ELSEVIER

Journal of Nuclear Materials 247 (1997) 235–239

journal of nuclear materials

Enthalpies of formation of $CeNi_2$ and $CeNi_5$ by calorimetry

B. Prabhakara Reddy, R. Babu, K. Nagarajan, P.R. Vasudeva Rao *

Fuel Chemistry Division, Chemical Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, Tamil Nadu, India

Abstract

The enthalpies of formation of the intermetallic compounds, $CeNi_2$ and $CeNi_5$ at 298.15 K have been determined by high temperature solution calorimetry. The thermal effects of dissolution of nickel, cerium and the intermetallic compounds in liquid aluminum at 1095.15 K were determined as a function of concentration of the solutes from which the respective thermal effects of dissolution at infinite dilution were derived. The enthalpies of formation of the compounds at 298.15 K were computed from these values of thermal effects of dissolution at infinite dilution. The enthalpies of formation of $CeNi_2$ and $CeNi_5$ at 298.15 K thus obtained are -115.8 ± 7.3 and -201.9 ± 11.9 kJ mol^{-1}, respectively. The present enthalpy of formation of $CeNi_5$ is compared with the earlier literature values. In the case of $CeNi_2$ the study provides the only experimental data for the enthalpy of formation. © 1997 Elsevier Science B.V.

1. Introduction

Metallic alloys of U–Pu–Zr are among the promising fuels for future fast reactors. Austenitic stainless steel D-9 has been considered to be one of the suitable cladding materials for these fuels. The diffusion of the lanthanide fission products into the clad as well as the diffusion of some of the clad components into the fuel have been observed during the post-irradiation examination of these irradiated fuels [1]. Hence the thermodynamic properties of the rare earth-nickel systems are of importance. There has been considerable interest in the thermochemistry of rare earth-nickel systems in energy applications as well, since the intermetallic compounds of these systems have been considered as a suitable storage medium for hydrogen gas [2]. The enthalpy of formation of the intermetallic compound $CeNi_5$ at 298.15 K was earlier determined by Colinet et al. [3] by aluminum solution calorimetry and by Yamaguchi et al. [4] by tin solution calorimetry. They are not in agreement with each other, the enthalpy value obtained by Colinet et al. being more exothermic than the value reported by Yamaguchi et al. There are no experimental data for the enthalpy of formation of $CeNi_2$. In this work, we have determined the enthalpy of formation of $CeNi_2$ and $CeNi_5$ at 298.15 K by aluminum solution calorimetry.

2. Experimental

2.1. Sample preparation

High purity nickel (99.95%) from Aldrich, USA, and cerium (99.9%) from Metals and Byproducts, USA, were used for the preparation of the samples. The intermetallic compounds, $CeNi_2$ and $CeNi_5$ were prepared by melting stoichiometric amounts of nickel and cerium under argon atmosphere in an arc-melting set up. The buttons thus prepared were wrapped in tantalum foils and sealed in quartz tubes under argon atmosphere at sub-ambient pressure. $CeNi_2$ was annealed at 973 K for 168 h, whereas $CeNi_5$ was annealed at 973 K for 168 h and then at 1173 K for 168 h. The X-ray diffraction patterns of the annealed samples confirmed the presence of the respective single phase intermetallic compound. The samples were stored in an argon atmosphere glove box until measurement.

2.2. Equipment

The calorimetric measurements were carried out by using a high temperature differential calorimeter (model

---

* Corresponding author. Tel.: +91-4114 40 229/40 398; fax: +91-4114 40 365/40 396; e-mail: vasu@igcar.ernet.in.

0022-3115/97/$17.00
PII S0022-3115(97)00072-X

Table 1
Experimental data for the measurement of thermal effects of dissolution of nickel in liquid aluminum at 1095.15 K

Calibration [a]

No.	Weight of Al added (mg)	Peak area (counts)
1	35.77	219.0
2	30.79	164.0
3	34.86	195.0
4	31.42	163.5

Measurement

No.	Weight of Ni (mg)	Peak area (counts)	$\langle \text{Ni} \rangle_{298.15} \to [\text{Ni}]_{(\text{Al},1095.15)}$	
			x_{Ni} (at.%)	Q^{E}_{Ni} (kJ mol^{-1})
1	13.66	−123.0	0.80	−120.1
2	12.78	−115.0	1.54	−120.0
3	14.01	−127.0	2.34	−120.9
4	11.45	−102.0	2.98	−118.8
5	13.12	−114.0	3.71	−115.9

$Q^{\text{E},\infty}_{\text{Ni}} = -(119.1 \pm 2.0)$ kJ mol^{-1}

[a] Initial amount of aluminum taken = 642.41 mg. Total mass of aluminum = 775.25 mg. Calibration constant = 0.2272 J count^{-1}.

