

Thermodynamics of Aluminium-Nickel Alloys

N C OFORKA

Department of Applied Chemistry, University of Port Harcourt, Port Harcourt, Nigeria

Received 14 October 1985; revised and accepted 29 April 1986

Activity measurements have been made with a Knudsen cell mass spectrometer on aluminium-nickel alloys over the temperature range 1173-1483 K. The activities of aluminium and nickel at the entire composition range show pronounced negative deviation from ideality at 1423 K. The properties $\Delta\bar{G}_{Al}$, $\Delta\bar{G}_{Ni}$, $\Delta\bar{G}_{Al}^{ex}$, $\Delta\bar{G}_{Ni}^{ex}$, ΔG and ΔG^{ex} have been calculated using the experimental data.

There are few publications in recent literature on the thermodynamic properties of aluminium-nickel alloys. The thermodynamic properties so far investigated are: heats of formation¹, molar enthalpy of formation², activity data of aluminium in aluminium-nickel alloys^{3,5}, partial molar free energy of mixing by emf technique⁴ integral molar free energy of mixing⁶ etc. Schaeffer⁷ carried out the most exhaustive work on the aluminium-nickel system and with the help of a high temperature galvanic cell, obtained activity data for the entire range of the aluminium-nickel phase diagram at 1273 K. His activity data at 1273 K differed from those of the previous workers, and the assessment of Kaufman and Nesor⁸.

The present work re-investigates the thermodynamic properties of the aluminium-nickel alloys by the Knudsen cell mass spectrometric technique and compares the results with selected literature data.

Materials and Methods

Experimental methods used were generally the same as described in the papers published by Moore *et al.*⁹, Argent *et al.*^{10,11} and Oforka¹². Fine turnings or crushed samples of alloys were taken in an alumina cell sealed with an orifice plate (diameter of orifice ~0.35 mm). Clausing factors reported by Freeman and Edwards¹³ were used to convert ion intensities into those expected from an orifice of standard geometry. The temperature stabilities of the specimens were ± 0.5 K over 30 minutes at 1423 K and the absolute accuracy of the temperature was ± 2 K as determined by melting point determinations on nickel and iron. An argon reference was used to correct for day-to-day variations in instrumental sensitivity.

Results and Discussion

The measurement of the partial pressure (P_i) of a component i of an alloy and that (P_i^0), of the pure component, leads to the determination of the activity

(a_i) of component i as the ratio of the two partial pressures (Eq. 1).

$$a_i = P_i/P_i^0 \quad \dots (1)$$

In the Knudsen cell mass spectrometric technique, the partial pressure of the species is related to the intensity of the species by Eq. (2).

$$P_i = K \cdot I_i^+ \cdot T \quad \dots (2)$$

where K is a constant and contains all instrumental and geometrical factors, I_i^+ is the intensity of the species i (counts per second) and T is the absolute temperature at which the measurement is made. The measurements were repeated at various temperatures and the results of least-squares fits to standardised intensities in the form of Eq. (3) were used to calculate intensities at 1423 K.

$$\ln(I/T) = A + B/T \quad \dots (3)$$

In Eq. (3) I is the intensity, T is the absolute temperature and A and B are constants. The ratio of the intensity of a species in an alloy to that in pure standard gives the activity of that species. The standards used were pure solid nickel and liquid aluminium. The activities determined were treated to get partial and excess partial molar quantities. The partial molar free energy change for the species i when dissolved in a solvent is given by Eq. (4).

$$\Delta\bar{G}_i = RT \ln a_i \quad \dots (4)$$

where R is the gas constant, T is the absolute temperature and a_i is the activity of the component. The deviation of a partial quantity from its value in an ideal solution is the excess partial quantity and is given by Eq. (5).

$$\begin{aligned} \Delta\bar{G}_i^{ex} &= \Delta\bar{G}_i - \Delta\bar{G}_i^{id} \\ &= RT \ln a_i - RT \ln X_i = RT \ln \gamma_i \quad \dots (5) \end{aligned}$$

where $\Delta\bar{G}_i^{ex}$ is the excess partial free energy of mixing, $\Delta\bar{G}_i^{id}$ is the ideal partial free energy of mixing, γ_i is the activity coefficient of i ($=a_i/X_i$) and X_i is the

Table 1—Composition Dependence of Partial and Integral Molar Quantities of Solid Aluminium-Nickel Alloys at 1423 K

