The Ruthenium–Yttrium System: An Experimental Calorimetric Study with a Phase Diagram Optimization

N. Selhaoui,* J. Charles,† O. J. Kleppa,‡ L. Bouirden,* and J. C. Gachon†,[1]

* Laboratoire de Thermodynamique Métallurgique et Rhéologie des Matériaux, Faculté des Sciences d'Agadir, Université Ibnou Zohr, BP 28/S Agadir, Morocco;
† Laboratoire de Chimie du Solide Minéral, UMR 7555, Service de Thermodynamique Métallurgique, Université Henri Poincaré, Nancy I, BP 239,
F54506 Vandoeuvre lès Nancy Cedex, France; and ‡James Franck Institute, University of Chicago, 5640 S. Ellis Avenue, Chicago, Illinois 60637

After an experimental determination of the standard enthalpies of formation of $Ru_{0.67}Y_{0.33}$ and $Ru_{0.286}Y_{0.714}$, the Ru–Y system was numerically assessed with the help of NANCYUN software to check the consistency between our experimental results and the phase diagram proposed in the literature. © 1998 Academic Press

Key Words: **Ru–Y phase diagram; standard enthalpies of formation; optimization; thermodynamic properties**

I. INTRODUCTION

After a systematic calorimetric study of systems involving a transition metal (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt) and a rare earth metal (Y, Sc, La, Ce, Lu) to determine their standard enthalpies of formation by high-temperature drop calorimetry (1–4), we present here our numerical results on the Ru–Y system.

The Ru–Y phase diagram (Fig. 1) was drawn by Moffatt (5), who modified the diagram of Savitsky *et al.* (6), which included only Ru_2Y and RuY_3, by adding Ru_2Y_3 and Ru_2Y_5 reported by Sharifrazi *et al.* (7) and $Ru_{25}Y_{44}$ reported by Fornasini *et al.* (8). Similarity to the Gd–Ru and Dy–Ru systems was assumed.

The temperatures and compositions of the liquid–solid equilibria are approximate, except for the eutectic Ru/liquid/Ru_2Y and RuY_3/liquid/α-Y plateaux, which were determined experimentally. We reinvestigated this system by numerical assessment with the help of NANCYUN software (9, 10).

II. HIGH-TEMPERATURE DIRECT REACTION CALORIMETRY

The experiments were carried out at 1473 ± 2 K in a single-unit differential microcalorimeter. Details of the

---

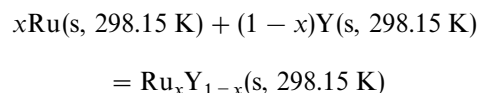[1] To whom correspondence should be addressed. E-mail: gachon@ltm.u-nancy.fr.

method have already been published (1). Here, we will simply recall the principle. The standard enthalpy of formation of the compound Ru_xY_{1-x}, where x is the Ru atom fraction, is obtained from the difference between two sets of measurements. In the first set, the following reaction took place in the calorimeter:

$$x\text{Ru(s, 298.15 K)} + (1 - x)\text{Y(s, 298.15 K)}$$
$$= Ru_xY_{1-x}\text{(s, 1473 K)} \qquad [1]$$
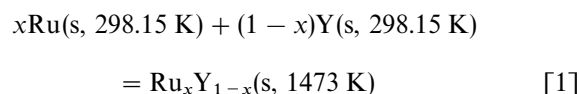
The products of reaction [1] were reused in a subsequent set of measurements to determine their heat contents.

$$Ru_xY_{1-x}\text{(s, 298.15 K)} = Ru_xY_{1-x}\text{(s, 1473 K)} \qquad [2]$$

From Eqs. [1] and [2] we get

$$x\text{Ru(s, 298.15 K)} + (1 - x)\text{Y(s, 298.15 K)}$$
$$= Ru_xY_{1-x}\text{(s, 298.15 K)}$$

The standard enthalpy of formation, $\Delta_f H(298.15 \text{ K})$, is given by:

$$\Delta_f H(298.15 \text{ K}) = \Delta H_m(1) - \Delta H_m(2)$$

where $\Delta H_m(1)$ and $\Delta H_m(2)$ are the enthalpy changes per mole of atoms for reactions [1] and [2]. Calibration of the calorimeter was performed by dropping weighed pieces of 2-mm-diameter, high-purity copper wire at room temperature into the calorimeter at 1473 ± 2 K. The enthalpy change of pure copper between room temperature and 1473 K was taken from Hultgren *et al.* (11), 46,465 J mol^{-1}. The calibrations were reproducible within $\pm 1.5\%$.