HT-1500 of Setaram, France) which is described elsewhere [6].

2.3. Procedure

About 600 mg of aluminum (purity 99.999%) was taken in an alumina crucible which was loaded into the calorimeter and heated to the temperature of measurement above the melting temperature of aluminum. Calibration runs were carried out by successively dropping aluminum samples, each weighing around 25 to 40 mg and initially maintained at the ambient temperature, 298.15 K. After this, 10 to 25 mg lots of solute samples (metal or alloy), maintained at the ambient temperature, were dropped successively into liquid aluminum. The calorimetric signals recorded correspond to the thermal effects of dissolution (Q^{E}) of the solute metal or intermetallic compound in liquid aluminum. The amounts of solute samples (10 to 25 mg) were so chosen as to result in dilute solutions of the solute in the aluminum solvent. The thermal effects of dissolution of Ni, Ce, CeNi_2 and CeNi_5 in liquid aluminum at 1095.15 K were measured in separate experiments under flowing argon.

3. Results

The thermal effects of dissolution of nickel (Q^{E}_{Ni}) and cerium (Q^{E}_{Ce}) in liquid aluminum at 1095.15 K, individually measured as a function of the concentration of nickel and cerium respectively are given in Tables 1 and 2. Similar results for the intermetallic compounds of CeNi_2 and CeNi_5 at 1095.15 K are given in Tables 3 and 4, respectively. As can be seen from these tables, the thermal effects of dissolution of Ce, Ni, CeNi_2 and CeNi_5 (the Q^{E} values) are independent of the concentration of the respective solutes in liquid aluminum within experimental errors. Hence the mean of the Q^{E} values was taken as $Q^{\text{E},\infty}$, the thermal effects of dissolution at infinite dilution. These values are also given in the respective tables along with their standard deviations. From the thermal effects of dissolution at infinite dilution, the enthalpies of formation of the compounds at 298.15 K (kJ mol^{-1}) were computed by using the following equation:

$$\Delta_{\text{f}} H^0_{298.15} \langle \text{CeNi}_n \rangle = Q^{\text{E},\infty}_{\text{Ce}} + n Q^{\text{E},\infty}_{\text{Ni}} - (n+1) Q^{\text{E},\infty}_{\text{Ce}_x\text{Ni}_{1-x}}. \tag{1}$$

The partial enthalpies of dissolution at infinite dilution of nickel and cerium in liquid aluminum ($\Delta \bar{H}^{\infty}_{\text{Ni}}$, $\Delta \bar{H}^{\infty}_{\text{Ce}}$) were derived from the thermal effects of dissolution at infinite dissolution ($Q^{\text{E},\infty}_{\text{Ni}}$, $Q^{\text{E},\infty}_{\text{Ce}}$) given in Tables 1 and 2 and the literature data for the enthalpy of nickel and cerium from Hultgren et al. [7] by using the following equation:

$$\Delta \bar{H}^{\infty}_{\text{Me}} = Q^{\text{E},\infty}_{\text{Me}} - \left(H^0_T - H^0_{298.15} \right)_{\text{Me}} - \Delta_{\text{m}} \text{H}^0_{\text{Me}}, \tag{2}$$

Table 2
Experimental data for the measurement of thermal effects of dissolution of cerium in liquid aluminum at 1095.15 K

Calibration [a]

No.	Weight of Al added (mg)	Peak area (counts)
1	34.88	197.0
2	30.22	165.0
3	35.75	220.0
4	31.85	189.0
5	31.86	200.5

Measurement

No.	Weight of Ce (mg)	Peak area (counts)	$\langle \text{Ce} \rangle_{298.15} \to [\text{Ce}]_{(\text{Al},1095.15)}$	
			x_{Ce} (at.%)	Q^{E}_{Ce} (kJ mol^{-1})
1	23.86	−117.5	0.56	−147.7
2	22.74	−113.0	1.09	−149.0
3	23.45	−119.0	1.63	−152.2
4	18.36	−91.0	2.04	−148.6
5	21.03	−107.0	2.52	−152.6

$Q^{\text{E},\infty}_{\text{Ce}} = -(150.0 \pm 2.2)$ kJ mol^{-1}

[a] Initial amount of aluminum taken = 650.94 mg. Total mass of aluminum = 815.50 mg. Calibration constant = 0.2140 J count^{-1}.