X_{Ni}	a_{Ni}	a_{Al}	γ_{Ni}	γ_{Al}	$\Delta\bar{G}_{Ni}$ kJ/mol	$\Delta\bar{G}_{Al}$ kJ/mol	$\Delta\bar{G}_{Ni}^{ex}$ kJ/mol	\bar{G}_{Al}^{ex} kJ/mol	G kJ/mol	G^{ex} kJ/mol
0.15	0.000011	0.65	7.33×10^{-5}	0.7647	-135.0950	- 5.0971	-112.6485	- 3.1741	-24.5968	-19.5953
0.27	0.000098	0.35	3.63×10^{-4}	0.4795	-109.2172	- 12.4217	- 93.7251	- 8.6980	-38.5564	-31.6553
0.42	0.000098	0.35	2.33×10^{-4}	0.6035	-109.2172	- 12.4217	- 98.9530	- 5.9764	-53.0758	-45.0265
0.48	0.015	0.013	0.0313	0.0250	- 59.7696	- 28.6894	- 51.0881	- 43.6474	-55.4095	-47.2189
0.58	0.103	0.00039	0.1776	9.29×10^{-4}	- 26.8948	- 92.8747	- 20.4495	- 82.6105	-54.6064	-46.5571
0.65	0.231	0.00022	0.3554	6.29×10^{-4}	- 18.8670	- 99.6490	- 13.7699	- 87.2274	-47.1407	-39.4800
0.725	0.231	0.00022	0.3136	8.0×10^{-4}	- 18.8670	- 99.6490	- 15.0619	- 84.3739	-41.0820	-34.1227
0.77	0.343	0.000056	0.4519	2.44×10^{-4}	- 12.4895	-115.8387	- 9.3970	-98.4491	-36.2598	-29.8790
0.90	0.63	0.000032	0.7000	3.2×10^{-4}	- 5.4669	-122.4601	- 4.2202	-95.2156	-17.1662	-13.3197

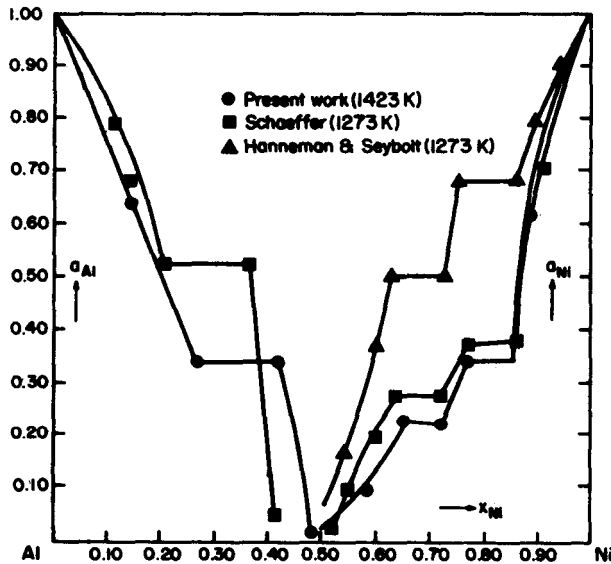


Fig. 1—Activity data of Al and Ni in Al-Ni binary alloys.

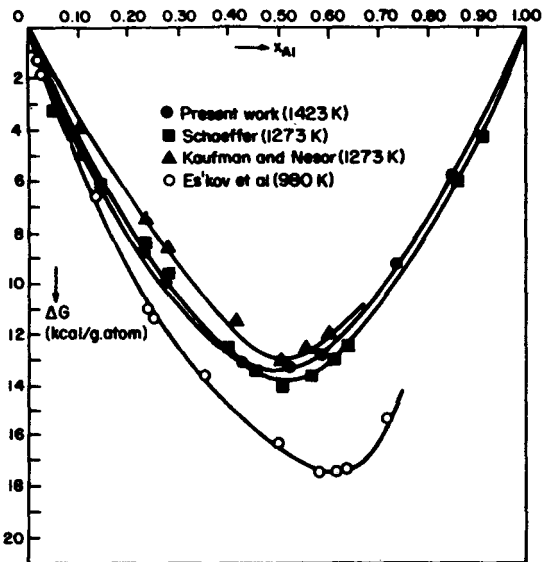


Fig. 3—Integral free energies (ΔG) of mixing of Al-Ni binary alloys.