The yttrium lump was stored in a vacuum desiccator and fine filings (-80 mesh) were prepared just before
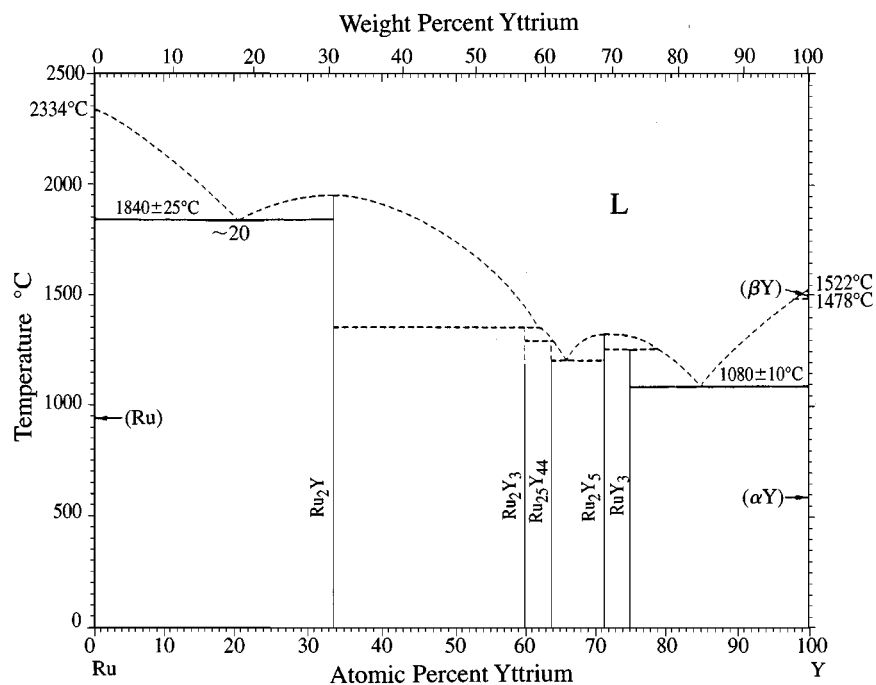
FIG. 1. Experimental Ru–Y phase diagram proposed by Moffatt (5).

the two components (powders of Ru and Y) were mixed in suitable proportion at room temperature. The metals were purchased from Johnson Matthey, AESAR Group.

A summary of the experimental results is given in Table 1. The reported $\Delta H_m(1)$ and $\Delta H_m(2)$ are averages of four to six experiments with standard deviations δ_1 and δ_2. The uncertainty in $\Delta_f H(298.15\ K)$ was calculated from $\delta = (\delta_1^2 + \delta_2^2)^{1/2}$.

After the experiments, the alloy samples were examined by powder X-ray diffraction and by SEM and energy-dispersive X-ray (EDX) microanalyses without any further heat treatment. Our X-ray diffraction experiments showed traces of Ru in the Ru$_2$Y samples. Examination of the products by SEM and EDX confirmed the presence of small

amounts of Ru in Ru$_2$Y. Thus, we considered our calorimetric result for Ru$_2$Y as indicative.

III. NUMERICAL OPTIMIZATION

According to Charles *et al.* (9), the excess Gibbs energy of the liquid phase is represented through a polynomial expansion using Legendre polynomials:

$$g^E(x,T) = x(1-x) \sum_{i=0}^{n} [a_i + b_i T] L_i(x)$$

where $x = x_B$ is the atomic fraction of B in the A–B system, a_i and b_i are independent of temperature and composition $L_i(x)$ is the Legendre polynomial of ith order:

$$iL_i(x) = (2x - 1)(2i - 1)L_{i-1}(x) - (i - 1)L_{i-2}(x)$$

$$L_0 = 1 \quad \text{and} \quad L_1(x) = 2x - 1$$

The degree n of the polynomial expansion relative to the liquid phase must be defined by the user before the computer begins to build the equation set. The Gibbs energy of formation for a stoichiometric compound is written $\Delta_f G = \Delta_f H - T\Delta_f S$, assuming that, in a first approximation, $\Delta_f H$ and $\Delta_f S$ are temperature independent.

For each equilibrium equation or experimental information, a weighting factor is chosen to represent as well as possible its reliability.