Table 3
Experimental data for the measurement of thermal effects of dissolution of $CeNi_2$ in liquid aluminum at 1095.15 K

Calibration [a]

No.	Weight of Al added (mg)	Peak area (counts)
1	34.01	197.5
2	38.20	222.5
3	24.52	136.0
4	31.22	190.0
5	27.89	178.0

Measurement

No.	Weight of $CeNi_2$ (mg)	Peak area (counts)	$\langle Ce_xNi_{1-x}\rangle_{298.15} \rightarrow [xCe + (1-x)Ni]_{\{Al,1095.15\}}$	
			$X_{Ce_{1/3}Ni_{2/3}}$ (at%)	$Q^{E}_{Ce_{1/3}Ni_{2/3}}$ (kJ mol^{-1})
1	12.35	−61.0	0.34	−89.3
2	12.09	−62.0	0.67	−92.7
3	15.36	−78.0	1.08	−91.8
4	10.24	−52.0	1.35	−91.8
5	18.45	−90.0	1.83	−88.2

$Q^{E,\infty}_{Ce_{1/3}Ni_{2/3}} = -(90.8 \pm 1.9)$ kJ mol^{-1}

[a] Initial amount of aluminum taken = 613.01 mg. Total weight of aluminum = 776.10 mg. Calibration constant = 0.2128 J count^{-1}.

where Me = Ni or Ce and $\Delta_m H^0_{Me}$ is the enthalpy of fusion at 1095.15 K of the respective elements. However the enthalpy of fusion of nickel at 1095.15 K has been assumed to be the same as that at its normal melting temperature. The values thus obtained are given in Table 6.

4. Discussion

The enthalpy of formation of $CeNi_5$ at 298.15 K from the present study is compared with the values calculated by Miedema's model [5] and the literature data in Table 5.

Table 4
Experimental data for the measurement of thermal effects of dissolution of $CeNi_5$ in liquid aluminum at 1095.15 K

Calibration [a]

No.	Weight of Al added (mg)	Peak area (counts)
1	34.38	183.0
2	33.91	199.0
3	35.71	193.0
4	34.41	206.0
5	31.46	167.5

Measurement

No.	Weight of $CeNi_5$ (mg)	Peak area (counts)	$\langle Ce_xNi_{1-x}\rangle_{298.15} \rightarrow [xCe + (1-x)Ni]_{\{Al,1095.15\}}$	
			$X_{Ce_{1/6}Ni_{5/6}}$ (at.%)	$Q^{E}_{Ce_{1/6}Ni_{5/6}}$ (kJ mol^{-1})
1	22.56	−125.5	0.87	−90.6
2	23.72	−132.0	1.76	−90.6
3	23.86	−135.0	2.64	−92.1
4	20.18	−111.0	3.37	−89.5
5	22.98	−127.0	4.18	−90.0

$Q^{E,\infty}_{Ce_{1/6}Ni_{5/6}} = -(90.6 \pm 1.0)$ kJ mol^{-1}

[a] Initial amount of aluminum taken = 633.82 mg. Total weight of aluminum = 810.77 mg. Calibration constant = 0.2261 J count^{-1}.

Table 5
Enthalpies of formation of the intermetallic compounds of $CeNi_2$ and $CeNi_5$ at 298.15 K

Compound	$-\Delta_f H^0_{298.15}$ (kJ mol^{-1}) $\langle Ce\rangle + n\langle Ni\rangle \rightarrow \langle CeNi_n\rangle$	Refs.
$CeNi_2$	115.8 ± 7.3	this work
	123	Miedema's model
$CeNi_5$	201.9 ± 11.9	this work
	146	Miedema's model
	199	[3]
	166	[4]

Table 6
The partial enthalpies of solution of Ni and Ce in aluminum at infinite dilution

Metal	Solvent	T (K)	$-\Delta \bar{H}^{\infty}$ (kJ mol^{-1})	Refs.
Ni	Al	1095	161.6 ± 2.0	this work
		1030	160.2	[8]
		1000	154.8	[9]
		1023	156.7	[10]
		1100	154.0	[11]
		948	157.4	[12]
		1173	146.3	[13]
Ce	Al	1095	184.6 ± 2.2	this work
		966	188.7	[14]
		1125	179.7	[15]
		1013	218.6	[16]
		1870	218.5	[17]

The value obtained in this study agrees fairly well with the one obtained by Colinet et al. [3]. But, the data obtained by Yamaguchi et al. [4] by tin solution calorimetry is very much less exothermic than both these values. In fact, their samples had an effective stoichiometry of $CeNi_{5.13}$ and thus contained excess of nickel than the amount corresponding to the stoichiometry, $CeNi_5$. They applied corrections to their measured values on these samples to arrive at the enthalpy of formation of $CeNi_5$. According to the Ce–Ni phase diagram, their samples would have been a two phase mixture of $\langle CeNi_5\rangle + \langle Ni\rangle$ rather than single phase $CeNi_5$. Perhaps the discrepancies in their enthalpy of formation could be attributed to the additional errors that might have been caused by such a correction procedure. The enthalpy of formation of $CeNi_5$ computed by using Miedema's model is also very much less exothermic than the measured value from the present work as well as from the earlier experimental data [3]. Our results are the first experimental data for the enthalpy of formation of $CeNi_2$. This value is only slightly less exothermic than the one obtained by computation by using Miedema's model.

