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Equilibrium Partition Coefficients between Solid and Liquid Phases and Activity Coefficients of Solute Elements in Ni Base Binary Dilute Alloys

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The equilibrium partition coefficients k_o^x between solid and liquid phases of various solute elements were measured in Ni base binary dilute alloys and the activity coefficients of those elements in both solid and liquid phases of Ni base dilute alloys at the melting point of pure Ni were calculated from a thermodynamic solution model with the values of k_o^x.

Gleichgewichtsverteilungskoeffizient zwischen fester und flüssiger Phase und Aktivitätskoeffizient der gelösten Elemente in verdünnten binären Ni-Basis-Legierungen

Der Gleichgewichtsverteilungskoeffizient k_o^x zwischen fester und flüssiger Phase verschiedener gelöster Elemente in Ni wurde gemessen. Dazu wurden mit der Mikrosonde die Konzentrationen in einer Probe bestimmt, die längere Zeit in einem schwachen Temperaturgradienten so geglüht wurde, daß sich eine stationäre Grenzfläche fest – flüssig bildete und dann abgeschreckt wurde. Die Aktivitätskoeffizienten dieser Elemente in verdünnten flüssigen und festen Ni-Basislegierungen beim Ni-Schmelzpunkt wurden aus den gemessenen k_o^x nach einem thermodynamischen Lösungsmodell berechnet.

1 Introduction

Various thermodynamic values are needed for an investigation of some refining processes for highly pure Ni. For example, the equilibrium partition coefficients between solid and liquid phases k_o^x, which is defined as the ratio of the equilibrium concentration of an solute element X in solid phase to that in liquid phase, of various solute elements are indispensable to analyse a concentration profile in the specimen when a zone-melting technique is applied for refinig Ni. In addition, the information on activity coefficients γ_x^o of solute elements in Ni base infinitely dilute alloys is also quite significant to investigate the refining of Ni. The value of γ_x^o as well as the vapour pressure of element X is considered as an important factor controlling evaporation of it from the Ni solvent. Further, the values of γ_x^o give us some suggestions on the solubility limit of oxygen in Ni base dilute alloys when an oxide of element X coexists. The information on k_o^x and γ_x^o in Ni base dilute alloys, however, has not been obtained systematically so far.

The purpose of this work is to measure the equilibrium partition coefficients k_o^x of various elements between the γ phase and liquid in Ni base binary dilute alloys and also to obtain the values of activity coefficients of those elements in both the liquid and solid phases of those alloys on the basis of the above measured k_o^x and a thermodynamic model derived recently by the authors1)2)3).

2 Measurement of Equilibrium Partition Coefficients of Solute Elements

A stationary interface method developed by Umeda et al.4)5), was applied for the determination of the equilibrium partition coefficients k_o^x of solute element X in Ni base binary dilute alloys. In the case of a small temperature difference between solidus and liquidus of the alloy, the plain interface between solid and liquid phases can be obtained by means of this method in a rod specimen which is set in a furnace with a small temperature gradient along the specimen. This method is useful for the measurement of k_x^o in dilute alloys because it is quite difficult to keep the temperature of the specimen within the region of coexistence of liquid and solid.

The composition of the specimens used for the measurement are given in Table 1. Figure 1 shows the experimental