TABLE 1
Observed Heats of Reaction, Average Heat Contents at 1473 K, and Calculated Standard Enthalpies of Formation of Ru–Y Compounds in Kilojoules per Mole of Atoms (Referred to Solid Ru and α-Y)

Compound	$\Delta H_{obs} = \Delta H_m(1)$	Heat content = $\Delta H_m(2)$	$\Delta_f H(298.15\ K)$
Ru$_{0.67}$Y$_{0.33}$	13.31 ± 1.00 (5)[a]	32.83 ± 1.01 (4)[a]	−19.5 ± 1.4
Ru$_{0.286}$Y$_{0.714}$	17.14 ± 1.44 (5)[a]	44.39 ± 2.74 (4)[a]	−27.3 ± 3.1

[a] (x) = number of experiments averaged.

TABLE 2
Thermodynamic Data for Pure Elements (12)

Pure element	Melting enthalpy $(J\,mol^{-1})$	$T^{melting}$ (K)	Melting entropy $(J\,mol^{-1}\,K^{-1})$
α-Y	11,397.22	1799	6.34
Ru	38,589.03	2607	14.80

III-1. Experimental Data

The experimental information introduced in the program is as follows:

1. Enthalpies of melting and melting points of Ru and Y pure elements (Table 2) taken from the Scientific Group Thermodata Europ (S.G.T.E.) (12).
2. Coordinates (T, x) of binary liquid–solid equilibria taken from the experimental phase diagram proposed by Moffatt (5) (Table 3).
3. Enthalpies of formation of $Ru_{0.67}Y_{0.33}$ and $Ru_{0.286}Y_{0.714}$ determined by direct synthesis drop calorimetry (1) (Table 4). We modified the reference state for Y (α for the experimental value and β for the calculation).
4. Estimates of melting entropies for all the stoichiometric compounds in order to have a sufficient number of equations (Table 4). Small weighting factors were applied to these entropy values.

III-2. Results of the Optimization

The excess Gibbs energy of the liquid referred to liquid Ru and Y is represented with a polynomial expansion of order $n = 1$:

$$g^E(x, T) = x(1 - x)[(a_0 + b_0 T) + (a_1 + b_1 T)(2x - 1)]$$

TABLE 3
Coordinates (T, x) of Points Taken from the Experimental Liquid–Solid Equilibria[a]

Types of equilibria	Temperature (K)	N_1	x_1	N_2	x_2	Weighting factors
Eutectic	2113	1	0.200	2	0.000	3
Y, liq, YRu_2	2113	1	0.200	3	0.333	3
Peritectic	1623	1	0.620	3	0.333	1
liq, YRu_2, Y_3Ru_2	1623	1	0.620	4	0.600	1
Peritectic	1573	1	0.640	4	0.600	5
liq, Y_3Ru_2, $Y_{44}Ru_{25}$	1573	1	0.640	5	0.638	5
Eutectic	1523	1	0.660	5	0.638	1
$Y_{44}Ru_{25}$, liq, Y_5Ru_2	1523	1	0.660	6	0.714	1
Peritectic	1523	1	0.780	6	0.714	5
liq, Y_5Ru_2, YRu_3	1523	1	0.780	7	0.750	5
Eutectic	1353	1	0.850	7	0.750	3
Y, liq, Y_3Ru	1353	1	0.850	8	1.000	3
Equilibrium	1623	1	0.940	8	1.000	1
Y, liq	1473	1	0.880	8	1.000	1
Equilibrium	1773	1	0.590	3	0.333	1
YRu_2, liq	1973	1	0.520	3	0.333	1
Y_3Ru, liq	1473	1	0.810	7	0.750	1
Equilibrium: Ru, liq	2273	1	0.150	2	0.000	1
Congruent melting points						
YRu_2, liq	2223	1	0.333	3	0.333	5
Y_5Ru_2, liq	1618	1	0.714	6	0.714	3
Metastable estimated congruent melting points						
Y_3Ru, liq	1573	1	0.750	7	0.750	1
$Y_{44}Ru_{25}$, liq	1573	1	0.638	5	0.638	1
Y_3Ru_2, liq	1598	1	0.600	4	0.600	1

[a] x = yttrium atomic fraction.
[b] The different phases are numbered as follows: 1, liquid phase; 2, pure ruthenium; 3, stoichiometric compound YRu_2; 4, stoichiometric compound Y_3Ru_2; 5, stoichiometric compound $Y_{44}Ru_{25}$; 6, stoichiometric compound Y_5Ru_2; 7, stoichiometric compound Y_3Ru; 8, pure yttrium.

