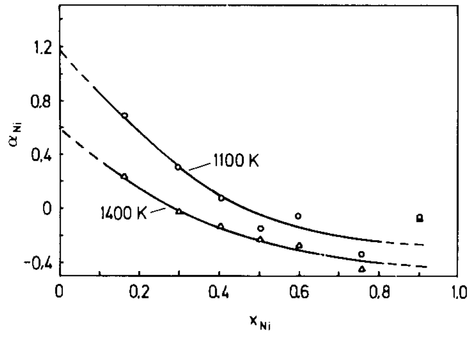

FIG. 3. α function for nickel in rhodium–nickel alloys.

ing at lower temperatures. There must be considerably larger negative deviations to result in ordering at lower temperatures. This was shown for the systems nickel–platinum (*3*) and iron–platinum (*17*). The positive deviation from ideality at lower nickel concentrations shows that there is a tendency for unmixing in these concentration ranges. This tendency for unmixing is seen to be considerably larger at lower temperatures. The present activity–composition data indicate that a miscibility gap may be expected to exist in the system rhodium–nickel at temperatures below those of the present investigation.

The excess integral molar entropy of mixing, ΔS_M^E, determined from the slopes of the measured potential-temperature curves, is shown in Fig. 4. The excess entropy at 1400K is positive and asymmetric with a maximum value at $x_{Ni} = 0.42$. At a composition of $x_{Ni} = 0.500$, ΔS_M^E is 2.61 J mole^{-1} K^{-1}.

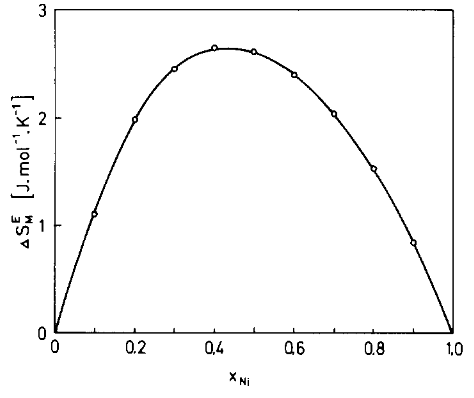

FIG. 4. Excess integral entropy of mixing at 1400K.

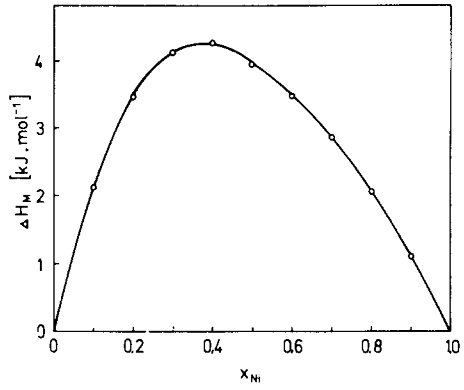

FIG. 5. Integral enthalpy of mixing of rhodium–nickel alloys at 1400K.

Although the derivation of the integral molar enthalpy of mixing, ΔH_M, from emf measurements is not the most advantageous method, the integral enthalpies of mixing were calculated and are presented in Fig. 5.

The integral enthalpy of mixing is also positive and asymmetric with a maximum at about $x_{Ni} = 0.400$.

The major factor to be considered for the large positive entropies and enthalpies of mixing is the considerable atomic size difference of the two pure metals. The size difference causes a "loosening" of the lattice, as evidenced by the large positive deviation of the lattice parameters from Vegard's law. This is in agreement with other systems with positive deviations from Raoult's law and Vegard's law, such as gold–nickel (*1*, *2*).

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