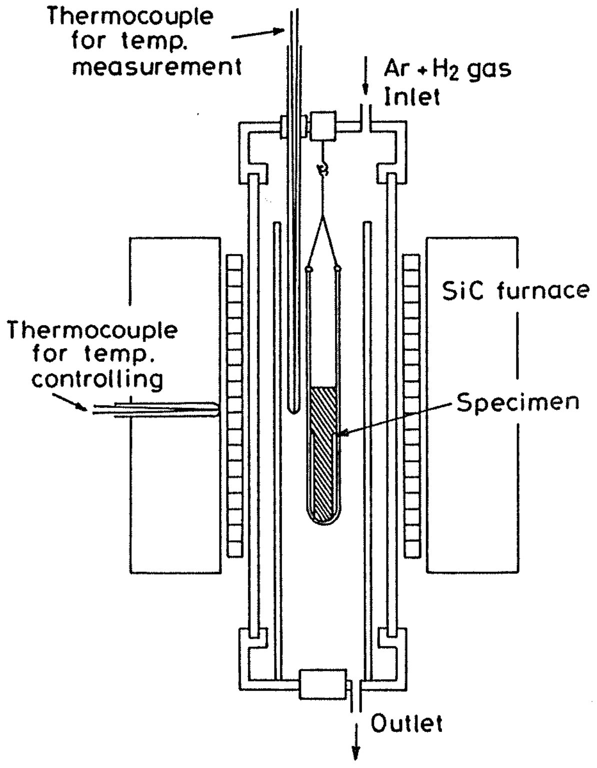

Fig. 1. Experimental apparatus for quenching specimens.

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Table 1. Chemical compositions of Ni base binary alloys used for the measurement of k_0^x.

Solute	Concentration (at.%)
Cu	1.0
Ge	1.0
In	1.5
Mo	1.0
Nb	0.91
P	5.6
Sb	1.4
Si	1.1
Sn	1.0
Ta	1.1
Ti	1.2
V	1.1

Table 2. Experimental results of k_0^x of solute elements in Ni base binary alloys.

Solute	k_0^x
Cu	0.78
Ge	0.56
In	0.12
Mo	1.00
Nb	0.39
P	0.06
Sb	0.16
Si	0.62
Sn	0.18
Ta	0.79
Ti	0.70
V	1.00