TABLE 4
Comparison between Calculated Results (Present Work) and Experimental Data for the Stoichiometric Compounds in the Ru–Y System[a]

	Primary data and their weighing factors (WF)					Calculated values[b]			
Stoichiometric compound	$\Delta_f H$ $(J\,mol^{-1})$ experimental	WF	$\Delta S^{melting}$ $(J\,mol^{-1}\,K^{-1})$ estimates	WF		$\Delta_f H$ $(J\,mol^{-1})$	$\Delta_f S$ $(J\,mol^{-1}\,K^{-1})$	$\Delta S^{melting}$ $(J\,mol^{-1}\,K^{-1})$	$T^{melting}$ congruent (K)
$Y_{0.67}Ru_{0.33}$	−21,147	1	6.00	500		−21,178	−5.638	7.63	2253
$Y_{0.60}Ru_{0.40}$			7.00	500		−32,767	−14.21	6.94	1587
$Y_{0.638}Ru_{0.362}$			7.00	500		−32,963	−14.59	6.86	1570
$Y_{0.714}Ru_{0.286}$	−30,864	1	7.00	500		−30,854	−13.87	6.18	1577
$Y_{0.75}Ru_{0.25}$			7.00	500		−28,796	−13.21	6.02	1524

[a] The thermodynamic functions are relative to 1 mol of atoms and referred to solid β-yttrium and solid ruthenium.
[b] Coefficients of the optimization: $a_0 = -171,268.06$, $b_0 = 84.64$, $a_1 = -60,789.44$, $b_1 = 47.40$.
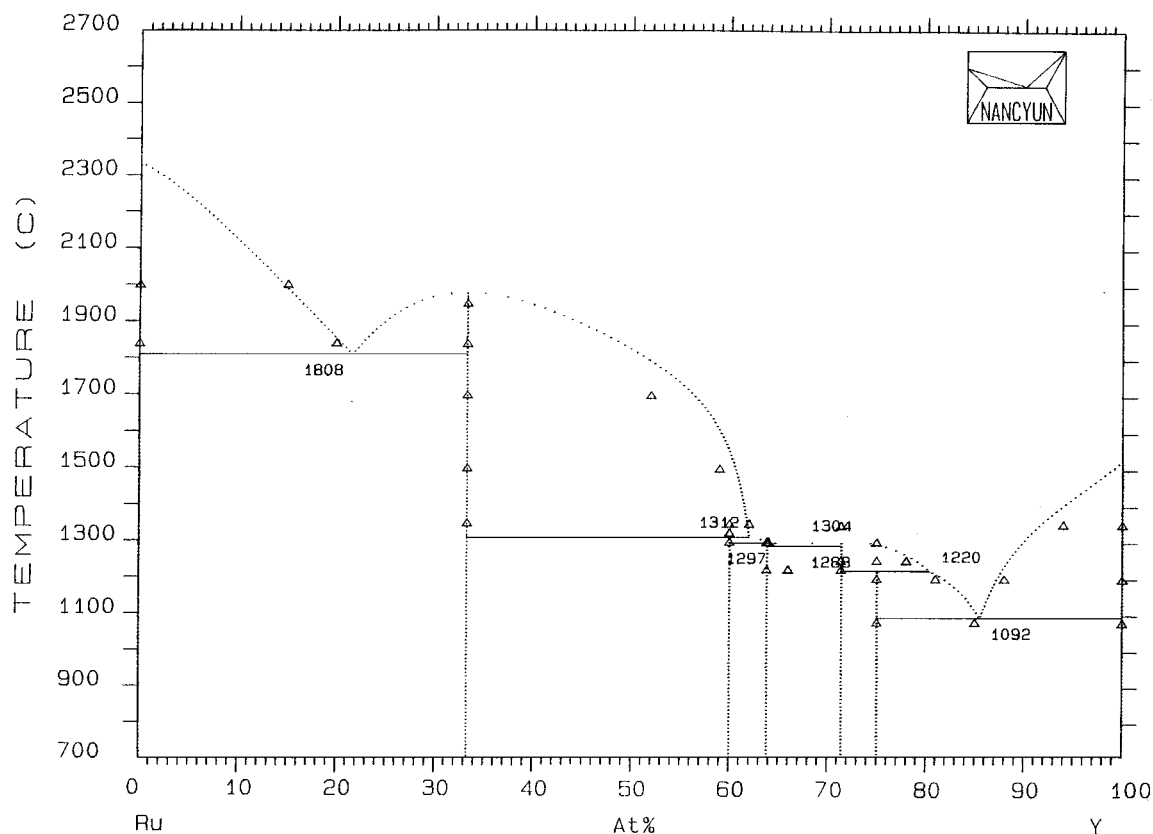
FIG. 2. Computed Ru–Y phase diagram. Triangles indicate the experimental or estimated points taken from Moffatt (5) for the numerical assessment.

