Vapor Pressure and Thermodynamic Study of the Co-Ni System

J. VÁŠTAL and J. KUČERA

Cobalt and nickel evaporation rates between 1420° and 1600°K were measured by the effusion method in six Co-Ni alloys covering the whole concentration range. The partial thermodynamic functions in the Co-Ni system for nickel and cobalt were obtained by processing data simultaneously for both the components so that the Duhem-Margules equation was fulfilled. The investigated system shows slight negative deviations from Raoult's law.

In our previous paper we have reported thermodynamic functions in the Co-Ni system by the isotope exchange method. The partial thermodynamic functions for cobalt were measured directly, whereas the values for nickel were calculated by integrating the Gibbs-Duhem equation. The results showed that negative deviations from Raoult’s law prevail in the Co-Ni system. An attempt was made to interpret these results in terms of ordering processes in the Co-Ni system using the Birchannell model. In this system short-range order can be assumed according to the Puzey and Goman’kov measurements of the magnetic anisotropy constant. On the other hand, however, neutron diffraction did not indicate the existence of a long- or short-range order, and thus the question of ordering processes near the Ni-Co composition remains open. With regard to the complications connected with the isotope exchange method, the temperature dependence of the cobalt vapor pressure was determined from a small number of points only and therefore the accuracy of the vapor pressure values evaluated in the previous paper was not too high (from 30 to 55 pct—see Ref. 1, Table II).

In this work, we have performed a new series of measurements of cobalt vapor pressure by the effusion method to achieve more accurate values and to verify the reproducibility of the results obtained by both methods. Further, we have carried out another series of measurements for the second component (nickel) of the Ni-Co system by the effusion method in order to avoid the inaccuracies caused by integrating the Gibbs-Duhem equation.

EXPERIMENTAL

The evaporation rate was measured for pure cobalt, pure nickel and the Co-Ni alloys which were kindly provided by the Centre National de Recherches Métallurgiques Liege, Belgium. The compositions of the alloys are given in Table I. The cobalt used in these alloys contained the following impurities: 0.016 wt pct Fe, 0.014 wt pct Cu, 0.01 wt pct Mn. Other elements were present in much lower concentrations. Nickel used for the preparation of sample No. 70 contained iron and silicon as impurities in an amount less than 0.01 wt pct (Mond Nickel Co.).

In this work the measurements were carried out by the effusion method described in detail in our previous paper. During the measurement by this method a thin sample (~50 μm thick) was placed in a sintered alumina crucible 11 mm high and 8 mm in diam. The crucible was enclosed by a 0.1 mm molybdenum foil with a cylindrical orifice 0.6 mm in diam. The crucible was held in a molybdenum cell (32 mm high and 28 mm OD) heated by a high frequency generator. The quantity of vapor which passed through the effusion aperture in a certain time interval at a constant temperature was determined by making radioactivity measurements on metal condensates from water-cooled copper targets. For cobalt vapor pressure measurements the isotope 60Co was used and the samples were prepared by the irradiating of fragments of alloys, 5 to 10 mg, in the nuclear reactor of the Institute of Nuclear Research of the Czechoslovak Academy of Sciences. Their activity was measured with the help of a scintillation γ-detector connected with the amplitude analyzer which enabled the selective recording of pulses in the energy range 1.0 to 1.4 mev. Corrections with respect to the decay of 60Co and to the instability of the electronic part of the device were performed using standard samples.

For measurements of nickel vapor pressure the isotope 63Ni was used and the samples were prepared as follows: a layer containing 63Ni was electrolytically deposited from the 3 pct solution of H3BO3 on nickel foils or Co-Ni alloy foils, respectively—Nos. 65 to 69, Table I. Each foil with the 63Ni layer was placed between other foils of the same material and remelted by high-frequency heating. The resulting chemical

<table>
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<th>Table I. Composition of the Samples During Measurements</th>
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<td>No. of Sample</td>
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<td>61</td>
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composition of the samples after the remelting, quoted in Table II (Nos. 71 to 75), was calculated from the bulk of foils and of the deposited nickel layer. After rolling the fragments, the remelting was repeated in order to achieve a homogeneous distribution of the isotope in samples. The specific activity of each fragment was determined as follows: the fragment was dissolved in a drop of 5N-HNO₃ in a volumetric flask, and a thin layer of this solution was deposited on a copper target (identical with targets used for vapor condensation in the Knudsen device), weighed, and evaporated. The β-activity of ⁶⁰Ni in the deposited layer was measured with the Geiger-Müller tube having an aperture thickness of 1.48 mg per sq cm.

The size of the aperture in the molybdenum cover of the effusion container was determined by a planimeter analysis of the photograph of the aperture made with a metallographic microscope at a known magnification. The temperature in the effusion container heated by the high-frequency generator was measured by a Pt/Pt-Rh thermocouple calibrated in situ to the melting points of Ag, Au, Cu, and Ni of at least 99.99 pct purity. In the course of measurements, the temperature was kept at a constant value ±3°C by an automatic controller. The effect of temperature variation was eliminated with the help of a photographic record of the temperature during the measurements. The values of cobalt and nickel vapor pressure measured with the use of ⁶⁰Co and ⁶³Ni isotopes were corrected to the molecular mass of cobalt and nickel corresponding to the natural isotopic mixture.⁸

RESULTS AND ANALYSIS

The evaporation rates of cobalt and nickel by the effusion method were measured in the temperature range 1420°C to 1600°C. The checking of specific activity of the samples before and after the measurements proved that the composition of alloys changed during the anneals (cobalt depletion), very probably due to the reaction of cobalt vapor with the sintered alumina evaporation container in which the samples were deposited during the anneal. The evaporation rate w was calculated from the experimental data with the use of the initial specific activity of the alloy and the vapor pressure, p, was determined from the relation

\[ p = w \sqrt{\frac{2\pi RT}{M}} \]  

where \( R \) is the gas constant, \( M \) the molecular mass of vapor and \( T \) the absolute temperature. The vapor pressure related to the initial composition of each alloy, Table I, satisfied the linear dependence, Fig. 1.

\[ \log p = A \cdot \frac{10^4}{T} + B \]  

where \( A \) and \( B \) are constants.

By checking the activity of the samples Nos. 66 and 68 as a function of annealing time it was found that the cobalt content in the samples decreased approximately linearly with time, Fig. 2, because of the reaction of cobalt with the sintered alumina container. The microprobe measurements on foils with 50.7 at. pct Co not annealed and annealed at 1570°C for 12 hr proved that the cobalt component remained approximately uniform across the samples during the course of anneal, Fig. 3. From this it follows that the straight lines in Fig. 1 represent somewhat lower cobalt concentrations, which could be found from the initial and final cobalt concentrations in the samples as their average values given in Table I. The vapor pressures given in Fig. 1 were considered as functions of two variables, i.e. the temperature and the average chemical composition, \( \log p_{Co} = f(1/T, x_{Co}) \). From these

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**Fig. 1**—Temperature dependence of cobalt vapor pressure for different Co-Ni alloy compositions (a part of the total plot).  
-●●● = alloy No. 61;  
-■■■ = alloy No. 65;  
-△△△ = alloy No. 66;  
-××× = alloy No. 68;  
-○○○ = alloy No. 69.

**Fig. 2**—Cobalt content in samples Nos. 66 and 68 as a function of annealing time.