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Thermodynamic Assessment of the Ni-Ru System

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The Ni-Ru system is assessed using the CALPHAD technique. The only available experimental information for this system concerns phase equilibria, whereas no thermochemical information has been found. The THERMO-CALC software is applied to obtain Gibbs energy (*G*) functions for the individual phases. The phase diagram calculated from the new *G* functions is in excellent agreement with the experimental diagram, and all the thermodynamic parameters are given in the Appendix. In addition, tentative activity diagrams and the metastable miscibility gaps in fcc and hcp phases are calculated from the new thermodynamic description.

1. Introduction

Ruthenium (Ru) is considered to be a potential substitute for platinum (Pt) in the bond coat in gas turbine engines.[1] Thus, there is a need to compare the thermodynamics and kinetics of the two elements in various alloys. As a first step, it should be interesting to compare the thermodynamic properties and the ternary phase diagrams of the Ni-Al-Ru and Ni-Al-Pt systems. The Ni-Al system has already been assessed by Ansara et al.[2], Dupin and Ansara,[3] and Sundman,[4] and the Al-Ru system has been assessed by Prins et al.[5] The purpose of the present report is to assess the Ni-Ru system. The ternary system Ni-Al-Ru will be assessed in a coming report.

2. Experimental Data

Pure nickel (Ni) is face-centered-cubic (fcc), whereas Ru is hexagonal-close-packed (hcp). The form of the Ni-Ru phase diagram is well known.[6] It is a simple peritectic with high mutual solubilities in the two solid phases. To the knowledge of the present author, no thermochemical data are available in the literature. Thus, the assessment must be based on phase diagram data only.

Raub and Menzel[7] and Kornilov and Myasnikova[8] used thermal analysis to measure the liquidus and solidus temperatures for a series of alloys. In both cases, the composition was evaluated from the x-ray lattice parameter data.

No measurements have been made on the hcp liquidus with Ru content higher than 50 atomic percent (at.%), but Kornilov and Myasnikova[8] determined the hcp solidus up to 62 at.%. The experimental uncertainties could not be found in the articles. However, the data of Raub and Menzel[7] and Kornilov and Myasnikova[8] are in good agreement for the hcp liquidus and solidus, but are not in equally good agreement for the fcc liquidus and solidus.

Tryon and Pollock[9] investigated three diffusion couples of nominally pure Ni and Ru at temperatures of 1000 °C, 1100 °C, and 1250 °C, and used EPMA to obtain concentration profiles from which phase diagram data were obtained. Their error estimate for their solvus values is on the order of 1 at.%, and their determinations are in close accord with the data of both Raub and Menzel[7] and Kornilov and Myasnikova[8] in the temperature region of measurement (Fig. 1).

One series of alloys was prepared and annealed to determine the Ni-rich solvus and the Ru-rich solvus by Raub and Menzel,[7] and another was prepared by Kornilov and Myasnikova.[8]Raub and Menzel[7] annealed the specimens under vacuum in quartz tubes at temperatures up to 1000 °C. For higher temperatures, they used a vacuum furnace or flowing Ar. The specimens were quenched after the annealing. Kornilov and Myasnikova[8] quenched the specimens from 1200 °C, 1000 °C, 900 °C, or 800 °C after holding for 24, 50, 100, or 200 h, respectively. At 600 °C, the annealing time was 400 h, followed by cooling in the furnace.

Raub and Menzel[7] reported the peritectic temperature to be 1490 °C, whereas Kornilov and Myasnikova[8] reported 1550 ± 10 °C. The peritectic temperature is the biggest difference between the two sets of data. However, the peritectic temperature of 1490 °C is not entirely consistent with the reported liquidus and solidus data, and, moreover, the purity of the materials used by Raub and Menzel[7] was lower than that used by Kornilov and Myasnikova.[8]

Kornilov and Myasnikova[8] reported the composition of the fcc phase at the peritectic temperature to be 41 at.% Ru, which differs from the value 29.7 at.% Ru given by Raub and Menzel.[7] The composition of the hcp phase at the peritectic temperature was reported by Kornilov and Myasnikova[8] to be 53 at.% Ru, and by Raub and Menzel it was reported to be 51.3 at.% Ru.