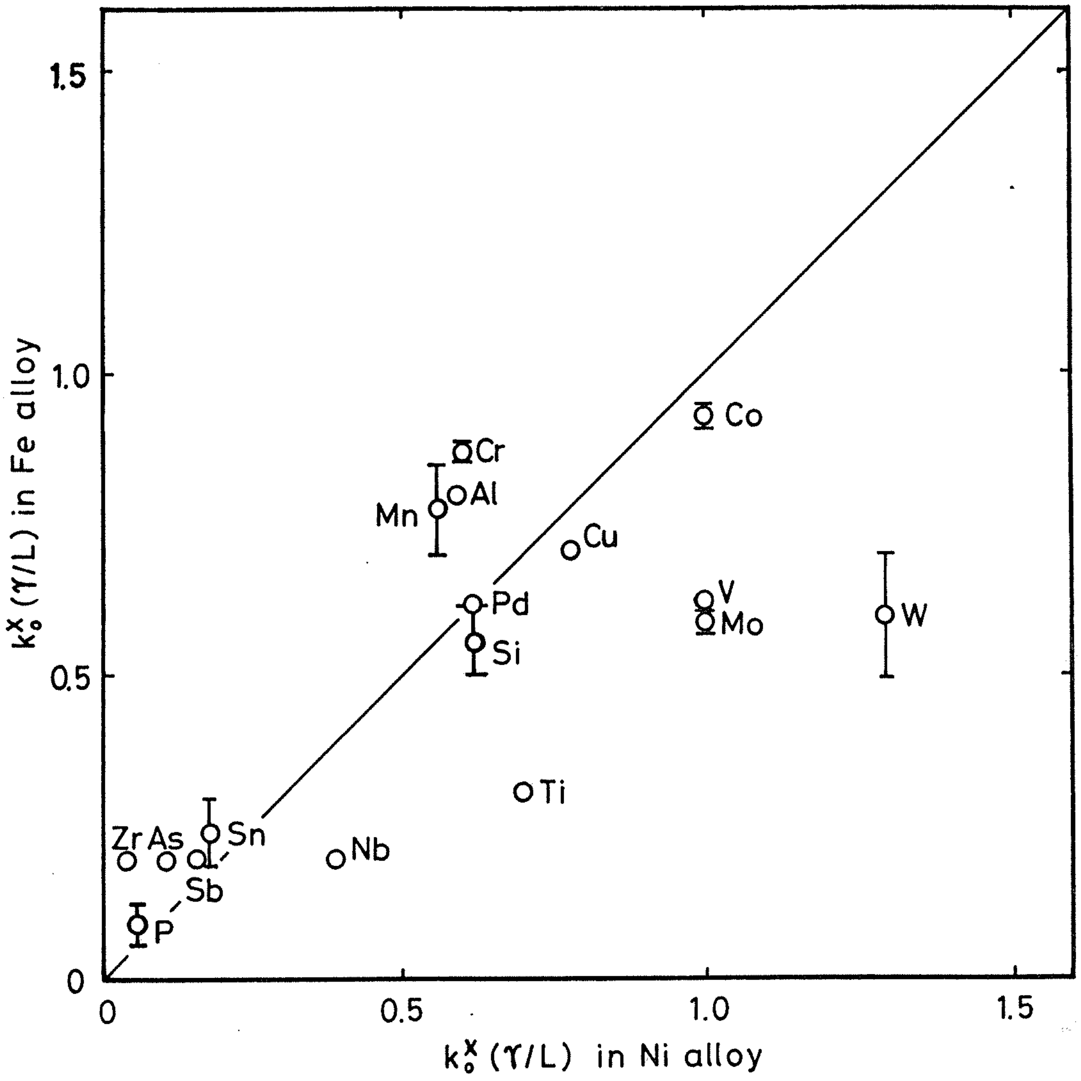

Fig. 2. Comparison of the equilibrium partition coefficients, k_0^x, in Ni alloys with those in Fe alloys.

apparatus. An alumina cell containing the specimen 120 mm long was set in the furnace having a small temperature gradient as shown in Fig. 1. After the temperature gradient was controlled so as to melt only the upper part of the rod specimen, it was held for a given time. Then, the specimen in the alumina cell was quenched into a water bath to fix the solid-liquid interface. From preliminary experiments it was confirmed that the plain solid-liquid interface could be obtained after being held at that temperature for 3 h. After the specimen being cut and polished, the concentrations of the solute elements in the γ phase and the quenched liquid parts near the solid-liquid interface were measured by electron probe micro analysis to determine k_x^o following the definition in Eq. (1).

$$k_x^o = N_x^{\text{Solid}}/N_x^{\text{Liquid}} \qquad (1)$$

where N_x^{Solid} and N_x^{Liquid} are the concentrations of solute X in solid γ and liquid, respectively.

The conditions adopted for the measurement by the electron probe micro analyser were described in details in the previous reports⁶)⁷).

3 Results and Discussion

3.1 Equilibrium Partition Coefficients of Solute Elements

Table 2 shows the measured values of the equilibrium partition coefficients k_x^o of the solute elements in Ni base binary alloys. The comparison of k_x^o in Ni alloys with those between the γ and the liquid phase in Fe alloys is shown in Table 3 and Fig. 2. In these table and figure, the values of k_x^o in Ni alloys except the measured k_x^o in this work are also included. These values are not always accurate because they were determined from the tangents on liquidus and solidus line at the melting point of pure Ni in those binary phase diagrams[8]. The values of k_x^o in Fe alloys were quoted from the compilation[9]. As shown in Fig. 2, most of k_x^o in Ni base binary alloys are greater than those in iron alloys. This seems to correspond to the difference of the maximum solubility of the solute elements in the γ phases of Ni and Fe alloys shown in Fig. 3, which were obtained from the phase diagrams[8][10].

3.2 Activity Coefficients of Solute Elements

Some of the authors[1][2][3] have proposed a thermodynamic solution model to predict a partial excess entropy $\Delta\overline{S}_x^{\mathrm{Ex,Liq}}$, a partial excess Gibbs energy $\Delta\overline{G}_x^{\mathrm{Ex,Liq}}$ and activity coefficient $\gamma_x^{\mathrm{o,Liq}}$ of solute element X in infinite dilution of liquid alloys by using a partial enthalpy of mixing $\Delta\overline{H}_x^{\mathrm{MIX,Liq}}$ obtained by Miedema's semi-empirical method[11]. This model can evaluate the value of non-configurational excess entropy and can also explain the temperature dependence of the relationship between $\Delta\overline{H}_x^{\mathrm{MIX,Liq}}$ and $\Delta\overline{S}_x^{\mathrm{Ex,Liq}}$ in liquid binary alloys. Since the derivation of the model has been described in details in the previous works[1][2], only the final equations are shown here.