As shown in Table 6, the partial enthalpy of dissolution of nickel ($\Delta \bar{H}^{\infty}_{Ni}$) in liquid aluminum at 1095.15 K obtained in the present study is in good agreement with the values reported in the literature [8–12] within the error limits except that of Pool et al. [13] where the value of these authors is less exothermic. In the partial enthalpy values reported in the literature, the investigators have not taken into account the enthalpy of fusion of Ni to derive the partial enthalpy from the thermal effects of dissolution. However, the values given in Table 6 were obtained by adding the enthalpy of fusion to the reported data [8–13].

The partial enthalpy of dissolution of cerium ($\Delta \bar{H}^{\infty}_{Ce}$) in liquid aluminum at 1095.15 K, obtained in the present study, agrees fairly well with that obtained by Colinet et al. [14]. The value obtained by Sommer et al. [15] is slightly less exothermic than our measured value. The partial enthalpies of solution of cerium in liquid aluminum value obtained by Yamshchikov et al. [16] and Esin et al. [17] are in very good agreement with each other, but are more exothermic than our measured value. The reason for these discrepancies is not known. These two references could not be directly accessed and hence the values have been taken from the compilation of data on the thermodynamic properties of rare earth alloy systems by Colinet and Pasturel [18].

5. Conclusions

This study provides the only experimental data for enthalpy of formation of $CeNi_2$. Our data on enthalpy of formation of $CeNi_5$ agree very well with the reported literature data.

Acknowledgements

The authors are grateful to Shri I. Kaliappan for the help rendered in preparation of the intermetallic compounds and to Dr K.V.G. Kutty for the characterization of the samples.

References

[1] R.G. Pahl, D.L. Porter, C.E. Lahm, G.L. Hofman, Metall. Trans. 21A (1990) 1863.
[2] K.H.J. Buschow, H.H. van Mal, J. Less-Common Met. 29 (1972) 203.
[3] C. Colinet, A. Pasturel, Phys. Status Solidi (a)80 (1983) K75.
[4] K. Yamaguchi, D.Y. Kim, M. Ohtsuka, K. Itagaki, J. Alloys Comp. 221 (1995) 161.
[5] F.R. de Boer, R. Boom, W.C.M. Mattens, A.R. Miedema, A.K. Niessen, Cohesion in Metals (North-Holand, Amsterdam, 1988).
[6] K. Nagarajan, R. Saha, R. Babu, C.K. Mathews, Thermochim. Acta 90 (1985) 279.
[7] P. Hultgren, P.D. Desai, T. Hawkins, M. Glaser, K.K. Kelly, D.D. Wagmann, Selected Values of the Thermodynamic

Properties of the Elements (American Society for Metals, Metals Park, OH, 1973).

[8] P.A. Gomozov, Yu.V. Zasypalov, B.M. Mogutnov, Russ. J. Phys. Chem. 60(8) (1986).

[9] M. Jeymond, D. Landaud, M. Lagardeur, A. Pasturel, Thermochim. Acta 55 (1982) 301.

[10] H.D. Dannohl, H.L. Lukas, Z. Metallkd. 65 (1974) 642.

[11] E.Th. Henig, H.L. Lukas, Z. Metallkd. 66 (1975) 98.

[12] C.C. Colinet, H. Diaz, J.C. Matieu, Ann. Chim. 4 (1979) 657.

[13] H.J. Pool, J. Starr, W.W. Griffith, Symposium Thermodynamik der Legierungen, Munster, 1972.

[14] A. Pasturel, C.C. Colinet, A.P. Guegan, J.C. Achard, J. Less-Common Met. 90 (1983) 21.

[15] F. Sommer, M. Keita, J. Less-Common Met. 136 (1987) 95.

[16] L.F. Yamshchikov, V.A. Lebedev, I.F. Nichkov, S.P. Raspopin, V.G. Shein, Sov. Non Ferrous Met. Res. 11 (1983) 128.

[17] Yu.O. Esin, G.M. Ryss, P.V. Geld, Russ. J. Phys. Chem. 53 (1979) 1360.

[18] C. Colinet, A. Pasturel, in: Handbook on the Physics and Chemistry of Rare Earths, eds. K.A. Gschneidner Jr., L. Eyring, G.H. Lander and G.R. Choppin, Vol. 19, Lanthanides/Actinides Physics II (Elsevier, Amsterdam, 1994).