3. Thermodynamic Model for the Pure Elements

As mentioned, the stable phase for Ni is fcc, and for Ru it is hcp. For a pure element, the Gibbs energy (*G*) is expressed as ${}^0G\text{-}H^{\mathrm{SER}}$, where SER denotes the so-called stable-element reference [Scientific Group Thermodata Europe (SGTE), Ref. 10]. The temperature dependence is written as a power series expansion of the type:

$$^0G - H^{\mathrm{SER}} = a + bT + cT\ln T + \sum_{\mathrm{n}} d_{\mathrm{n}} T^{\mathrm{n}}$$

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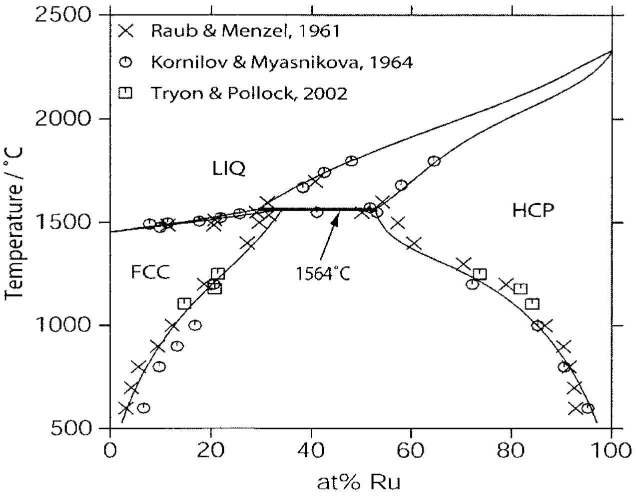

Fig. 1 Calculated Ni-Ru phase diagram with experimental data

Data for the pure elements were taken from the SGTE unary data base.[10]

4. Thermodynamic Model for Solution Phases

In this assessment, a regular solution type of model was used. This assumes random mixing in all three substitutional phases (i.e., liquid, fcc, and hcp). The molar G for a phase ϕ is written:

$$G_m^\phi = x_{Ni}^\phi\,{}^0G_{Ni}^\phi + x_{Ru}^\phi\,{}^0G_{Ru}^\phi + RT[x_{Ni}\ln(x_{Ni}) + x_{Ru}\ln(x_{Ru})] + {}^EG_m^\phi$$

where ${}^EG_m$ is the excess G expressed by a Redlich-Kister expansion:

$${}^EG_m^\phi = x_{Ni}x_{Ru}I_{Ni,Ru}^\phi \qquad I_{Ni,Ru}^\phi = \sum_k {}^kL_{Ni,Ru}^\phi(x_{Ni} - x_{Ru})^k$$

$${}^kL_{Ni,Ru}^\phi = A_k + B_kT$$

where k = 0, 1, and 2, respectively, specifies regular, subregular, and sub-sub-regular solution parameters. A and B are constants to be optimized.

5. Optimization

The optimization was performed in the Parrot module of THERMO-CALC. This module fits the model parameters to the experimental data by a least mean squares method that minimizes the quadratic errors.