$$\Delta\overline{G}_x^{\mathrm{Ex,Liq}} = RT\ln\gamma_x^{\mathrm{o,Liq}} = \Delta\overline{H}_x^{\mathrm{MIX,Liq}} - T\Delta\overline{S}_x^{\mathrm{Ex,Liq}} \tag{2}$$

Table 3. Equilibrium partition coefficients between liquid and γ phases of various elements in Ni and Fe base binary alloys.

Solute	k_o^x in Ni	k_o^x in Fe[c])
Al	0.59[a])	0.80
As	0.11[a])	0.20
Co	1.00[a])	0.91 ~ 0.95
Cr	0.60[a])	0.85 ~ 0.88
Cu	0.78[b])	0.70 ~ 0.72
Mn	0.56[a])	0.70 ~ 0.85
Mo	1.00[b])	0.57 ~ 0.61
Nb	0.39[b])	0.20
P	0.06[b])	0.06 ~ 0.13
Pd	0.62[a])	0.62
Sb	0.16[b])	0.20
Si	0.62[b])	0.50 ~ 0.61
Sn	0.18[b])	0.19 ~ 0.3
Ti	0.70[b])	0.30 ~ 0.32
V	1.00[b])	0.62 ~ 0.63
W	1.30[a])	0.50 ~ 0.70
Zr	0.04[a])	0.20

[a]) Data from Ref. [8]), [b]) present work and [c]) data from Ref. [9]).

$$\Delta\overline{H}_x^{\mathrm{MIX,Liq}} = \Omega_{\mathrm{Ni\text{-}X}} \tag{3}$$

$$\Delta\overline{S}_x^{\mathrm{Ex,Liq}} = 3/2 \cdot R \cdot [(L_{\mathrm{Ni}} - L_x)^2/(L_{\mathrm{Ni}}L_x) + \{4U_{\mathrm{Ni}}U_x - 2\Omega_{\mathrm{Ni\text{-}X}}(U_{\mathrm{Ni}} + U_x) - (U_{\mathrm{Ni}} + U_x)^2\} / (2U_{\mathrm{Ni}}U_x)] \tag{4}$$

$$L_i = 1/2(2^{1/2}V_i/N_o)^{1/3} \qquad (i = \mathrm{Ni\ or\ X}) \tag{5}$$

$$U_i = -685.3 \cdot \beta_i^2 \cdot T_{m,i} \,/\, \mathrm{J \cdot mol^{-1}} \ (i = \mathrm{Ni\ or\ X}) \tag{6}$$

where R gas constant = 8.3144 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$, T temperature/K, $\Omega_{\mathrm{Ni\text{-}X}}$ exchange energy/$\mathrm{J \cdot mol^{-1}}$, V_i molar volume of pure element i/$\mathrm{cm^3 \cdot mol^{-1}}$ (i = Ni or X), N_o Avogadro's number, $T_{m,i}$ melting point of pure element i/K (i = Ni or X) and β_i Coefficient of pure element i to transform a frequency of an atom in solid state into that in liquid state at