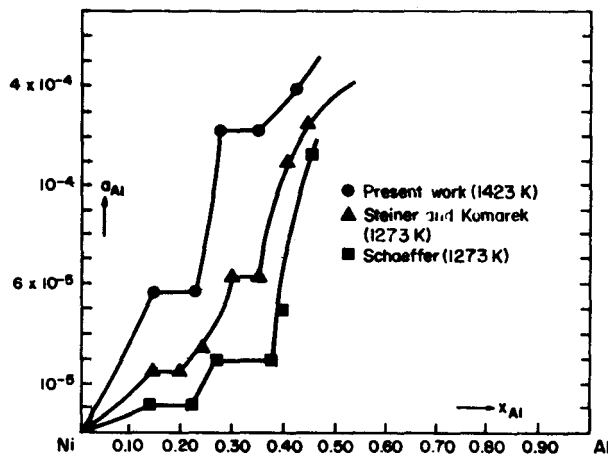


Fig. 2—Activity data of Al in Al-Ni binary alloys

concentration of component i (in mol fraction). The compositions of the alloys are given in Table 1 together with the activities of the species (a_i), activity coefficients (γ_i), the partial molar free energy of mixing ($\Delta\bar{G}_i$), the excess partial molar free energy of mixing ($\Delta\bar{G}_i^{ex}$), the

integral free energy of mixing (ΔG) and the excess integral free energy of mixing ($\Delta\bar{G}^{ex}$).

The activities of the species were measured with an accuracy of $\pm 10\%$. The heats of formation of aluminium-nickel alloys were high negative quantities (Table 1) and the system showed strong negative deviations from ideality as expected. At low nickel concentrations (0-30 atom % Ni) the activity of nickel was too low to be measured. In this low concentration range, the activity of nickel was obtained by integration using the experimentally determined aluminium activities. The present results at 1423 K are in reasonable agreement with those of Schaeffer⁷ and lower than the results of Hanneman and Seybolt⁵ (Fig. 1) at the nickel-rich end of the aluminium-nickel phase diagram. At high nickel concentrations end of the diagram (Fig. 2) the aluminium activities are significantly greater than those obtained by either Schaeffer⁷ or Steiner and Komarek³. This is as expected, since an increase in temperature should be obtained in the present work. This is in good agreement

increase the value of the activity coefficients towards unity and the solution approximates to ideality and hence higher activity values. Figure 3 compares the integral free energies of mixing and satisfactory agreement is once again obtained with Schaeffer's work⁷ and with Kaufman and Nesor's assessment⁸. The values given by Es' Kov *et al.*⁶ are considerably more negative since these relate to 980 K. A minimum ΔG value of -56.5 kJ/mol at 50 atom % Ni has been obtained in the present work. This is in good agreement with that of Schaeffer⁷ (-58.58 kJ/mol). Kaufman and Nesor's assessment⁸ also gives at the composition of NiAl phase a minimum ΔG value of -54.39 kJ/mol at 1273 K. The minimum ΔG value of -73.64 kJ/mol obtained by Es' Kov *et al.*⁶ at 39 atom % Ni (the composition of Ni₂Al₃ phase) differs from those reported by other workers.

Acknowledgement

The author wishes to express his thanks to Prof. B.B. Argent of the University of Sheffield, England for laboratory facilities and guidance and to the University of Port Harcourt for financial grant.

References

- 1 Kubaschewski O, *Trans Faraday Soc*, **54** (1958) 818.
- 2 Sandakov V M, Esin Yu O & Geld P V, *Zhur Fiz Khim*, **46** (1972) 1567.
- 3 Steiner A & Komarek K L, *Trans Met Soc AIME*, **230** (1964) 786.
- 4 Malkin V I & Pokidyshev V V, *Dokl Akad Nauk SSSR*, **166** (1966) 1390.
- 5 Hanneman R E & Seybolt A U, *Trans Met Soc AIME*, **245** (1969) 434.
- 6 Es' Kov V M, Samokhval V V & Vecher A A, *Izvest Akad Nauk SSSR Metaly*, **2** (1974) 199.
- 7 Schaeffer S C, Bureau of Mines report (US Department of Interior, Washington D C) 1975.
- 8 Kaufman L & Nesor H, Bureau of Mines report (US Department of Interior, Washington D C) 1975, 293.
- 9 Moore R H, Robinson D & Argent B B, *J phys Educ*, **8** (1975) 4641.
- 10 Argent B B, Jones K & Kirkbride B J, *The industrial use of thermochemical data*; Supplement Pub 34 (Chemical Society, London), 1980, 379.
- 11 Argent B B, Ellis M & Effenberg G, *High temperature-high Press*, **14** (1982) 409.
- 12 Oforka N C, *Indian J Chem*, **25A** (1986) 263.
- 13 Freeman R D & Edwards T G, *Characterization of high temperature vapours*, edited by J L Margrave (John Wiley, New York) 1967.