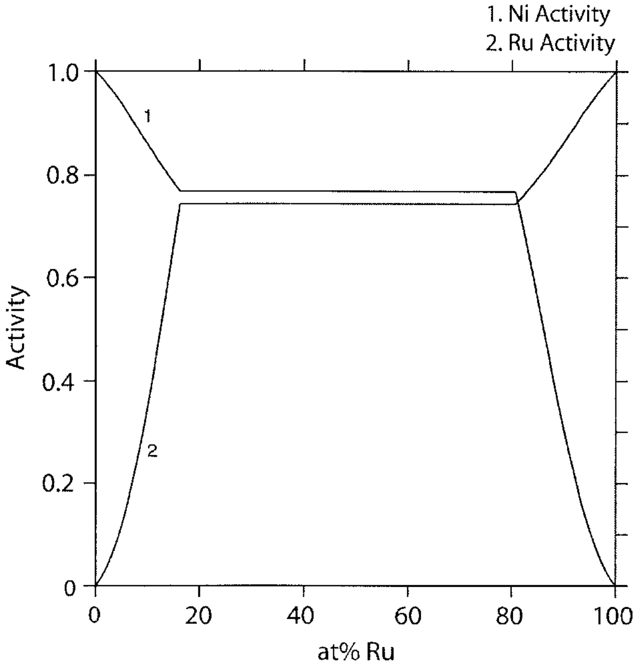

Fig. 2 Calculated Ni and Ru activities at 1100 °C

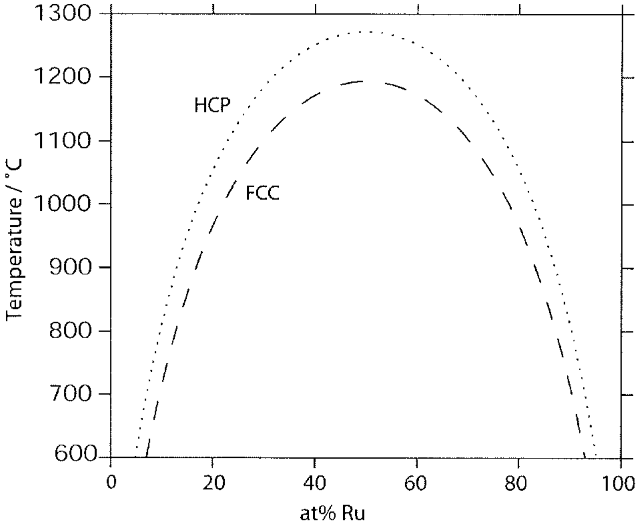

Fig. 3 Calculated metastable miscibility gaps in the fcc and hcp phases

6. Results and Discussion

Two Redlich-Kister coefficients, the regular and sub-sub-regular, were used for each phase to optimize the excess G. The parameters for the fcc and hcp phases were set equal in the early stage of the optimization. Since the structures are very similar, their parameters were not expected to differ very much. It was later shown to be necessary to introduce a difference in enthalpy to fit the calculated phase diagram with the experimental data (see the list of parameters in the Appendix). A total of eight parameters were optimized. This is regarded as a low value but is justified by the limited amount of experimental data. It was not possible to fit the calculated phase diagram with the experiments when regular and sub-regular parameters were optimized. The best fit was obtained when regular and sub-sub-regular parameters were optimized. This is believed to be partially due to the lack of thermochemical data.

Figure 1 shows the resulting phase diagram. It shows excellent agreement with the experimental data. The invariant equilibrium is located at 1564 °C, which is higher than that reported in both Ref. 7 and 8. The maximum solubilities in the fcc and hcp phases were calculated to be 34.1 and 52.6 at.% Ru, respectively.

Figure 2 shows the Ni and Ru activities as functions of composition calculated at 1100 °C from the new description. As already mentioned, there is no experimental information to support those calculations, but some readers may find them valuable. In addition, the calculated metastable miscibility gaps in the fcc and hcp phases are given in Fig. 3.

Acknowledgments

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Appendix: List of Parameters

$G_{\mathrm{Ru}}^{\mathrm{SER}} = \text{Ref. } 10$
$-7561.873 + 127.866233 \times T - 22.9143287 \times T \times \ln(T)$
$-4.062566 \times 10^{-3} \times T^2 + 0.17641 \times 10^{-6} \times T^3 + 56377 \times T^{-1}$
$298.15 < T < 1500$
$-59\,448.103 + 489.516214 \times T$
$-72.3241219 \times T \times \ln(T)$
$+18.726245 \times 10^{-3} \times T^2 - 1.952433 \times 10^{-6} \times T^3$
$+11\,063\,885 \times T^{-1}$
$1500 < T < 2607$
$-38\,588\,773.031 + 168\,610.517\,401 \times T$
$-21\,329.7050475 \times T \times \ln(T)$
$+5221.638997 \times 10^{-3} \times T^2 - 240.245985 \times 10^{-6} \times T$
$+13\,082\,992\,629 - T^{-1}$
$2607 < T < 2740$
$-55\,768.304 + 364.482314 \times T - 51.8816 \times T \times \ln(T)$
$2740 < T < 4500$

$G_{\mathrm{Ni}}^{\mathrm{SER}} = \text{Ref. } 10$
$-5179.159 + 117.854 \times T - 22.096 \times T \times \ln(T)$
$-4.8407 \times 10^{-3} \times T$
$298.15 < T < 1728$
$-27\,840.655 + 279.135 \times T - 43.10 \times T \times \ln(T)$
$+1.12754 \times 10^{31} \times T^9$
$1728.00 < T < 3000$