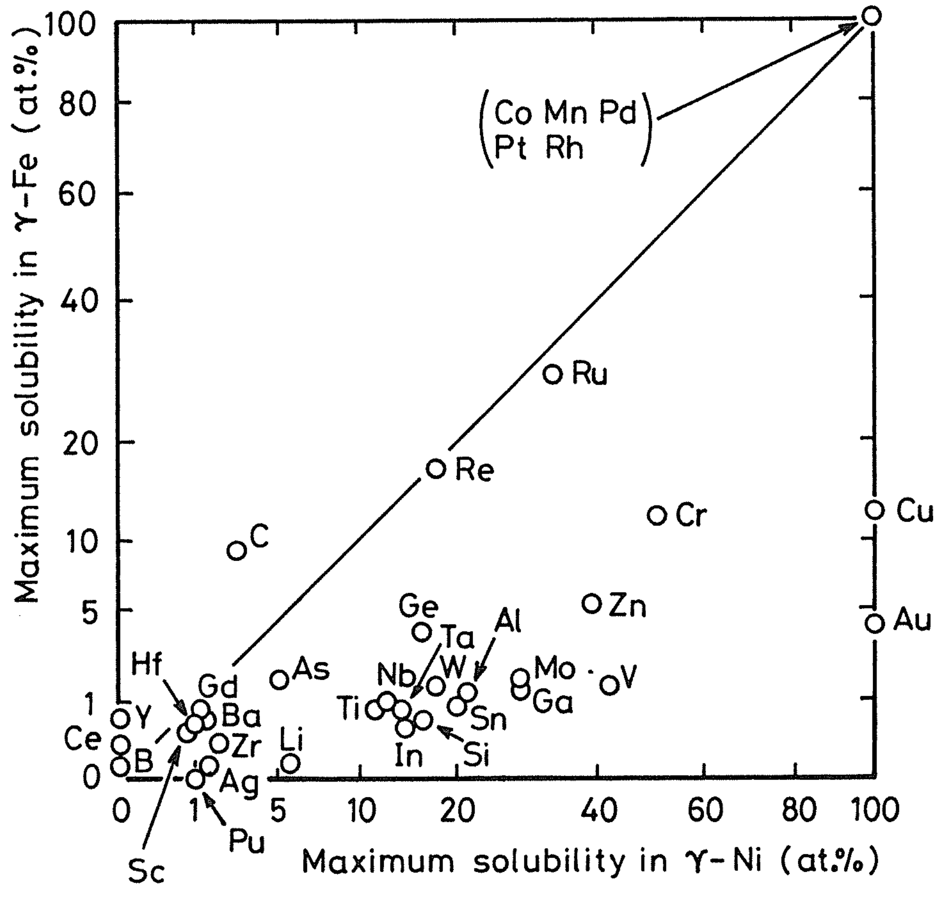

Fig. 3. Comparison of the maximum solubilities of various elements in γ phase of Ni alloys with those of Fe alloys.

Table 4. Calculated results for $\Delta\overline{S}_X^{Ex,Liq}$, $\Delta\overline{G}_X^{Ex,Liq}$ and $\gamma_X^{o,Liq}$ of solute elements in Ni base liquid alloys with the values used for the calculation of $\gamma_X^{o,Liq}$.

Solute	$\Delta\overline{H}_X^{MIX,Liq}$ (kJ · mol^{-1})	$T_{m,i}$ (K)	V_i (cm^3 · mol^{-1})	β_i	$\Delta\overline{S}_X^{Ex,Liq}$ (J · K^{-1} · mol^{-1})	$\Delta\overline{G}_X^{Ex,Liq}$ (kJ · mol^{-1})	$\gamma_X^{o,Liq}$
Al	−96	933	9.99	0.52	−12.3	−74.7	5.5×10^{-3}
Co	−1	1765	6.69	0.48	−0.1	−0.8	0.95
Cr	−27	2178	7.23	0.50	−3.0	−21.9	0.22
Cu	14	1356	7.12	0.46	1.1	12.2	2.3
Ge	−51	1232	9.87	0.50	−5.5	−41.5	0.056
In	8	430	15.74	0.68	−0.6	9.0	1.87
Mn	−33	1517	7.35	0.50	−3.1	−27.6	0.15
Mo	−32	2895	9.39	0.50	−4.8	−23.7	0.19
Nb	−135	2740	10.81	0.50	−11.9	−114.5	3.5×10^{-4}
Ni	–	1728	6.60	0.47	–	–	–
Pd	0	1828	8.89	0.50	−0.1	0.1	1.01
Sb	−7	904	16.96	0.40	−6.3	3.9	1.31
Si	−98	1687	8.61	0.38	−13.2	−75.2	5.3×10^{-3}
Sn	−21	505	16.30	0.64	−4.1	−13.9	0.38
Ta	−133	3123	10.81	0.50	−12.4	−111.5	4.3×10^{-4}
Ti	−154	1998	10.58	0.50	−13.1	−131.4	1.1×10^{-4}
V	−75	1973	8.36	0.50	−6.7	−63.5	0.012
W	−14	3655	9.55	0.50	−5.8	−3.9	0.76
Zr	−236	2130	14.00	0.50	−19.2	−202.8	7.4×10^{-7}