where

$$a_0 = -171,268.06, \qquad b_0 = 84.64,$$

$$a_1 = -60,789.44, \quad \text{and} \quad b_1 = 47.40.$$

Table 4 compares the calculated values of the thermodynamic functions of the stoichiometric compounds referred to both solid pure elements (Ru and β-Y) to the experimental ones. It can be seen that the consistency between all the input data is satisfactory. Differences between measured and fitted enthalpies of formation are less than the experimental standard deviations. However, the calculated congruent melting points differ a little bit from the estimated data (estimates by Moffatt (5)) ($\Delta T = 22$ K for Ru_2Y and 40 K for Ru_2Y_5). In this table we also report the temperatures and entropies of fusion of the compounds when assuming congruent melting points for them.

Figure 2 shows the computed diagram, where the input experimental points are also presented. It can be seen that the experimental points (T, x) taken from the Moffatt diagram are not exactly on the computed lines. This is also shown in Table 5 (the maximum temperature difference is for the eutectic plateau $Ru_{25}Y_{44}/\text{liquid}/Ru_2Y_5 : \Delta T = 60$ K).

IV. DISCUSSION AND CONCLUSION

Our assessment gives mixed results. On the one hand, the enthalpies of formation which have been computed are very close to the experimental ones. This point is satisfactory because we measured the enthalpies of formation of two compounds which are not neighbors and this is good for

TABLE 5
Comparison between Experimental and Calculated Values of Composition and Temperature for the Invariant Points

Invariant points	Temperature (K)		Composition x_Y	
	Experimental or estimates	Calculated	Experimental or estimates	Calculated
Ru/liquid/YRu$_2$	2113[a]	2081	0.200[a]	0.217
liquid/YRu$_2$/Y$_3$Ru$_2$	1623	1585	0.620	0.620
liquid/Y$_3$Ru$_2$/Y$_{44}$Ru$_{25}$	1573	1570	0.640	0.647
Y$_{44}$Ru$_{25}$/liquid/Y$_5$Ru$_2$	1498	1561	0.660	0.671
liquid/Y$_5$Ru$_2$/Y$_3$Ru	1523	1493	0.780	0.804
Y$_3$Ru/liquid/Y	1353[a]	1364	0.850[a]	0.855

[a] Experimental.

scaling the computed figures. On the other hand, the invariant temperatures, peritectic as well as eutectic, are not well reproduced. This suggests that some experimental work remains to be done to give more credibility to these values before trying a new assessment whose goal will be to give a better description of the liquid phase.

REFERENCES

1. N. Selhaoui and O. J. Kleppa, *J. Chim. Phys.* **90,** 435 (1993).
2. N. Selhaoui and O. J. Kleppa, *J. Alloys Compd.* **191,** 145 (1993).
3. N. Selhaoui and O. J. Kleppa, *J. Alloys Compd.* **191,** 155 (1993).
4. N. Selhaoui and O. J. Kleppa, *Z. Metallkd.* **84,** 11 (1993).
5. M. G. Moffatt, "The Handbook of Binary Phase Diagrams." Genium, Schenectady, NY, 1984.
6. E. M. Savitsky, V. P. Polyakova, and N. R. Roshan, *Russ. Metall.* (*Engl. Transl.*) **5,** 97 (1972).
7. P. Sharifrazi, R. C. Mohanty, and A. Raman, *Z. Metallkd.* **75**, 801 (1984).
8. M. L. Fornasini, A. Mugnoli, and A. Palenzona, *J. Less-Common Met.* **154,** 149 (1989).
9. J. Charles, J. C. Gachon, and J. Hertz, *Calphad* **9,** 35 (1985).
10. J. Charles, M. Notin, M. Rahmane, and J. Hertz, *J. Phase Equilib.* **13,** 497 (1992).
11. R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley, and D. D. Wagnam, *in* "Selected Values of Thermodynamic Properties of the Elements," p. 154. ASM, Metals Park, OH, 1973.
12. A. T. Dinsdale, NPL Report D. M. A. (A), 195, 1989.