Liquid
$G_{\mathrm{Ni}}^{\mathrm{liq}}(T) - {}^0H_{\mathrm{Ni}}^{\mathrm{fcc}}(298.15) = \text{Ref. } 10$
$+16\,414.686 - 9.397 \times T - 3.82318 \times 10^{-21} \times T^7 + G_{\mathrm{Ni}}^{\mathrm{SER}}$
$298.15 < T < 1728$
$+18\,290.88 - 10.537 \times T - 1.12754 \times 10^{31} \times T^9 + G_{\mathrm{Ni}}^{\mathrm{SER}}$
$1728.00 < T < 3000$

$G_{\mathrm{Ru}}^{\mathrm{liq}}(T) - {}^0H_{\mathrm{Ru}}^{\mathrm{hcp}}(298.15) = \text{Ref. } 10$
$+27\,480.616 - 8.398748 \times T + G_{\mathrm{Ru}}^{\mathrm{SER}}$
$298.15 < T < 800$
$+58\,389.105 - 307.684793 \times T + 42.4536697 \times T \times \ln(T)$
$-22.461602 \times 10^{-3} \times T^2 + 1.49129 \times 10^{-6} \times T^3$
$-39\,175\,02 \times T^{-1} + G_{\mathrm{Ru}}^{\mathrm{SER}}$
$800 < T < 1500$
$+110\,275.336 - 669.334775 \times T + 91.8634629 \times T \times \ln(T)$
$-45.150413 \times 10^{-3} \times T^2 + 3.620272 \times 10^{-6} \times T^3$
$-14\,925\,010 \times T^{-1} + G_{\mathrm{Ru}}^{\mathrm{SER}}$
$1500 < T < 2607$
$+38\,571\,611.223 - 168\,260.84384 \times T + 21\,277.8234475 \times T$
$\times \ln(T)$
$-5221.638997 \times 10^{-3} \times T^2 + 240.245985 \times 10^{-6}\, T^3$
$-13\,082\,992\,629 \times T^{-1} + G_{\mathrm{Ru}}^{\mathrm{SER}}$
$2607 < T < 2740$
$+38\,606.496 - 14.808753 \times T + G_{\mathrm{Ru}}^{\mathrm{SER}}$
$2740 < T < 4500$

${}^0L_{\mathrm{Ni,Ru}}^{\mathrm{liq}} = 64790 - 40.115 \times T$
${}^2L_{\mathrm{Ni,Ru}}^{\mathrm{liq}} = -12022$

FCC
$G_{\mathrm{Ni:Va}}^{\mathrm{fcc}}(T) - {}^0H_{\mathrm{Ni}}^{\mathrm{fcc}}(298.15) = \{\text{Ref. } 10\} = G_{\mathrm{Ni}}^{\mathrm{SER}}$
$298.15 < T < 3000$
$G_{\mathrm{Ru:Va}}^{\mathrm{fcc}}(T) - {}^0H_{\mathrm{Ru}}^{\mathrm{fcc}}(298.15) = \text{Ref. } 10$
$12\,500 - 2.4 \times T + G_{\mathrm{Ru}}^{\mathrm{SER}}$
$298.15 < T < 4500$
${}^0L_{\mathrm{Ni,Ru:Va}}^{\mathrm{fcc}} = 73\,973 - 45.109 \times T$
${}^2L_{\mathrm{Ni,Ru:Va}}^{\mathrm{fcc}} = -41324 + 16.864 \times T$

HCP
$G_{\mathrm{Ni:Va}}^{\mathrm{hcp}}(T) - {}^0H_{\mathrm{Ni}}^{\mathrm{hcp}} = \text{Ref. } 10$
$1046 + 1.2552 \times T + G_{\mathrm{Ni}}^{\mathrm{SER}}$
$298.15 < T < 3000$
$G_{\mathrm{Ru:Va}}^{\mathrm{hcp}}(T) - {}^0H_{\mathrm{Ru}}^{\mathrm{hcp}} = \{\text{Ref. } 10\} = G_{\mathrm{Ru}}^{\mathrm{SER}}$
$298.15 < T < 4500$
${}^0L_{\mathrm{Ni,Ru:Va}}^{\mathrm{hcp}} = {}^0L_{\mathrm{Ni,Ru:Va}}^{\mathrm{fcc}} + 6139$
${}^2L_{\mathrm{Ni,Ru:Va}}^{\mathrm{hcp}} = {}^2L_{\mathrm{Ni,Ru:Va}}^{\mathrm{fcc}}$

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