$\Delta\overline{H}_X^{MIX,Liq}$, V_i Ref. 11) and $T_{m,i}$, β_i Ref. 12).

the melting point. The values of β_i were obtained from the experimental data for surface tension of pure liquid metals as follows12) (i = Ni or X):

$$\beta_i = 1.1 \times 10^3\ V_{i,m}^{1/3} \cdot (\sigma_{i,m}/RT_{m,i})^{1/2}/(1.97 \cdot \eta_{m,i}^{1/3} - 1) \qquad (7)$$

In the above equation, $V_{i,m}$(m^3 · g-atom^{-1}), σ_i(mN · m^{-1}) and $\eta_{m,i}$ are molar volume, surface tension and packing fraction of pure liquid i at its melting point. When values of β_i are not available, it can be set to 0.5 approximately12).

Substituting $\Delta\overline{H}_X^{MIX,Liq}$ given by Miedema's semi-empirical method and the values of V_i11), $T_{m,i}$12) and β_i12) into the above Eqs. (2) to (6), $\Delta\overline{S}_X^{Ex,Liq}$, $\Delta\overline{G}_X^{Ex,Liq}$ and $\gamma_X^{o,Liq}$ can be obtained. The calculated results are shown in Table 4 with the data needed for the calculation. Although this model can be applied for the calculation of $\gamma_X^{o,Liq}$ in liquid dilute alloys, the values of activity coefficients of solute X $\gamma_X^{o,Sol}$ in the γ phase can be also obtained from the following equilibrium relationship between solid γ phase and liquid one6)7) with the value of k_o^X.

$$RT \ln (N_X^{Solid}/N_X^{Liquid}) = RT \ln k_o^X = \Delta G_X^{Fusion} + RT \ln (\gamma_X^{o,Liq}/\gamma_X^{o,Sol}) \qquad (8)$$

where ΔG_X^{Fusion} is the Gibbs energy of fusion of pure element X, i.e., Gibbs energy change of pure element X for the transformation from the γ phase to the liquid phase.

The calculated results for $\gamma_X^{o,Sol}$ are shown in Table 5 with the values13) to 20) of ΔG_X^{Fusion}. The values of k_o^X, $\gamma_X^{o,Liq}$ and $\gamma_X^{o,Sol}$ obtained in this work can be used for an analysis of segregation behaviours and equilibria of Ni dilute alloys with nitrides or oxides of solute elements.

4 Summary

In this work, the equilibrium partition coefficients of some elements were measured by means of the stationary interface method and the activity coefficients of the solute elements in both solid and liquid phases of Ni base dilute alloys were calculated from the thermodynamic solution model. These values will be used for an investigation of various refining processes of highly pure Ni.

Table 5. Calculated results for $\gamma_X^{o,Sol}$ at 1728 K (melting point of pure Ni) in γ phase of Ni base binary dilute alloys.

Solute	$RT \ln k_o^X$ (kJ · mol^{-1})	ΔG_X^{Fusion} (kJ · mol^{-1})	Ref.	$\gamma_X^{o,Sol}$
Cu	−3.6	−3.6	13)	2.3
Ge	−8.3	−19.5	14)	0.026
In	−30.5	−9.4	15)	8.1
Mo	0	−1.7	16)	0.17
Nb	−13.5	−6.7	16)	5.5×10^{-4}
Sb	−26.3	−33.3	15)	0.81
Si	−6.9	−21.0	17)	2.0×10^{-3}
Sn	−24.6	−11.1	18)	0.97
Ta	−3.4	−2.2	19)	4.6×10^{-4}
Ti	−5.1	−3.7	20)	1.2×10^{-4}
V	0	−11.4	19)	5.4×10^{-3}

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